4.1 Introduction

This chapter describes the synthesis, characterization and the *in vitro* antimicrobial activity of a series of complexes of the heterocyclic N, O donor Schiff base 5-(hydroxymethyl)-4-{(1-Z)-[2-N(2-hydroxylphenyl)ethanimidoyl]-2-methyl}pyridine-3-ol-hydrochloride (HMHPMP\textsuperscript{a}-L\textsubscript{2}), structure 4.1. The complexes synthesized are with the general formula [Ln(L\textsubscript{2})\textsubscript{2}X\textsubscript{2}]X and [Ln(L\textsubscript{2})\textsubscript{2}X]X\textsubscript{2} where X= NO\textsubscript{3}\textsuperscript{-}, Cl\textsuperscript{-} and ClO\textsubscript{4}\textsuperscript{-}, Ln = La, Ce, Pr, Nd, Sm, Eu, Gd, Tb, Dy and Er.

The ligand, L\textsubscript{2}\textsuperscript{a} consists of azomethine nitrogen and two phenolic oxygen atoms as potential donor sites, and the ligand is expected to act as a tridentate chelating one. When this ligand forms complexes with metals, two chelate rings are formed resulting in highly stable complexes and its metal complexes are bioactive with improved hydrophilic/lipophilic character.
4.2 Experimental

The details of the preparation of metal salts and the synthesis of the Schiff base are described in chapter 2.

4.3 Synthesis of the complexes

4.3.1 Lanthanide(III) nitrate complexes (B-27 to B-35)

A solution of Ln(NO$_3$)$_3$.6H$_2$O (Ln = La, Ce, Pr, Nd, Sm, Eu, Gd, Dy and Er) in methanol (1mmol, 20mL) and ligand suspension (2mmol, 30mL) in hot methanol was mixed and stirred on a magnetic stirrer for 2hours, refluxed on a water bath for 5hours and allowed to cool in air. The dark brown solids separated on concentration was washed with ethyl acetate followed by methanol, finally purified by extraction with acetone and dried under vacuum over P$_4$O$_10$ [240]. The yield and melting point: B-27 = 62%, 258°C, B-28 = 65%, 255°C, B-29 = 68%, 265°C, B-30 = 64%, 268°C, B-31 = 78%, 260°C, B-32 = 64%, 258°C, B-33 = 80%, 255°C, B-34 = 70%, 265°C, B-35 = 63%, 268°C.

4.3.2 Lanthanide(III) chloride complexes (B-36 to B-41)

Syntheses of all complexes were done under similar conditions. A solution of LnCl$_3$.6H$_2$O (Ln = La, Pr, Nd, Sm, Eu and Tb) in methanol (1.5mmol, 20mL) was added to the solution of ligand (3mmol, 60mL) in
Studies on lanthanide complexes of 5-(Hydroxymethyl)-4-{1-Z)-[2-N(2-hydroxyphenyl](….

hot methanol. 10mL 2M solution of KOH was added to maintain the pH at 6-7. The mixture was refluxed on a water bath for 4hours. The precipitate was filtered, washed with dichloromethane followed by ether and dried under vacuum over P$_4$O$_{10}$ [241]. The yield and melting point: B-36 = 72%, 187°C, B-37 = 65%, 188°C, B-38 = 78%, 191°C, B-39 = 76%, 194°C, B-40 = 68%, 187°C, B-41 = 68%, 203°C.

4.3.3 Lanthanide(III) perchlorate complexes (B-42 to B-48)

All the complexes were synthesised under similar conditions. A solution of ligand (3mmol, 40mL) in methanol was boiled and to the boiling solution, methanolic solution of the respective Ln(ClO$_4$)$_3$.6H$_2$O (Ln = La, Pr, Nd, Sm, Eu, Tb and Er) (1.5mmol, 30mL) was added. The medium was made neutral by adding slight amount of dil. KOH, refluxed for 5hours, and then kept on a hot plate for slow heating. A thick layer of the precipitate settled was washed with methanol followed by ether, dried under vacuum over P$_4$O$_{10}$ [246]. The yield and melting point: B-42 = 60%, 175°C, B-43 = 62%, 180°C, B-44 = 66%, 185°C, B-45 = 62%, 190°C, B-46 = 65%, 185°C, B-47 = 65%, 185°C, B-48 = 68%, 178°C.

4.4 Results and Discussion

The procedural details of the analysis and physiochemical studies of the complexes are described in chapter 2

4.4.1 Lanthanide(III) nitrate complexes

4.4.1.1 Appearance and solubility of the complexes

Lanthanide(III) nitrate complexes B-27 to B-35 were dark brown colored and non-hygroscopic in nature. The complexes were soluble in methanol, ethanol, acetone, DMF, DMSO and insoluble in benzene and toluene.
4.4.1.2 Elemental analysis

The percentages of metal [197], nitrogen, hydrogen and carbon were analysed and the data is presented in Table 4.1. The data suggest that the complexes B-27 to B-35 may be formulated as $\text{Ln}(L^2)_2(\text{NO}_3)_3$ where $\text{Ln} = \text{La}, \text{Ce}, \text{Pr}, \text{Nd}, \text{Sm}, \text{Eu}, \text{Gd}, \text{Dy}$ and $\text{Er}$.

Table 4.1. Analytical data of $\text{Ln}(L^2)_2(\text{NO}_3)_3$ Complexes B-27 to B-35

<table>
<thead>
<tr>
<th>Complex</th>
<th>% C (Obs/Calc)</th>
<th>% H (Obs/Calc)</th>
<th>% N (Obs/Calc)</th>
<th>% Metal (Obs/Calc)</th>
</tr>
</thead>
<tbody>
<tr>
<td>B – 27</td>
<td>46.1(45.1)</td>
<td>4.1(4.4)</td>
<td>9.9(10.1)</td>
<td>13.6(14.1)</td>
</tr>
<tr>
<td>B – 28</td>
<td>37.8(36.6)</td>
<td>4.3(3.6)</td>
<td>10.6(10.7)</td>
<td>15.2(15.5)</td>
</tr>
<tr>
<td>B – 29</td>
<td>36.6(39.2)</td>
<td>3.6(4.9)</td>
<td>10.6(10.6)</td>
<td>15.3(15.8)</td>
</tr>
<tr>
<td>B – 30</td>
<td>36.3(36.5)</td>
<td>3.6(4.1)</td>
<td>10.6(9.8)</td>
<td>15.6(16.1)</td>
</tr>
<tr>
<td>B – 31</td>
<td>31.7(32.5)</td>
<td>3.3(4.5)</td>
<td>9.2(10.1)</td>
<td>13.8(14.0)</td>
</tr>
<tr>
<td>B – 32</td>
<td>38.6(36.1)</td>
<td>5.7(3.6)</td>
<td>8.2(10.5)</td>
<td>14.6(15.0)</td>
</tr>
<tr>
<td>B – 33</td>
<td>50.1(35.9)</td>
<td>4.5(3.6)</td>
<td>8.8(10.5)</td>
<td>16.5(16.2)</td>
</tr>
<tr>
<td>B – 34</td>
<td>39.5(38.4)</td>
<td>4.2(4.8)</td>
<td>9.1(10.1)</td>
<td>15.6(15.0)</td>
</tr>
<tr>
<td>B – 35</td>
<td>31.1(32.8)</td>
<td>5.5(4.8)</td>
<td>8.4(8.7)</td>
<td>16.1(15.8)</td>
</tr>
</tbody>
</table>

4.4.1.3 Molar conductance

The molar conductance data of complexes B-27 to B-35 in acetone, acetonitrile and DMF are presented in Table 4.2.

For complexes B-27 to B-29, the values (in ohm$^{-1}$ mol$^{-1}$ cm$^2$) are in the range 170-210, 215-260 and 140-165 respectively in acetone, acetonitrile and DMF that correspond to electrolyte of 1:2 types [204]. Molar conductance values for complexes B-30 to B-35 in acetone are in the range 100-140, 120-150 in acetonitrile and 65-85 in DMF respectively, which are corresponding to 1:1 electrolyte [204]. Hence the complexes B-27 to B-29 are represented as $[\text{Ln}(L^2)_2\text{NO}_3](\text{NO}_3)_2$ and complexes B-30 to B-35 are represented as $[\text{Ln}(L^2)_2(\text{NO}_3)_2](\text{NO}_3)$.
Studies on lanthanide complexes of 5-(Hydroxymethyl)-4-{1-Z)-[2-N(2-hydroxylphenyl]….

Table 4.2 Molar conductance* of Complexes B-27 to B-35

<table>
<thead>
<tr>
<th>Solvent</th>
<th>B-27</th>
<th>B-28</th>
<th>B-29</th>
<th>B-30</th>
<th>B-31</th>
<th>B-32</th>
<th>B-33</th>
<th>B-34</th>
<th>B-35</th>
</tr>
</thead>
<tbody>
<tr>
<td>CH₃COCH₃</td>
<td>170</td>
<td>180</td>
<td>210</td>
<td>115</td>
<td>110</td>
<td>120</td>
<td>130</td>
<td>138</td>
<td>125</td>
</tr>
<tr>
<td>CH₃CN</td>
<td>245</td>
<td>215</td>
<td>260</td>
<td>145</td>
<td>124</td>
<td>126</td>
<td>130</td>
<td>147</td>
<td>150</td>
</tr>
<tr>
<td>DMF</td>
<td>140</td>
<td>165</td>
<td>145</td>
<td>73</td>
<td>68</td>
<td>69</td>
<td>85</td>
<td>75</td>
<td>83</td>
</tr>
</tbody>
</table>

*10⁻³M solution

4.4.1.4 Infrared spectra

In order to study the binding mode of the Schiff base to the metal in complexes, the IR spectrum of L² and the spectra of the complexes were compared. Data summarized in Table 4.3.

