CHAPTER - 3
RESULTS AND DISCUSSION
**PART A: Results and Discussion**

The variations in the Oscillator Strength values (Tables OS 2.1.1 to OS 2.7.2), Judd Ofelt symmetry parameters (TL 2.1 to TL 2.7) and the radiative properties are recorded in (2.1.1 to 2.7.2) various tables in chapter 2 Part C as preliminary data.

A perusal of oscillator strength values for various binary and mixed ligand complexes exhibits a variation with respect to the metal ion environment which may be compared with the oscillator strength values obtained for the aquo complexes of the Ln(III) cation (Recorded in tables OS - 2.0.0).

The system undertaken in the present investigation includes simple binary complexes of three aromatic amino acid ligands and an antituberculosis drug Pyrazinamide.

The complexation equilibrium under investigation may be expressed as follows

\[ [\text{Ln(III).aqua}] + [L] \rightleftharpoons [\text{Ln(III).L}] + \text{aqua} \quad ...1 \]

where the incoming ligand undergoes complexation displacing the aqua ions. This causes a change in the metal ions environment consisting of a change in the electronic spectral parameter. Therefore, a comparison of the binary [ML] complexes with the corresponding aqua complexes shows a change in the electronic spectral parameters. A systematic investigation of the variations in the electronic spectral parameter with respect to ligand environment characteristics is the major aim of present work.

Lanthanoids are hard acid or class A accepter with large cationic radii and show a preference toward O-O donors ligand than the O-N and N-N donor ligands [1,2]. Since all the ligands in the present series are categorically O-N donor ligand, the complexation
equilibria are more facile. The ligands are expected to form zwitterions in lower buffer region on the basis of their soft basic nature and the presence of basic nitrogen. It, therefore, decreases the possibility of any metal-ligand interaction in this buffer region. The proton dissociation, however, increases as we move towards the higher buffer region increasing the degree of complexation. Keeping in view the pH dependence of the complexation equilibria, the pH ranges selected for the present studies vary between 3.5 to 5.5. The studies in the higher buffer regions beyond this buffer region have, however, been avoided keeping in view the hydrolysis of lanthanoid. Use of very dilute solution has also been made so as to avoided formation of any polymeric complexes [3].

The above stated studies have been carried out in our pilot investigation using pH-potentiometry so as to confirm and select the exact pH region for studies. The results of those studies have, however, not been reported for brevity [4]. The formation of mixed ligand complexes takes place following the equilibrium [5]

\[
\text{[Ln(III)] + [A] } \leftrightarrow \text{[Ln(III).A]} ;
\]

\[
[\text{Ln(III).A} + [L] ] \leftrightarrow \text{[Ln(III).A.L]} 
\]

which differs from the binary complexations equilibria in the fact that here the [L] combine with the [Ln(III)] which is already connected to a primary ligand [A], a situation similar to that in binary complexation equilibria where the [L] cobines with [Ln(III)] which is already in aquo complex form. Ethylene Diamine Tetra Actic acid (EDTA) has been chosen as a primary ligand in the present studies which is a robust ligand in nature [6]. The large coordination number, also restricts the formation of any higher complex species like 1:2 and even more. The strong complexing nature of EDTA also directs the
mixed ligand complexation equilibria

\[ [\text{Ln(III)}] + [A] \leftrightharpoons [\text{Ln(III).A}] \]
\[ [\text{Ln(III).A}] + [L] \leftrightharpoons [\text{Ln(III).A.L}] \]

where the complexations of \([\text{Ln(III).A}]\) is complete before the combination of \([L]\) with \([\text{Ln(III)}A]\) begins. The hard acid character of \(\text{Ln(III)}\) allows the primary complex \([\text{MA}]\) to retain some residual acid character which allows combination of \([L]\) with \([\text{Ln(III)}]\) which is already combined to \([A]\). This, however, increases the steric strain on the mixed-ligand complex which thereby affects the stability of the complex. This gets reflected in the electronic spectral parameters[7]. However, the large cationic size of \(\text{Ln(III)}\) where coordination number varies from 6 to 12 extends enough space for the secondary ligand to reside upon the remaining coordination sites left over after EDTA complexation.

The maximum coordination number extended by the central metal ion in the ternary complexes investigated in the present studies shows a maximum of 9 (in some cases 8). The \(\text{Ln(III)}\) metal ions chosen in the present studies include \(\text{Pr(III)}, \text{Nd(III)}, \text{Sm(III)}, \text{Eu(III)}, \text{Dy(III)}, \text{Er(III)}, \text{Tm(III)}\) where the first four \(\text{Ln(III)}\) belong to the lighter Lanthanoid series where the remaining last three belong to the heavier \(\text{Ln(III)}\) series.

In other words the first four elements represent the pre-Gd series whereas the other three represent the post-Gd element of the series. The concomitant lanthanoid contraction [8] causing a decrease in the ionic size leads to a change in the coordination number. The lighter lanthanoids have been reported to have shown a coordination number of nine (and even higher) whereas the higher lanthanoids in general show a coordination number eight [9].