Table 4.3 Infrared spectral data (in cm⁻¹) of L² and its nitrate complexes (B-27 to B-35)

<table>
<thead>
<tr>
<th>Compound</th>
<th>C=N</th>
<th>C-O</th>
<th>C-O</th>
<th>Ln-N</th>
<th>Ln-O</th>
</tr>
</thead>
<tbody>
<tr>
<td>L²</td>
<td>1623.9s</td>
<td>1201s</td>
<td>1323m</td>
<td>-</td>
<td>-</td>
</tr>
<tr>
<td>B-27</td>
<td>1602s,sh</td>
<td>1217s</td>
<td>1302m</td>
<td>427  w</td>
<td>466w</td>
</tr>
<tr>
<td>B-28</td>
<td>1633s,sh</td>
<td>1197s</td>
<td>1301m</td>
<td>430  w</td>
<td>470w</td>
</tr>
<tr>
<td>B-29</td>
<td>1604s,sh</td>
<td>1191s</td>
<td>1314m</td>
<td>426  w</td>
<td>464w</td>
</tr>
<tr>
<td>B-30</td>
<td>1633s,sh</td>
<td>1193s</td>
<td>1336m</td>
<td>420  w</td>
<td>458w</td>
</tr>
<tr>
<td>B-31</td>
<td>1631s,sh</td>
<td>1217s</td>
<td>1334m</td>
<td>423  w</td>
<td>464w</td>
</tr>
<tr>
<td>B-32</td>
<td>1601s,sh</td>
<td>1193s</td>
<td>1277m</td>
<td>421  w</td>
<td>458w</td>
</tr>
<tr>
<td>B-33</td>
<td>1635s,sh</td>
<td>1193s</td>
<td>1276m</td>
<td>419  w</td>
<td>466w</td>
</tr>
<tr>
<td>B-34</td>
<td>1629s,sh</td>
<td>1191s</td>
<td>1319m</td>
<td>430  w</td>
<td>466w</td>
</tr>
<tr>
<td>B-35</td>
<td>1629s,sh</td>
<td>1195s</td>
<td>1334m</td>
<td>415  w</td>
<td>465w</td>
</tr>
</tbody>
</table>

s: strong, sh: sharp, w: weak, m: medium

The IR spectra of the Schiff base ligand have strong and sharp vibrational frequency band at 1623cm⁻¹ ascribed to \(\nu(C=\text{N})\), intense and broad band at 3342cm⁻¹, 3353cm⁻¹ characteristic of \(\nu(\text{O-H})\). A medium band observed at 1323cm⁻¹ is attributed to \(\nu(\text{C-O pyridyl ring})\). Medium
bands at 1201 cm\textsuperscript{-1} attributed to $\nu$(C–O phenyl ring) and the other at 1110 cm\textsuperscript{-1} attributed to $\nu$(C–O) of the primary alcoholic group.

In the spectra of all the complexes, stretching vibrational frequency band of the azomethine group is shifted to $\pm 30$ cm\textsuperscript{-1} and appeared in the range 1601–1635 cm\textsuperscript{-1} indicated the involvement of the azomethine group in coordination [235].

The typical medium band at 1323 cm\textsuperscript{-1} and 1201 cm\textsuperscript{-1} of the ligand was shifted to $\pm 20$ cm\textsuperscript{-1} in all complexes ascertaining the participation of both O-H groups in chelation [236]. In all the complexes, these bands appeared in the range of 1301–1336 cm\textsuperscript{-1} and 1191–1217 cm\textsuperscript{-1} respectively.

The medium band displayed in the ligand at 1110 cm\textsuperscript{-1} remained unaffected, indicating the non-participation of this OH in coordination. The band appearing at 605 cm\textsuperscript{-1} is due to the bending of (O–H). Existence of this band is a strong support for the nonparticipation of the alcoholic O–H in coordinate bond formation. Medium frequency band at 590–710 cm\textsuperscript{-1} attributed to the out of plane vibrations of O-H. All these observations suggest that the primary alcoholic O–H was non-hydrogen bonded [252].

A broad band observed in the region 3300–3400 cm\textsuperscript{-1} in the ligand may probably be due to the hydrogen bonding between the azomethine nitrogen and phenolic –OH. This band was disappeared in the complexes indicating the breakage of hydrogen bonding.

The characteristics absorption bands resulting from the skeletal vibrations of the aromatic rings of the Schiff base ligand were observed at $\sim$1440 cm\textsuperscript{-1}. Unaffected band at 3100–3200 cm\textsuperscript{-1} confirms the non-involvement of ring nitrogen during complex formation.
In addition, new vibrational frequency bands which were absent in the ligand, appeared in all the complexes. These are characteristic of nitrate ion vibrations. The data is presented in Table 4.4.

High intensity absorption bands were observed at ~1450-1520 cm\(^{-1}\), medium bands at ~1260-1285 cm\(^{-1}\), ~1025-1035 cm\(^{-1}\) and ~750 cm\(^{-1}\) which are attributed to \(\nu_4\), \(\nu_1\), \(\nu_2\) and \(\nu_3\) modes respectively of bidentatively coordinated nitrate group [199]. The strong and intense band observed at ~1517 cm\(^{-1}\) and ~1280 cm\(^{-1}\) attributed to \(\nu_N=O(\nu_4)\) and \(\nu_{(asym)}NO_2(\nu_1)\) respectively are attributed to coordinated nitrate group of C\(_2\)v symmetry. In all the complexes, \(\nu_1\) was observed at 1258-1290 cm\(^{-1}\), \(\nu_2\) band was observed in region 1025-1035 cm\(^{-1}\) and \(\nu_3\) bands were observed in the range 742-755 cm\(^{-1}\) and \(\nu_5\) at ~640-672 cm\(^{-1}\). Lever separation rule was applied to establish the coordination nature of nitrate ion. Accordingly, the separation of \(\nu_4-\nu_1\) is used to recognize whether the coordination is monodentate or bidentate. A value ~200 cm\(^{-1}\) in all the complexes conclude that nitrate ion is coordinated to the metal ion in a bidentate fashion. Lever separation rule is extended to the combination bands also. The separation of \((\nu_5+\nu_2)\) and \((\nu_2+\nu_3)\) is good enough in the order of ~50 cm\(^{-1}\) and reveals that nitrate ion is considered as covalently bonded to metal ion in a bidentate fashion [212,213]. Upon coordination, the bands at 680 cm\(^{-1}\) split into two bands, and the magnitude of splitting is in the range of 20 cm\(^{-1}\) is also supporting evidence for the bidentate coordination of the nitrate ion to the metal ion.

Appearance of new bands at ~458–470 cm\(^{-1}\) due to the Ln–O vibrations and bands at ~415–430 cm\(^{-1}\) attributed to Ln–N vibrations conclude that the ligand act as tridentate chelating one, the possible coordination sites being azomethine nitrogen atom and the two phenolic oxygen atoms [235].
All these spectral and analytical inferences in conformity with electrical conductance measurements reveal a coordination number of eight for La, Ce and Pr complexes and for Nd, Sm, Eu, Gd, Dy and Er complexes, coordination number ten was assigned.

Table 4.4 IR spectral bands (in cm\(^{-1}\)) of nitrate ion in complexes B-27 to B-35

<table>
<thead>
<tr>
<th>Complex</th>
<th>(\nu_4)</th>
<th>(\nu_1)</th>
<th>(\nu_2)</th>
<th>(\nu_3)</th>
<th>(\nu_5)</th>
<th>Ionic NO(_3)</th>
</tr>
</thead>
<tbody>
<tr>
<td>B-27</td>
<td>1434s</td>
<td>1257m</td>
<td>1033m</td>
<td>758</td>
<td>672w</td>
<td>1380s 817m</td>
</tr>
<tr>
<td>B-28</td>
<td>1451s</td>
<td>1260m</td>
<td>1030m</td>
<td>742</td>
<td>649w</td>
<td>1382s 820m</td>
</tr>
<tr>
<td>B-29</td>
<td>1515s</td>
<td>1278m</td>
<td>1024m</td>
<td>748w</td>
<td>650w</td>
<td>1382s 810m</td>
</tr>
<tr>
<td>B-30</td>
<td>1456s</td>
<td>1258m</td>
<td>1020m</td>
<td>758w</td>
<td>655w</td>
<td>1382s 811m</td>
</tr>
<tr>
<td>B-31</td>
<td>1517s</td>
<td>1282m</td>
<td>1035m</td>
<td>750w</td>
<td>657w</td>
<td>1382s 819m</td>
</tr>
<tr>
<td>B-32</td>
<td>1454s</td>
<td>1278m</td>
<td>1003m</td>
<td>738w</td>
<td>640w</td>
<td>1374s 814m</td>
</tr>
<tr>
<td>B-33</td>
<td>1452s</td>
<td>1256m</td>
<td>1031m</td>
<td>748w</td>
<td>655w</td>
<td>1384s 810m</td>
</tr>
<tr>
<td>B-34</td>
<td>1456s</td>
<td>1282m</td>
<td>1034m</td>
<td>750w</td>
<td>656w</td>
<td>1382s 811m</td>
</tr>
<tr>
<td>B-35</td>
<td>1456s</td>
<td>1282m</td>
<td>1035m</td>
<td>750w</td>
<td>655w</td>
<td>1382s 817m</td>
</tr>
</tbody>
</table>

s: strong, m: medium, w: weak

4.4.1.5 UV-Visible spectra

The UV-Visible spectra recorded in DMF for all the complexes are reported in Table 4.5. The electronic spectra of the ligand are characterized by three main absorption bands in the region 200-600nm. The high intensity bands observed in the region 240-255nm are attributed to the \(\pi\rightarrow\pi^*\) transition of the benzene ring. Another band at 285nm corresponds to \(\pi\rightarrow\pi^*\) transition of the azomethine C=N while another at 365nm attributed to \(n\rightarrow\pi^*\) transition. Absorption at \(~410nm\) may be due to the intraligand transitions. All the complexes of Ln(III) metal ions gave similar spectra, which indicate similar structure for all the complexes. Since the \(f-f\) transitions are Laporte forbidden, they were found to be very weak. Hence, the involvement of \(f\) orbitals is usually not visible. On coordination, some perturbations were observed and some new absorption bands were
Studies on lanthanide complexes of 5-(Hydroxymethyl)-4-\{1-Z\}-[2-N(2-hydroxylphenyl)…
detected [253]. Absorption spectra of complexes differ from the free ions, due to coupling of vibrational transitions with electronic transitions.

In the spectra of the complexes, slight red shifts were observed for $n\rightarrow\pi^*$ and $\pi\rightarrow\pi^*$ transition and appeared in the region 369-377nm and 287-296nm respectively. This observation is in accordance with other analytical data, which support the coordinate bond formations of the ligand to the metal ion. This means the crystal field effect upon the interelectronic repulsion between the 4$f$ electrons of the metal ion is negligible [220].

Table 4.5 Electronic spectral bands (nm) of complexes B-29 to B-35

<table>
<thead>
<tr>
<th></th>
<th>B-29</th>
<th>B-30</th>
<th>B-31</th>
<th>B-32</th>
<th>B-33</th>
<th>B-34</th>
<th>B-35</th>
</tr>
</thead>
<tbody>
<tr>
<td>$n\rightarrow\pi^*$ ($\nu_{max}$)</td>
<td>369</td>
<td>372</td>
<td>377</td>
<td>373</td>
<td>374</td>
<td>376</td>
<td>374</td>
</tr>
<tr>
<td>$\pi\rightarrow\pi^*$ ($\nu_{max}$)</td>
<td>294</td>
<td>287</td>
<td>292</td>
<td>288</td>
<td>290</td>
<td>293</td>
<td>296</td>
</tr>
</tbody>
</table>

A comparison of the hypersensitive bands and that of the aquo ions were done for the complexes B-30 and B-31. The ratio can be used to calculate the bonding parameters such as nephelauxetic effects $\beta$, angular overlap parameter $\eta$, interelectronic repulsion parameter $b^{1/2}$ and covalency parameter $\delta\%$. The results were presented in Table 4.6.

The hypersensitive transitions observed in these complexes have been used to study the nature of the coordination of the metal ion to the ligand. The coordination chemistry of the complexes of $L^2$ with lanthanide nitrate ion as counter ion was investigated using the absorption spectroscopy. The $f-f$ transition were used for band assignments of the $f$ electrons [141,243].

Analysis of the hypersensitive bands were done and qualitatively compared with the spectra obtained from previous similar studies and were
found to be similar to the spectra observed for ten coordinate complexes [238,239,243,253]. All these results were in agreement with the electrical conductance measurement data. Based on the results, a coordination number eight was assigned for the metal ions in complexes B-27 to B-29 and ten in complexes B-30 to B-35.

The spectrum of Tb(III) complex consists of bands at 488, 545, 585 and 623 nm. The spectrum is mainly due to the $^5\text{D}_4 \rightarrow \;^7\text{F}_5$ transition around 18348 cm$^{-1}$. Absorption spectrum of Tb(III) in the visible and UV region were found to be weak and $f$-$f$ transitions occur between different terms. For this reason, the spectra overlap considerably and not easy to interpret.

The Dy(III) complex, the spectrum was dominated by two intense peaks, one at 17420 cm$^{-1}$ corresponds to $^4\text{F}_{9/2} \rightarrow ^6\text{H}_{13/2}$ and another at 20840 cm$^{-1}$ corresponds to $^4\text{F}_{9/2} \rightarrow ^6\text{H}_{15/2}$ transitions. The absorption spectra of Nd(III) in DMF (Fig 4.1) give the characteristic transitions for the $^4\text{I}_{9/2}$ ground state. Two peaks at 798 nm and 800 nm corresponding to $^4\text{I}_{9/2} \rightarrow ^4\text{F}_{5/2}, ^2\text{H}_{9/2}$ and another one at 866 nm corresponding to $^4\text{I}_{9/2} \rightarrow ^4\text{F}_{3/2}$ [239,243].

![Fig. 4.1 UV-Visible spectrum of B-30](image-url)
The spectrum of the Er(III) complex, **B-35** (Fig 4.2) exhibit one single broad emission at 468nm.

![UV-Visible spectrum of B-35](image)

**Fig. 4.2** UV-Visible spectrum of B-35

<table>
<thead>
<tr>
<th>Complex</th>
<th>ν&lt;sub&gt;complex&lt;/sub&gt; cm&lt;sup&gt;-1&lt;/sup&gt;</th>
<th>ν&lt;sub&gt;aq&lt;/sub&gt; cm&lt;sup&gt;-1&lt;/sup&gt;</th>
<th>Transitions</th>
<th>β</th>
<th>b&lt;sup&gt;1/2&lt;/sup&gt;</th>
<th>δ</th>
<th>η</th>
</tr>
</thead>
<tbody>
<tr>
<td>B-30</td>
<td>15503</td>
<td>15660</td>
<td>^4^I_{9/2} → ^4^F_{9/2}</td>
<td>0.9963</td>
<td>0.0304</td>
<td>0.3676</td>
<td>0.0609</td>
</tr>
<tr>
<td></td>
<td>13380</td>
<td>13510</td>
<td>^4^I_{9/2} → ^2^S_{3/2}, ^4^F_{7/2}</td>
<td>0.9903</td>
<td>0.0490</td>
<td>0.0676</td>
<td>0.0485</td>
</tr>
<tr>
<td></td>
<td>13333</td>
<td>13410</td>
<td>^4^I_{9/2} → ^4^F_{7/2}, ^4^S_{3/2}</td>
<td>0.9942</td>
<td>0.0378</td>
<td>0.5775</td>
<td>0.0759</td>
</tr>
<tr>
<td></td>
<td>12498</td>
<td>12540</td>
<td>^4^I_{9/2} → ^2^H_{9/2}, ^4^F_{5/2}</td>
<td>0.9966</td>
<td>0.0289</td>
<td>0.3360</td>
<td>0.0579</td>
</tr>
<tr>
<td></td>
<td>11494</td>
<td>11560</td>
<td>^4^I_{9/2} → ^4^F_{3/2}</td>
<td>0.9942</td>
<td>0.0377</td>
<td>0.5742</td>
<td>0.0757</td>
</tr>
<tr>
<td></td>
<td>21186</td>
<td>21300</td>
<td>^4^I_{9/2} → ^2^K_{15/2}, ^4^G_{11/2}</td>
<td>0.9946</td>
<td>0.0365</td>
<td>0.5380</td>
<td>0.0733</td>
</tr>
<tr>
<td></td>
<td>20900</td>
<td>21030</td>
<td>^4^I_{9/2} → ^2^K_{15/2}, ^4^G_{11/2}</td>
<td>0.9938</td>
<td>0.0365</td>
<td>0.6220</td>
<td>0.0788</td>
</tr>
<tr>
<td></td>
<td>19080</td>
<td>19100</td>
<td>^4^I_{9/2} → ^4^G_{7/2}, ^2^K_{13/2}, ^4^G_{9/2}</td>
<td>0.9989</td>
<td>0.0101</td>
<td>0.1048</td>
<td>0.0323</td>
</tr>
<tr>
<td>B-31</td>
<td>17630</td>
<td>17710</td>
<td>^4^G_{5/2}, ^6^H_{9/2}</td>
<td>0.9954</td>
<td>0.0336</td>
<td>0.4537</td>
<td>0.0673</td>
</tr>
<tr>
<td></td>
<td>16660</td>
<td>16780</td>
<td>^4^G_{5/2}, ^6^H_{9/2}</td>
<td>0.9928</td>
<td>0.0422</td>
<td>0.7202</td>
<td>0.0848</td>
</tr>
<tr>
<td></td>
<td>15450</td>
<td>15608</td>
<td>^4^G_{5/2}, ^6^H_{9/2}</td>
<td>0.9898</td>
<td>0.0503</td>
<td>0.0226</td>
<td>0.1011</td>
</tr>
</tbody>
</table>

**Table 4.6.** Electronic spectral bands of complexes B-30 and B-31
4.4.1.6 Magnetic Moment Studies

The magnetic moment studies were carried out for all the complexes and the data is displayed in Table 4.7. The values show little variation with the values calculated for free ions. This is in conformity with the electronic properties of lanthanides. Due to the spatially confined nature of 4f electrons, the involvement of these electrons in bond formation is negligible. The values are comparable with Van Vleck values [209].

Magnetic susceptibility measurements revealed a diamagnetic nature for lanthanum complex. All other metal complexes show paramagnetic nature.

Table 4.7. Observed magnetic moment values of complexes B-27 to B-35

<table>
<thead>
<tr>
<th></th>
<th>B-27</th>
<th>B-28</th>
<th>B-29</th>
<th>B-30</th>
<th>B-31</th>
<th>B-32</th>
<th>B-33</th>
<th>B-34</th>
<th>B-35</th>
</tr>
</thead>
<tbody>
<tr>
<td>μ (BM)</td>
<td>-</td>
<td>2.55</td>
<td>2.63</td>
<td>3.65</td>
<td>2.55</td>
<td>7.6</td>
<td>8.1</td>
<td>4.6</td>
<td>8.26</td>
</tr>
</tbody>
</table>

4.4.1.7 ¹H NMR Spectra

NMR spectral data of complex B-27 is presented in Table 4.8. Signals of the diamagnetic lanthanum complex were found to be shifted to lower field compared to free ligand. Signals observed at δ = 8.1ppm appeared in the ligand attributed to azomethine proton exhibit a low field shift to δ = 8.4ppm. Signals appeared as multiplet at δ = 6.9ppm attributable to aromatic protons also displayed downfield shift in the region δ = 7-7.3ppm which suggest electronic changes due to coordination. The signal appeared as singlet at δ = 6.6ppm in the ligand attributed to -OH proton displayed downfield shift to δ = 6.8ppm. All the data support the
bond formation with the metal ion and the ligand through azomethine and the phenolic groups [248].

Table 4.8. Important $^1$H NMR signals of lanthanum complex (B-27) in δ w.r.to TMS(=ppm)

<table>
<thead>
<tr>
<th>Compound</th>
<th>HC=N</th>
<th>OH(phenolic)</th>
<th>OH(alc)</th>
<th>Phenyl</th>
<th>N-CH$_3$</th>
<th>C-CH$_3$</th>
</tr>
</thead>
<tbody>
<tr>
<td>L$^2$</td>
<td>8.1s,sh</td>
<td>6.6br</td>
<td>3.4br</td>
<td>6.9-7.1m</td>
<td>4.7s</td>
<td>2.9s,br</td>
</tr>
<tr>
<td>B-27</td>
<td>8.4s,sh</td>
<td>6.8br</td>
<td>3.4br</td>
<td>7-7.3m</td>
<td>4.7s</td>
<td>2.9s,br</td>
</tr>
</tbody>
</table>

4.4.1.8 Thermal analysis

Five representative complexes were selected for the TG, DTA analysis. DTA curve shows endothermic/exothermic peaks. The TG curve corresponds to decomposition of the sample in nitrogen atmosphere. All complexes gave similar decomposition pattern.

The two-stage decomposition pattern provides further evidence in proposing the structure of the complex. The complexes were stable up to $\sim$250-270°C. There was no mass loss observed up to 250°C. This observation suggests absence of water molecule or solvent molecule neither as crystal coordinated nor as lattice water [249,250].

In the first stage, a mass loss within the range of 31.5-34% was observed at a temperature range of 250-420°C with an exothermic shoulder at 261°C corresponding to the removal of one molecule of the ligand. The second stage of the decomposition occurred at the temperature range of 420-600°C, with an observed mass loss within the range of 33-35% corresponding to the removal of the second ligand molecule with an exothermic peak at 550°C. Finally, the complex was decomposed into the corresponding metal oxide [250].
The kinetic parameters for the thermal decomposition were investigated using Coats-Redfern equation, which provide additional evidence for the formation of the complex [250]. A plot of \( \log(\alpha/T^2) \) versus \( 1/T \) gives a straight line which is in accordance with the kinetics for a non-isothermal process. The energy of activation \( E_a \) and the frequency factor \( A \) for the decomposition in different stages calculated for complex B-28, B-30 and B-31 are presented in Table 4.9. The negative value of \( \Delta H \) indicates that the complexes are highly stable. Plots obtained for complex B-28 for stages I, (Fig. 4.3) and stage II, (Fig. 4.4), that of complex B-30, (Fig. 4.5 & 4.6) and for complex B-31, (Fig. 4.7 & 4.8) respectively are illustrated.

Table 4.9. Thermal decomposition data and kinetic parameters for B-28, B-30 & B-31

<table>
<thead>
<tr>
<th>Complex</th>
<th>Stages of decomposition</th>
<th>% mass loss</th>
<th>Temp. range</th>
<th>Molecule eliminated</th>
<th>DTG Peak</th>
<th>( E_a )</th>
<th>A</th>
</tr>
</thead>
<tbody>
<tr>
<td>B-28</td>
<td>I</td>
<td>34.0(33)</td>
<td>250-420</td>
<td>ligand</td>
<td>280</td>
<td>-51.74</td>
<td>0.1443</td>
</tr>
<tr>
<td></td>
<td>II</td>
<td>35.0(33)</td>
<td>420-650</td>
<td>ligand</td>
<td>440</td>
<td>-34.07</td>
<td>-1.6105</td>
</tr>
<tr>
<td>B-30</td>
<td>I</td>
<td>31.5(32)</td>
<td>200-450</td>
<td>ligand</td>
<td>295</td>
<td>-56.47</td>
<td>0.0732</td>
</tr>
<tr>
<td></td>
<td>II</td>
<td>33.0(32)</td>
<td>450-680</td>
<td>ligand</td>
<td>400</td>
<td>-127.22</td>
<td>6.26</td>
</tr>
<tr>
<td>B-31</td>
<td>I</td>
<td>34.0(33)</td>
<td>200-480</td>
<td>ligand</td>
<td>301</td>
<td>-34.91</td>
<td>-0.876</td>
</tr>
<tr>
<td></td>
<td>II</td>
<td>34.0(33)</td>
<td>480-680</td>
<td>ligand</td>
<td>481</td>
<td>-6.185</td>
<td>-3.365</td>
</tr>
</tbody>
</table>
Studies on lanthanide complexes of 5-(Hydroxymethyl)-4-{1-Z)-[2-N(2-hydroxyphenyl)…

Fig. 4.3 $\alpha$-T plot for B-28 (Stage I)

Fig. 4.4 $\alpha$-T plot for B-28 (Stage II)
Fig. 4.5 $\alpha$-T Plot for B-30 (stage I)

Fig. 4.6 $\alpha$-T Plot for B-30 (stage II)
Fig. 4.7 α-T Plot for B-31 (stage I)

Log $\alpha/T^2$ vs. $10^3/T$

Fig. 4.8 α-T Plot for B-31 (Stage II)

Log $\alpha/T^2$ vs. $10^3/T$
Chapter 4

Hence, it can be concluded that the ligand \( L^2 \) is a tridentate chelating ligand with coordination sites at azomethine nitrogen and the two phenolic oxygen atoms. The tentative structures of the complexes are given below:

![Structure 4.2 (a)](image)
Proposed structure for B-27 to B-29

![Structure 4.2 (b)](image)
Proposed structure for B-30 to B-35

4.4.2 Lanthanide(III) chloride complexes

4.4.2.1 Appearance and solubility of the complexes

All the complexes B-36 to B-41 are light brown in color, crystalline and non-hygroscopic in nature. All these complexes were soluble in methanol, ethanol, acetone, DMF, DMSO and insoluble in acetonitrile, benzene and carbon tetrachloride.

4.4.2.2 Elemental analysis

The percentage of metal, anion [197], carbon, nitrogen, and hydrogen in the complexes B-36 to B-41 were determined and presented in Table 4.10. The data suggest that these complexes may be formulated as \( \text{Ln}(L^2)_2\text{Cl}_3 \) where \( \text{Ln} = \text{La, Pr, Nd, Sm, Eu and Tb} \).
Table 4.10 Analytical data of complexes B-36 to B-41

<table>
<thead>
<tr>
<th>Complex</th>
<th>C% Obs(Cal)</th>
<th>H% Obs(Cal)</th>
<th>N% Obs(Cal)</th>
<th>M% Obs(Cal)</th>
<th>Cl % Obs(Cal)</th>
</tr>
</thead>
<tbody>
<tr>
<td>B-36</td>
<td>39.37(37.87)</td>
<td>3.42(3.85)</td>
<td>6.1(6.79)</td>
<td>15.8(16.8)</td>
<td>21.5(20.5)</td>
</tr>
<tr>
<td>B-37</td>
<td>38.0(38.62)</td>
<td>4.1(3.29)</td>
<td>6.0(6.93)</td>
<td>17.1(17.4)</td>
<td>21.3(19.8)</td>
</tr>
<tr>
<td>B-38</td>
<td>39.1(38.46)</td>
<td>3.9(3.23)</td>
<td>6.8(6.90)</td>
<td>15.1(17.7)</td>
<td>21.4(19.0)</td>
</tr>
<tr>
<td>B-39</td>
<td>39.2(38.17)</td>
<td>3.8(3.60)</td>
<td>6.2(6.85)</td>
<td>16.5(18.3)</td>
<td>21.2(20.8)</td>
</tr>
<tr>
<td>B-40</td>
<td>38.5(37.28)</td>
<td>4.2(3.37)</td>
<td>6.6(6.69)</td>
<td>15.4(18.1)</td>
<td>20.8(21.5)</td>
</tr>
<tr>
<td>B-41</td>
<td>38.1(37.75)</td>
<td>3.9(3.85)</td>
<td>6.7(6.29)</td>
<td>16.5(18.2)</td>
<td>20.6(21.8)</td>
</tr>
</tbody>
</table>

4.4.2.3 Molar conductance

Molar conductance data for chloride complexes B-36 to B-41 in acetone, methanol, ethanol and DMF were obtained in the range 25-40, 28-60, 8-15 and 28-40 ohm^{-1}mol^{-1}cm^{2} respectively (Table 4.11). The values suggest non-conducting nature for these complexes [204]. Hence, the chloride complexes may be formulated as: [Ln(L^2)_2Cl_3] where Ln = La, Pr, Nd, Sm, Eu and Tb.

Table 4.11 Molar conductance* of Complexes B-36 to B-41

<table>
<thead>
<tr>
<th>Complex</th>
<th>Molar Conductance (ohm^{-1}mol^{-1}cm^{2})</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>Acetone</td>
</tr>
<tr>
<td>B-36</td>
<td>25</td>
</tr>
<tr>
<td>B-37</td>
<td>32</td>
</tr>
<tr>
<td>B-38</td>
<td>28</td>
</tr>
<tr>
<td>B-39</td>
<td>40</td>
</tr>
<tr>
<td>B-40</td>
<td>35</td>
</tr>
<tr>
<td>B-41</td>
<td>30</td>
</tr>
</tbody>
</table>

*10^{-3}M solution

4.4.2.4 Infrared spectra

The important vibrational frequency bands observed in the spectra of the ligand and complexes are reported in Table 4.12. The ligand, L^2 show a very strong band of -C=N at frequency of 1623 cm^{-1}. In the complexes, the
bands associated with this azomethine were shifted to ± 2-10cm⁻¹. The shift of the bands in the complexes is an evidence for the coordination of azomethine nitrogen to lanthanide ion [235].

The two phenolic -OH in the ligand show frequency bands at ν(C–O) at 1201cm⁻¹ and 1323cm⁻¹. Bands at 1323cm⁻¹ were shifted to ± 5-15cm⁻¹ and observed in the range of 1301-1317cm⁻¹ indicate that bond formation has been taken place through this phenolic oxygen [235]. The νC–O bands appeared in the range 1201cm⁻¹ was shifted to the range of 1194-1217cm⁻¹. The primary alcoholic group present in the pyridoxal ring remained unaffected and no distinct change in the position or intensity of vibrational frequency of this –OH was observed. All these observations suggest that coordination of the ligand to metal ion has been taken place through azomethine nitrogen atom and the two phenolic oxygen atoms.

Appearance of additional non-ligand bands in the region 318-322cm⁻¹ was assigned to Ln-Cl. New bands appeared in the region 365-380cm⁻¹ were attributed to Ln-N, and new bands observed at 418-448cm⁻¹ were assignable to Ln-O [246]. From the infrared data, it is concluded that the Schiff base act as a tridentate chelating ligand.

| Table 4.12 Important IR spectral data (cm⁻¹) of complexes B-36 to B-41 |
|-----------------|--------|------|------|------|------|------|------|
| Compound        | C=N    | C-O  | C-O  | Ln-O | Ln-N | Ln-Cl |
| Ligand          | 1623s  | 1323m| 1201s| -    | -    | -    |
| B-36            | 1604s  | 1301m| 1195s| 438w | 365w | 320w |
| B-37            | 1627s  | 1305m| 1217s| 423w | 378w | 318w |
| B-38            | 1620s  | 1317m| 1206s| 348w | 367w | 322w |
| B-39            | 1628s  | 1310m| 1195s| 437w | 376w | 321w |
| B-40            | 1628s  | 1307m| 1194s| 448w | 380w | 319w |
| B-41            | 1629s  | 1303m| 1216s| 418w | 368w | 318w |

s: strong, m: medium, w: weak
4.4.2.5 UV–Visible spectra

Electronic spectra of the ligand show band maxima at 285nm and 365nm corresponding to the $\pi\rightarrow\pi^*$ and $n\rightarrow\pi^*$ transitions respectively. The $\pi\rightarrow\pi^*$ transitions were blue shifted to the region 265-280nm in all complexes. The $n\rightarrow\pi^*$ transitions were red shifted to the range 368-410nm (Table 4.13).

<table>
<thead>
<tr>
<th></th>
<th>B-36</th>
<th>B-37</th>
<th>B-38</th>
<th>B-39</th>
<th>B-40</th>
<th>B-41</th>
</tr>
</thead>
<tbody>
<tr>
<td>$n\rightarrow\pi^*$ ($\nu_{max}$)</td>
<td>370</td>
<td>372</td>
<td>369</td>
<td>368</td>
<td>410</td>
<td>400</td>
</tr>
<tr>
<td>$\pi\rightarrow\pi^*$ ($\nu_{max}$)</td>
<td>265</td>
<td>268</td>
<td>272</td>
<td>280</td>
<td>270</td>
<td>278</td>
</tr>
</tbody>
</table>

The $f/f$ transitions were monitored at 350-700nm. In the spectrum of $[\text{Sm(L}^2\text{)}_2\text{Cl}_3]$ (B-39), bands at 563nm, 602nm, 650nm and 703nm were observed. These transitions are attributed to $^4G_{5/2}\rightarrow^6H_{5/2}$, $^4G_{5/2}\rightarrow^6H_{7/2}$, $^4G_{5/2}\rightarrow^6H_{9/2}$, $^4G_{5/2}\rightarrow^6H_{11/2}$ respectively. For Eu$^{3+}$, the transitions were observed at 694nm corresponding to the transition $^5D_0\rightarrow^7F_{4}$, band at 649nm corresponding to $^5D_0\rightarrow^7F_{3}$ transition, 617nm corresponding to $^5D_0\rightarrow^7F_{2}$, and 591nm corresponding to $^5D_0\rightarrow^7F_{1}$ and the band at 581nm corresponding to $^5D_0\rightarrow^7F_{0}$. Spectra obtained for B-38 is illustrated (Fig.4.3)
The $f$-$f$ transitions observed in the solution state for a few chloride complexes and their tentative assignment are given in Table 4.14. These transitions were compared with those bands observed for the respective aqueous ions. The nephelauxetic effect $\beta$, which is a measure of the covalency in complexes, bonding parameter $b^{1/2}$, $\eta$ and Sinha parameter $\delta$ were calculated and presented in Table 4.14. The positive value of $b^{1/2}$ shows covalent nature of the metal-ligand band. The $\delta\%$ values were also found to be positive in the complexes indicating electron delocalization over $4f$ orbital which also indicates covalence nature between the metal ion and the ligand [151].

Table 4.14 Electronic transitions and tentative assignments of B-38 and B-41

<table>
<thead>
<tr>
<th>complex</th>
<th>$\nu_{(comp)}$ (cm$^{-1}$)</th>
<th>$\nu_{(aqua)}$ (cm$^{-1}$)</th>
<th>transition</th>
<th>$\beta$</th>
<th>$b^{1/2}$</th>
<th>$\delta$</th>
<th>$\eta$</th>
</tr>
</thead>
<tbody>
<tr>
<td>B-38</td>
<td>23200</td>
<td>23415</td>
<td>$^4I_{0,2} \rightarrow ^4D_{11/2}$</td>
<td>0.9908</td>
<td>0.0479</td>
<td>0.9267</td>
<td>0.0962</td>
</tr>
<tr>
<td></td>
<td>20800</td>
<td>20930</td>
<td>$^4I_{0,2} \rightarrow ^4G_{9/2}$</td>
<td>0.9937</td>
<td>0.0394</td>
<td>0.6250</td>
<td>0.0790</td>
</tr>
<tr>
<td></td>
<td>19440</td>
<td>19625</td>
<td>$^4I_{0,2} \rightarrow ^4G_{9/2}$</td>
<td>0.9905</td>
<td>0.0485</td>
<td>0.9516</td>
<td>0.0975</td>
</tr>
<tr>
<td></td>
<td>18520</td>
<td>18640</td>
<td>$^4I_{0,2} \rightarrow ^4G_{7/2}$</td>
<td>0.9935</td>
<td>0.0407</td>
<td>0.6479</td>
<td>0.0804</td>
</tr>
<tr>
<td></td>
<td>12500</td>
<td>12715</td>
<td>$^4I_{0,2} \rightarrow ^4G_{5/2}$</td>
<td>0.9830</td>
<td>0.0650</td>
<td>1.72</td>
<td>0.0311</td>
</tr>
<tr>
<td></td>
<td>12195</td>
<td>12300</td>
<td>$^4I_{0,2} \rightarrow ^4F_{5/2}$</td>
<td>0.9914</td>
<td>0.0461</td>
<td>0.8610</td>
<td>0.0927</td>
</tr>
<tr>
<td></td>
<td>16129</td>
<td>16310</td>
<td>$^4I_{0,2} \rightarrow ^4H_{11/2}$</td>
<td>0.9889</td>
<td>0.0526</td>
<td>1.122</td>
<td>0.1059</td>
</tr>
<tr>
<td></td>
<td>19047</td>
<td>19220</td>
<td>$^4I_{0,2} \rightarrow ^4G_{7/2}$</td>
<td>0.9909</td>
<td>0.0474</td>
<td>0.9082</td>
<td>0.0953</td>
</tr>
</tbody>
</table>

<table>
<thead>
<tr>
<th>complex</th>
<th>$\nu_{(comp)}$ (cm$^{-1}$)</th>
<th>$\nu_{(aqua)}$ (cm$^{-1}$)</th>
<th>transition</th>
<th>$\beta$</th>
<th>$b^{1/2}$</th>
<th>$\delta$</th>
<th>$\eta$</th>
</tr>
</thead>
<tbody>
<tr>
<td>B-41</td>
<td>20491</td>
<td>20620</td>
<td>$^5D_{4} \rightarrow ^7F_6$</td>
<td>0.9937</td>
<td>0.0395</td>
<td>0.6295</td>
<td>0.0793</td>
</tr>
<tr>
<td></td>
<td>18348</td>
<td>18415</td>
<td>$^5D_{4} \rightarrow ^7F_5$</td>
<td>0.9963</td>
<td>0.0301</td>
<td>0.3651</td>
<td>0.0604</td>
</tr>
<tr>
<td></td>
<td>17094</td>
<td>17200</td>
<td>$^5D_{4} \rightarrow ^7F_4$</td>
<td>0.9938</td>
<td>0.0392</td>
<td>0.6201</td>
<td>0.0787</td>
</tr>
<tr>
<td></td>
<td>16050</td>
<td>16225</td>
<td>$^5D_{4} \rightarrow ^7F_3$</td>
<td>0.9892</td>
<td>0.0519</td>
<td>1.090</td>
<td>0.1044</td>
</tr>
</tbody>
</table>

4.4.2.6 Magnetic Moment studies

The magnetic moments were calculated and presented in the Table 4.15. The values of $\mu_{\text{eff}}$ are close to those obtained by Van Vleck [209,235]. Only minute deviations were observed. The results showed that there was not much influence of the ligand field on $4f$ electrons of the lanthanide ions.
Table 4.15 Observed magnetic moment values for B-36 to B-41

<table>
<thead>
<tr>
<th></th>
<th>B-36</th>
<th>B-37</th>
<th>B-38</th>
<th>B-39</th>
<th>B-40</th>
<th>B-41</th>
</tr>
</thead>
<tbody>
<tr>
<td>$\mu$ (BM)</td>
<td>--</td>
<td>3.59</td>
<td>3.58</td>
<td>1.58</td>
<td>6.9</td>
<td>8.7</td>
</tr>
</tbody>
</table>

4.4.2.7 $^1$HNMR Spectra

NMR spectrum of lanthanum complex (B-36) was recorded and data presented in the Table 4.16. Signals of complex were shifted to lower field compared to free ligand. Signals observed at $\delta = 3.3$ppm was attributed to –OH(alcoholic) protons. Signals observed at $\delta = 8.1$ppm appeared in the ligand attributed to azomethine proton exhibit a low field shift to $\delta = 8.4$ppm in complex. Signals observed as multiplet at $\delta = 6.9$- 7.1ppm exhibit a downfield shift to $\delta = 7.2$ to 7.5ppm on complexation. The resonance appeared at $\delta = 6.6$ppm observed in the ligand exhibit a downfield shift to $\delta = 6.9$ppm during complex formation. The spectra obtained are consistent with assumed structure [244,248].

Table 4.16 Important $^1$H NMR signals of lanthanum complex (B-36) in $\delta$(ppm) w.r.to TMS

<table>
<thead>
<tr>
<th>Complex</th>
<th>HC=N</th>
<th>OH(phenolic)</th>
<th>OH(alc)</th>
<th>Phenyl</th>
<th>N-CH$_3$</th>
<th>C-CH$_3$</th>
</tr>
</thead>
<tbody>
<tr>
<td>B-36</td>
<td>8.4</td>
<td>6.9</td>
<td>3.3</td>
<td>7.2-7.5</td>
<td>4.7</td>
<td>2.9</td>
</tr>
</tbody>
</table>

4.4.2.8 Thermal analyses

Thermal decomposition data for the complex B-38 are presented in Table 4.17.

The thermal stability of the complex was examined with respect to TG curve. The complex shows two-stage decomposition. The first stage of decomposition occurred at the temperature range of 90-250°C and second stage occurred at 250-320°C. In the two stage decomposition, at each stage, elimination of the ligand moiety was observed corresponding to a mass loss of 33% in both stages. For each stage of decomposition, the kinetic study was
carried out and the energy of activation for the reaction was calculated and presented in Table 4.17. The $\alpha$-$T$ plot for the decomposition of complex B-38 for each stage is illustrated (stage I- Fig. 4.10, and stage II- Fig. 4.11).

Table 4.17 Thermal Analysis data of B-38

<table>
<thead>
<tr>
<th>Complex</th>
<th>Stages of decomposition</th>
<th>% mass loss</th>
<th>Temp. range</th>
<th>Molecule eliminated</th>
<th>DTG Peak</th>
<th>$E_a$ (kJ)</th>
<th>$A$ ($\text{min}^{-1}$)</th>
</tr>
</thead>
<tbody>
<tr>
<td>B-38</td>
<td>I</td>
<td>33</td>
<td>90-250</td>
<td>ligand</td>
<td>98</td>
<td>22.867</td>
<td>2.563x10$^7$</td>
</tr>
<tr>
<td></td>
<td>II</td>
<td>33</td>
<td>250-320</td>
<td>ligand</td>
<td>298</td>
<td>-17.21</td>
<td>1.226x10$^8$</td>
</tr>
</tbody>
</table>

Fig. 4.10 $\alpha$-$T$ Plot for B-38(Stage I)

Fig. 4.11 $\alpha$-$T$ Plot for B-38(Stage II)
Based on all experimental data, a coordination number nine is assumed to the metal ions in the chloride complexes. A tentative structure was proposed for the complexes. (Structure 4.3)

4.4.3 Lanthanide(III) perchlorate complexes
4.4.3.1 Appearance and solubility of the complexes

All complexes are solids, dark brown in color and non-hygroscopic. All complexes are soluble in common organic solvents like methanol, ethanol, DMF, DMSO and insoluble in nitrobenzene, chloroform and benzene.

4.4.3.2 Elemental analysis

The percentages of metal, anion [197], carbon, nitrogen and hydrogen content in the complexes B-42 to B-48 were determined and presented in Table 4.18. The data suggest that these complexes may be formulated as $\text{Ln} (\text{L}^2)_2 (\text{ClO}_4)_3$ where Ln = La, Pr, Nd, Sm, Eu, Tb and Er.
### Table 4.18 Analytical data of complexes B-42 to B-48

<table>
<thead>
<tr>
<th>Complex</th>
<th>% C (obs/cal)</th>
<th>% H (obs/cal)</th>
<th>% N (obs/cal)</th>
<th>% M (obs/cal)</th>
<th>% CI⁻ (obs/cal)</th>
</tr>
</thead>
<tbody>
<tr>
<td>B-42</td>
<td>31.2(30.4)</td>
<td>3.6(3.6)</td>
<td>5.6(5.5)</td>
<td>13.0(13.5)</td>
<td>17.0(17.3)</td>
</tr>
<tr>
<td>B-43</td>
<td>33.4(30.4)</td>
<td>4.1(3.6)</td>
<td>5.2(5.4)</td>
<td>13.8(13.7)</td>
<td>16.0(17.3)</td>
</tr>
<tr>
<td>B-44</td>
<td>29.1(26.6)</td>
<td>3.9(3.2)</td>
<td>5.2(4.9)</td>
<td>11.8(12.3)</td>
<td>16.0(15.1)</td>
</tr>
<tr>
<td>B-45</td>
<td>29.3(30.1)</td>
<td>4.0(3.6)</td>
<td>5.3(5.4)</td>
<td>12.0(14.5)</td>
<td>18.0(17.0)</td>
</tr>
<tr>
<td>B-46</td>
<td>28.9(30.1)</td>
<td>3.9(3.6)</td>
<td>5.6(5.4)</td>
<td>13.5(14.6)</td>
<td>17.0(17.1)</td>
</tr>
<tr>
<td>B-47</td>
<td>31.9(29.9)</td>
<td>4.2(3.6)</td>
<td>5.3(5.4)</td>
<td>14.0(15.2)</td>
<td>17.5(15.2)</td>
</tr>
<tr>
<td>B-48</td>
<td>29.0(29.6)</td>
<td>4.0(3.5)</td>
<td>5.3(5.3)</td>
<td>13.9(15.4)</td>
<td>16.0(16.8)</td>
</tr>
</tbody>
</table>

**4.4.3.3 Molar conductance**

The molar conductance values for the complexes B-42 to B-48 are reported in Table 4.19. The values are in the range 180-185, 240-284 and 138-165 ohm⁻¹ mol⁻¹ cm² in acetone, acetonitrile and DMF respectively for lanthanum and praseodymium complexes (B-42 and B-43). These values suggest that these complexes behave as 1:2 electrolyte and for complexes B-44 to B-48, the values are in the range 118-135, 130-160 and 70-90 ohm⁻¹ mol⁻¹ cm². The values are in conformity with 1:1 electrolytic nature [204].

Hence, these complexes may be formulated as $[\text{Ln}(L^2)^2\text{ClO}_4](\text{ClO}_4)_2$ where Ln = La and Pr (B-42, B-43), and $[\text{Ln}(L^2)^2(\text{ClO}_4)_2]\text{ClO}_4$ where Ln = Nd, Sm, Eu, Tb and Er (B-44 to B-48).

### Table 4.19 Molar conductance* of complexes B-42 to B-48

<table>
<thead>
<tr>
<th>Solvent</th>
<th>B-42</th>
<th>B-43</th>
<th>B-44</th>
<th>B-45</th>
<th>B-46</th>
<th>B-47</th>
<th>B-48</th>
</tr>
</thead>
<tbody>
<tr>
<td>CH₃COCH₃</td>
<td>180</td>
<td>185</td>
<td>120</td>
<td>135</td>
<td>133</td>
<td>118</td>
<td>125</td>
</tr>
<tr>
<td>CH₃CN</td>
<td>240</td>
<td>284</td>
<td>130</td>
<td>150</td>
<td>145</td>
<td>135</td>
<td>160</td>
</tr>
<tr>
<td>DMF</td>
<td>138</td>
<td>165</td>
<td>65</td>
<td>70</td>
<td>82</td>
<td>85</td>
<td>90</td>
</tr>
</tbody>
</table>

*10⁻³ M solution
4.4.3.4 Infrared spectra

The structurally significant IR bands observed in the spectra of free ligand are 1623cm\(^{-1}\) (vC=N), 1201cm\(^{-1}\) and 1323cm\(^{-1}\) (vC–O) attributable to C–O (phenyl) and C–O (pyridyl) respectively. A strong band at 1110cm\(^{-1}\) attributed to vC–O) of the primary alcoholic group [235].

In the spectra of complexes, the band due to azomethine (–HC=N) was shifted to ± 2–10cm\(^{-1}\) indicating the involvement of this nitrogen atom in coordinate bond formation [236].

The typical bands at 1323cm\(^{-1}\) and 1201cm\(^{-1}\) of the ligand was shifted to ± 7-15cm\(^{-1}\) in all complexes ascertaining the participation of both –O–H groups in chelation. In all the complexes, these bands appeared in the range 1290-1320cm\(^{-1}\) and 1215-1229cm\(^{-1}\) [210].

The medium band displayed in the ligand at 1110cm\(^{-1}\) remains unaffected, indicating the non-participation of this OH in coordination. In the present nitrate complexes, the spectra show a broad medium intensity band in the region 3340-3500cm\(^{-1}\) and at 3280cm\(^{-1}\) indicating the presence of C–OH vibrations. This also indicates the non-coordination of the alcoholic OH present in the ligand. The band appearing at 605cm\(^{-1}\) is due to the bending of (O–H). Existence of this band is a strong support for the presence of water molecules, either coordinated or lattice water.

Sharp bands appearing in the range 2875-2916cm\(^{-1}\) are due to v(C–H) of methyl groups. The characteristic absorption bands resulting from the skeletal vibrations of the aromatic rings from the Schiff base ligands were observed at ~1440cm\(^{-1}\). Unaffected band at 3100-3200cm\(^{-1}\) confirms the non-involvement of ring nitrogen in complex formation.
In the IR spectra of the complexes, new bands were appeared characteristic of perchlorate group. Two distinctly split bands appeared in the range of $\sim 1080-1090 \text{ cm}^{-1}$ and $\sim 1120-1130 \text{ cm}^{-1}$ in all the complexes indicate coordinated perchlorate group of $C_{3v}$ symmetry [199]. The split bands at 610-615 cm$^{-1}$ and 625-630 cm$^{-1}$ in all complexes support the conclusion that perchlorate ion is coordinated monodentately.

In addition, all of them show two unsplit bands. Bands in the region $\sim 620-628 \text{ cm}^{-1}$ and $\sim 1100-1115 \text{ cm}^{-1}$ are assignable to the $\nu_4$ and $\nu_3$ modes of perchlorate group of $T_d$ symmetry [199]. Thus, perchlorate groups are also present outside the coordination sphere. This is in conformity with the conductivity values, which support the strong evidence of ionic perchlorate groups in these complexes.

New bands appeared in the frequency range $\sim 440-476 \text{ cm}^{-1}$ (Ln–O) and $\sim 410-436 \text{ cm}^{-1}$ (Ln–N) suggest that coordinate bond is formed between metal ion and the donor atoms of the ligand. Hence it can be concluded that the ligand $L^2$ act as a bidentate chelating ligand.

### Table 4.20 Important IR bands (cm$^{-1}$) of complexes B-42 to B-48

<table>
<thead>
<tr>
<th>Complex</th>
<th>C=N</th>
<th>C-O</th>
<th>C-O</th>
<th>Ln-O</th>
<th>Ln-N</th>
<th>ClO$<em>4^-$ ($C</em>{3v}$)</th>
<th>ClO$<em>4^-$ ($C</em>{3v}$)</th>
<th>ClO$_4^-$</th>
<th>ClO$_4^-$</th>
</tr>
</thead>
<tbody>
<tr>
<td>B-42</td>
<td>1602s</td>
<td>1310s</td>
<td>1217m</td>
<td>468w</td>
<td>428w</td>
<td>1084s</td>
<td>1120s</td>
<td>610m</td>
<td>628m</td>
</tr>
<tr>
<td>B-43</td>
<td>1621s</td>
<td>1290s</td>
<td>1227m</td>
<td>440w</td>
<td>416w</td>
<td>1090s</td>
<td>1118s</td>
<td>612m</td>
<td>630m</td>
</tr>
<tr>
<td>B-44</td>
<td>1621s</td>
<td>1300s</td>
<td>1217m</td>
<td>459w</td>
<td>424w</td>
<td>1078s</td>
<td>1122s</td>
<td>615m</td>
<td>624m</td>
</tr>
<tr>
<td>B-45</td>
<td>1601s</td>
<td>1298s</td>
<td>1215m</td>
<td>476w</td>
<td>410w</td>
<td>1074s</td>
<td>1130s</td>
<td>614m</td>
<td>632m</td>
</tr>
<tr>
<td>B-46</td>
<td>1602s</td>
<td>1301s</td>
<td>1216m</td>
<td>465w</td>
<td>417w</td>
<td>1088s</td>
<td>1128s</td>
<td>615m</td>
<td>632m</td>
</tr>
<tr>
<td>B-47</td>
<td>1620s</td>
<td>1317s</td>
<td>1229m</td>
<td>458w</td>
<td>422w</td>
<td>1079s</td>
<td>1126s</td>
<td>615m</td>
<td>628m</td>
</tr>
<tr>
<td>B-48</td>
<td>1604s</td>
<td>1318s</td>
<td>1217m</td>
<td>463w</td>
<td>436w</td>
<td>1080s</td>
<td>1122s</td>
<td>614m</td>
<td>627m</td>
</tr>
</tbody>
</table>

s: strong, m: medium, w: weak
4.4.3.5 UV-Visible spectra

Electronic spectra of the ligand show band maxima at 285nm and 365nm corresponding to the $\pi \rightarrow \pi^*$ and $n \rightarrow \pi^*$ respectively were shifted in the range 265-280nm in complexes. In the $n \rightarrow \pi^*$ transition, the maxima was slightly red shifted in the range 370-392nm also (Table 4.21).

<table>
<thead>
<tr>
<th>Complex</th>
<th>$\nu_{\text{complex}}$(cm$^{-1}$)</th>
<th>$\nu_{\text{aq}}$(cm$^{-1}$)</th>
<th>Transition</th>
<th>$\beta$</th>
<th>$b^{1/2}$</th>
<th>$\delta$</th>
<th>$\eta$</th>
</tr>
</thead>
<tbody>
<tr>
<td>B-48</td>
<td>20300</td>
<td>20412</td>
<td>$^4I_{15/2} \rightarrow ^2H_{11/2}$</td>
<td>0.9945</td>
<td>0.0370</td>
<td>0.5517</td>
<td>0.0742</td>
</tr>
<tr>
<td></td>
<td>18640</td>
<td>18850</td>
<td>$^4I_{15/2} \rightarrow ^4S_{3/2}$</td>
<td>0.9888</td>
<td>0.0527</td>
<td>1.1266</td>
<td>0.1061</td>
</tr>
</tbody>
</table>

The $f-f$ transitions observed in the solution state for perchlorate complex (B-48) and its tentative assignment are listed in Table 4.22.

These transitions were compared with those of the respective aqueous ions. The nephelauxetic effect $\beta$, $b^{1/2}$, $\eta$ and Sinha parameter $\delta$ were calculated for typical complexes and were presented in Table 4.22. The positive value of $b^{1/2}$ shows covalent nature of the metal-ligand band. The $\delta$ values were also found to be positive in the complexes indicating electron delocalization over $4f$ orbital, which also indicate a covalence nature between the metal ion and the ligand [151].
4.4.3.6 Magnetic Moment Studies

The magnetic moments were determined at 298K on a Gouy balance and the values of $\mu_{\text{eff}}$ calculated were found to be close to those obtained by VanVleck [208,235]. Only small deviations were observed. The results indicate that there is not much influence of the ligand field on $4f$ electrons of the lanthanide ions. In the Ln-O bond formation, a nonparticipation of the $4f$ electrons of the lanthanide ions in their complexes can be inferred. A comparison of the observed values with those calculated for uncomplexed ions supports the non participation of the $f$-electrons in bond formation. The values obtained are displayed in Table 4.23

Table 4.23 Observed magnetic moment values for B-42 to B-48

<table>
<thead>
<tr>
<th></th>
<th>B-42</th>
<th>B-43</th>
<th>B-44</th>
<th>B-45</th>
<th>B-46</th>
<th>B-47</th>
<th>B-48</th>
</tr>
</thead>
<tbody>
<tr>
<td>$\mu$ (BM)</td>
<td>--</td>
<td>3.61</td>
<td>3.48</td>
<td>1.6</td>
<td>8.1</td>
<td>9.2</td>
<td>7.8</td>
</tr>
</tbody>
</table>

4.4.3.7 $^1$H NMR spectra

NMR spectra were recorded in DMSO-$d_6$. TMS was used as the internal reference. The spectral data is reported in Table 4.24. Signals of the diamagnetic lanthanum complex were shifted to lower field compared to $L^2$. Broad signals appeared at $\delta = 3.8$ppm was attributed to H$_2$O protons [221]. Signals observed at $\delta = 8.1$ppm appeared in $L^2$ attributed to azomethine proton exhibit low fields shift to $\delta = 8.5$ppm. The resonance appeared at $\delta = 6.6$ppm in $L^2$ attributed to phenolic proton displayed downfield shift to $\delta = 6.7$ppm. The spectra obtained are consistent with the proposed structure [248].
Table 4.24 The important NMR signals (δ in ppm) of complex B-42

<table>
<thead>
<tr>
<th>Compound</th>
<th>(H₂O)</th>
<th>(C-CH₃)</th>
<th>(N-CH₃)</th>
<th>OH(phenol)</th>
<th>OH(alc)</th>
<th>(C=N)</th>
</tr>
</thead>
<tbody>
<tr>
<td>L²</td>
<td>--</td>
<td>3.3</td>
<td>3.60</td>
<td>6.6</td>
<td>3.5</td>
<td>8.1</td>
</tr>
<tr>
<td>B-42</td>
<td>3.8</td>
<td>3.4</td>
<td>3.64</td>
<td>6.7</td>
<td>3.5</td>
<td>8.5</td>
</tr>
</tbody>
</table>

4.4.3.8 Thermal analysis

A few representative complexes were selected for thermal studies. Based on mass loss, intermediate products and final residue, the assignment of decomposition was made.

Complexes B-42 and B-43 show similar decomposition pattern. Thermal decomposition data for B-42 is presented in Table 4.25. The TG curve indicates three-stage decomposition. The first stage of decomposition occurred in the temperature range 120-180°C with an observed mass loss of 1.7% corresponding to the removal of one molecule of uncoordinated water. An endothermic peak was observed at 150°C on the DTG curve at this stage. In the second stage of decomposition, a mass loss of 24% was observed in the range of temperature 180-320°C with a DTG shoulder at 280°C which accounts for the elimination of two uncoordinated perchlorate ions and also one molecule of coordinated water molecule. The third stage of decomposition starts at 320°C and ends at 580°C with a DTG peak at 450°C with the removal of the two ligand molecules and finally converted into lanthanum chloride, which was confirmed by spectral analysis of the residue [249,250].

Table 4.25 Thermal decomposition data of B-42

<table>
<thead>
<tr>
<th>Complex</th>
<th>Stages of decomposition</th>
<th>Mass loss %</th>
<th>Temp. range</th>
<th>Molecule eliminated</th>
</tr>
</thead>
<tbody>
<tr>
<td>B-42</td>
<td>I</td>
<td>1.7</td>
<td>120-160</td>
<td>H₂O</td>
</tr>
<tr>
<td></td>
<td>II</td>
<td>24</td>
<td>160-320</td>
<td>H₂O+ClO₄</td>
</tr>
<tr>
<td></td>
<td>III</td>
<td>70</td>
<td>320-580</td>
<td>Ligand molecules</td>
</tr>
</tbody>
</table>
Chapter 4

An investigation of kinetic parameters of the decomposition reaction was also carried out. The extent of the reaction was examined by Coats-Redfern equation by plotting $\log g(\alpha)$ versus $1/T$ for the decomposition reaction from TG curve. A plot of $\log[(\alpha)/T^2]$ versus $\log(1/T)$ was found to be a straight line, which was in agreement with a non-isothermal process. The slope of the straight line gives the energy of activation $E_a$ and the y-intercept gives the frequency factor $A$. The $\alpha$–$T$ plot of B-42 for stage II is illustrated (Fig. 4.12). Data is presented in Table 4.26

<table>
<thead>
<tr>
<th>Complex</th>
<th>Stage</th>
<th>$\Delta H$ (mJ)</th>
<th>Peak Area</th>
<th>Peak Temp</th>
<th>$E_a$ (kJ)</th>
<th>$A$ (min$^{-1}$)</th>
</tr>
</thead>
<tbody>
<tr>
<td>B-42</td>
<td>II</td>
<td>-63.43</td>
<td>-1645</td>
<td>290</td>
<td>-68.353x10$^{-5}$</td>
<td>0.0170</td>
</tr>
</tbody>
</table>

![Graph](image)

Fig. 4.12 $\alpha$–$T$ plot for complex B-42.(Stage II)

Structure 4.4 is tentatively suggested for complexes B-42, B-43 and structure 4.5 for complexes B-44 to B-48.
Studies on lanthanide complexes of 5-(Hydroxymethyl)-4-{1-Z)-[2-N(2-hydroxylphenyl)…

Structure 4.4. Proposed structure for [LnL₂ClO₄H₂O](ClO₄)₂H₂O (B-42, B-43)

Structure 4.5. Proposed structure for [Ln(L³)₂(ClO₄)₂H₂O]|ClO₄ (B-44 to B-48)
Table 4.27 The formulae and coordination number of the synthesized complexes.

<table>
<thead>
<tr>
<th>Formula</th>
<th>Lanthanide</th>
<th>Coordination number</th>
</tr>
</thead>
<tbody>
<tr>
<td>(<a href="%5Ctext%7BNO%7D_3">\text{Ln}(\text{L}^2)_2(\text{NO}_3)_2</a>_2)</td>
<td>La, Ce and Pr (B-27, B-28, B-29)</td>
<td>8</td>
</tr>
<tr>
<td>([\text{Ln}(\text{L}^2)_2(\text{NO}_3)_2]\text{NO}_3)</td>
<td>Nd, Sm, Eu, Gd, Dy and Er (B-30, B-31, B-32, B-33, B-34, B-35 in order)</td>
<td>10</td>
</tr>
<tr>
<td>([\text{Ln}(\text{L}^2)_2\text{Cl}_3])</td>
<td>La, Pr, Nd, Sm, Eu and Tb (B-36, B-37, B-38, B-39, B-40, B-41 in order)</td>
<td>9</td>
</tr>
<tr>
<td>(<a href="%5Ctext%7BClO%7D_4">\text{Ln}(\text{L}^2)_2\text{ClO}_4\text{H}_2\text{O}\text{H}_2\text{O}</a>\text{H}_2\text{O})</td>
<td>La and Pr (B-42, B-43)</td>
<td>8</td>
</tr>
<tr>
<td>([\text{Ln}(\text{L}^2)_2\text{ClO}_4\text{H}_2\text{O}\text{ClO}_4])</td>
<td>Nd, Sm, Eu, Tb and Er (B-44, B-45, B-46, B-47 and B-48 in order)</td>
<td>9</td>
</tr>
</tbody>
</table>

4.4.4 Biological Study

In vitro screening of the antimicrobial activities of eighteen selected complexes were performed. Antibacterial assay shows that \(\text{L}^2\) is nontoxic against all bacterial strains and fungi tested. The complexes show enhanced activity against most of the bacteria, fungi and algae.

Among the complexes of lanthanum, the perchlorate complex B-42 exhibited antagonistic ability by inhibition of the growth of most of the pathogenic bacterial strains. \(S.\ \text{aureus}\) was inhibited to the greatest extent followed by \(B.\ \text{cereus}\) by B-42. All the three complexes of lanthanum displayed toxicity towards \(E.\ \text{coli}\) in varying range. Among the three different complexes of lanthanum, the nitrate and perchlorate complexes can be regarded as much more effective against \(E.\ \text{coli}\) than the chloride complex. The perchlorate complex exhibited moderate toxicity against \(P.\ \text{aeruginosa}\) while the chloride analogue exhibited a minimum activity,
whereas the nitrate complex was the least affected. The perchlorate complex inhibited the growth of *B. subtilis* and *K. pneumoniae* whereas the nitrate and chloride complexes were shown to be ineffective against these two bacterial strains. *S. typhimurium* was found resistant to the nitrate complex whereas chloride and perchlorate complexes exhibit similar inhibition property.

Praseodymium perchlorate complex was nontoxic against all the eight bacterial strains evaluated. The chloride complex exhibited growth inhibition against two of the bacterial strains, which are *S. aureus* and *Klebsiella sps*. All other organisms effectively resisted this complex. The nitrate complex exhibited moderate toxicity against *S. aureus*, *B. cereus*, *E. coli* and *S. typhimurium*.

Neodymium chloride complex was non toxic towards all species for which the assays were performed while the nitrate complex inhibited the growth of *E. coli*. The perchlorate analogue exhibited moderate toxicity against *E. coli*, *B. cereus*, *S. aureus* and *S. typhimurium*

All the eight bacterial strains were resistant to the nitrate complex of samarium whereas the chloride complex was effective to a lesser extent against *E. coli* and is ineffective against all other organisms. The perchlorate complex exhibited very low activity against *E. coli*, *P. aeruginosa*, *B. cereus*, *B. subtilis*, *K. pneumoniae* and *S. typhimurium*. It is non toxic towards *K. sps* and *S. aureus*. The most potent complex among the series was identified as europium nitrate complex, which was shown to be a promising toxic agent against *E. coli*. This was the only complex which shows activity against all bacterial strains examined. The information obtained in the present study suggests that promising results in controlling the growth of *S. aureus* and *B.*
cereus were achieved under laboratory conditions by the application of lanthanum perchlorate complex.

All complexes showed variation in the level of activity against fungi spores. All strains differ in sensitivity to the synthesized complexes. Altogether seventeen complexes were chosen for the antifungal evaluation from the three series. Only a few of the complexes were toxic towards the tested fungi. Complexes B-27, B-29, B-32, B-36, B-37, B-38, B-39, B-41, B-42, B-43, B-45 and L² were shown to be non-toxic towards all the organisms. B-30 (the nitrate complex of neodymium) was reported to be the most effective antifungal agent against *Aspergillus niger* among the complexes of L². This complex exhibit moderate activity against *Scopulariopsis acremonium* and minimum activity against *Pleurotus sajor caju.*

Algal studies revealed that B-32 inhibit the growth of *Dunaliella salina* while *Isochrysis, Marine chlorella* and *Nannochloropsis* remain uninhibited. B-35 inhibited the growth of *Isochrysis* only. Only one chloride complex, B-37 was shown to inhibit the growth of *Dunaliella salina* and *Marine chlorella.* Among the perchlorate complexes evaluated, B-41 exhibited promising inhibition against *Dunaliella salina.* Complex B-42 inhibits the growth of both *Nannochloropsis* and *Dunaliella salina.* The nitrate complex of erbium was proved the most effective inhibiting agent for *Aspergillus niger.*

Activity against *Dunaliella salina* was documented with complexes B-32, B-42, B-43 and B-37. Specific activity against *Isochrysis* was exhibited by complex B-35. Of particular note was the potent activity of complex B-37 against *Marine chlorella.* In addition, *Nannochloropsis* was inhibited by B-43.
4.4.5 Conclusion

The present research work involves the synthesis of Schiff base ligand, 5-(hydroxymethyl)-4-{(1-Z)-[2-N(2-hydroxyphenyl)ethanimidoyl]2-methyl} pyridine-3-ol-hydrochloride-(L\(^2\)) from pyridoxal hydrochloride and 2-aminophenol, and its complexes from the respective lanthanide(III) chloride, nitrate and perchlorate salts and characterized by various physicochemical methods and spectral analysis.

The physical characterization revealed that the nitrate complexes of La, Ce and Pr behave like 1:2 electrolytic complexes and represented as [Ln(L\(^2\))\(_2\)(NO\(_3\))]\((\text{NO}_3)\)\(_2\), rest of the series behave like 1:1 electrolyte type, represented as [Ln(L\(^2\))\(_2\)(NO\(_3\))]\((\text{NO}_3)\). The chloride complexes behave as neutral and hence represented as [Ln(L\(^2\))\(_2\)Cl\(_3\)] and perchlorate complexes are represented as [Ln((L\(^2\))\(_2\)(ClO\(_4\)))\((\text{ClO}_4)\)\(_2\)] where Ln = Nd, Sm, Eu, Gd, Tb, and Er and [Ln(L\(^2\))\(_2\)(ClO\(_4\))]\((\text{ClO}_4)\)\(_2\), where Ln = La and Pr. Magnetic moment determination suggests paramagnetic nature for all complexes except lanthanum.

IR spectral studies revealed that the Schiff bases behave as tridentate chelating ligand and the chelation occurs via two oxygen atoms of phenolic group present in the phenyl ring and pyridyl ring and through azomethine group. IR spectral studies also evidenced that nitrate ion is coordinated to the metal ion bidentately and perchlorate ion is coordinated to the metal ion monodentately. UV-Visible spectral studies provided idea about the bonding nature of the ligand to the metal ion and it was possible to quantify the bonding parameters like inter electronic repulsion, nephelauxetic effect, Sinha’s covalency parameter etc. The information obtained from the NMR data revealed the coordination nature of –OH group. It is concluded that
the phenolic group was participated in bond formation via deprotonation in perchlorate complexes. Thermal analysis evidenced the stability of complexes. The nitrate complexes are thermally stable up to ~250-260°C. The chloride and perchlorate complexes are thermally stable upto ~180-190°C. The different stages of decomposition were examined and the kinetic parameters like energy of activation $E_a$ and Arrhenius parameter $A$ for the decomposition reaction show that the thermal decomposition reactions are non-isothermal.

The in vitro screening of the antimicrobial activities were performed. The information obtained in the present study suggest that promising results in controlling the growth of $S$. aureus and $B$. cereus were achieved by lanthanum perchlorate complex. A few complexes were proved as the most effective inhibiting agents for Aspergillus niger. Activity against Dunaliella salina was documented with few complexes. Specific activity against Isochrysis was exhibited by B-35. Complex B-37 effectively inhibited the growth of Marine chlorella and Dunaliella salina.

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