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There are, however, disputes in the change in coordination number along the series, yet there are ample number of evidences both favouring and opposing the coordination number [10-12]. The studies reported from our laboratory, however, support a change in coordination number across Gadolinium (Gd(III)) in the series [13].

To investigate the effect of lanthanoid contraction and the concomitant changes in the coordination number and their reflections in the electronic spectral parameters is the second major aim of the present studies. The studies have been carried out in view of these two aims.

The changes in the ionic radii and the resulting changes in the coordination number cause a great change in the nephelauxetic parameters [14]. It has been reported that the changes in these parameters across the series are periodic in nature [15], where the periodicity has been sought to be on account of

i. - the spin (S) quantum number across the series,

ii. - changes in the orbital angular (L) quantum numbers across the series

iii. - the changes in the Total quantum number (J) across the series and

iv. - the changes in the stabilisation energy of the ground levels marked by the inter electronic repulsion (Racah) parameters and their coefficients.

The exhibition of the changes in these fundamental parameters in the solution properties of lanthanoids has also been reported to be on account of hydration [16], standard entropy [17], ionization potential [18] and several such properties. To investigate a probable possible role of these individual parameters in the electronic
spectral parameters is the additional part of the present investigations. The studies have been carried out in view of these aims.

The systematic investigation of the electronic spectral parameters under different ligand environments has been undertaken where the observed results have been interpreted in light of the above parameters.

In lanthanoids the 4f-shells are deeply seated and are less available for bonding. The high screening effect with strong shielding mechanism confines these orbitals within a definite region and thus get highly localised. This results in intense sharp peaks less interrupted by the ligand field and by the crystal field stabilisation. Thus the studies of the intense sharp peaks and its related parameters serve as a tool to investigate the symmetry changes, the changes in solution dielectrics and extent of metal ligand viscosity and the resulting entropy changes caused as a result of complexation[18]. The fundamental electronic spectral parameters which may be expressed by the oscillator strength values indicate the intensity of specific electronic transition or the susceptibility to which a specific transition is allowed. A picture of 4f - orbitals which are less perturbed by ligand field, the susceptibility of specific transition to the external field are determined by the tensor operators theoretically calculated by Carnall [19] and later on modified by Devlin [20] et al. The parameters may also be calculated [21] for various hosts / matrices making use of the S,L and J quantum numbers and the theoretical possibility of the transition states from ground levels and their free and forbidden transition modes. The oscillator strength values obtained for various metal ions (Pr(III) to Tm(III) ) in different ligand environments have been recorded in the previous chapter.
A perusal of the oscillator strength values in general shows a dependence on the pH values of the medium which in general appear to pass through a maxima at pH around 4 to 4.5. This may be attributed to a possible increase in the absorbing complex specie with pH of the medium. This is in agreement with the observation that the ligand dissociation increases with increased pH values which thereby increasing the concentration of complex specie. This in its turn increases the intensity of the specific allowed electronic transition. This trend continues with pH until a complete conversion of the free metal ion into complex form takes place. A dip in the intensity towards the higher buffer region may be due to formation of hydroxo complexes[22]. The strong complexing nature of the primary complexes does not allow any ligand replacement, at the same time the polydentate nature of EDTA rules out the possibility of any reproportionation or disproportional of the mixed ligand complex[23].

Tables (Tables OS2.1 to OS 2.7, chapter III) report 4 prominent allowed electronic transition for Pr (III), 9 for Nd(III), 4 for Sm (III), 5 for Eu (III), 7 for Dy (III), 9 for Er (III) and 4 for Tm (III) where the sequence within transition levels has been observed to be as follows:

Pr(III) \( ^3P_2 > ^3P_1, ^5H_6 > ^1D_2 > ^3P_0 \)

Nd(III) \( ^4G_{5/2}, ^2G_{7/2} > ^4D_{5/2} > ^4F_{7/2} > ^4F_{5/2} > ^2G_{7/2} > ^4F_{3/2} > ^2G_{9/2} > ^4F_{9/2} > ^2P_{1/2} \)

Sm(III) \( ^6P_{3/2} > ^4I_{13/2} > ^4I_{13/2} ( ^6P_{5/2} ) > ^4M_{15/2} ( ^4I_{11/2} ) \)

Eu(III) \( ^5L_6 > ^5H_6 > ^5L_7 > ^5G_6 > ^5D_2 \)

Dy(III) \( ^6P_7 > ^4K_{17/2} > ^4I_{15/2} > ^6F_{5/2} > ^4F_{9/2} > ^4G_{11/2} > ^6P_{5/2} \)

Er(III) \( ^4G_{11/2} > ^2H_{11/2} > ^4F_{7/2} = ^4G_{9/2} > ^4G_{9/2} > ^4F_{5/2} > ^2K_{15/2} > ^2G_{9/5} \)

Tm(III) \( ^3F_3, ^3F_2 > ^1P_2 > ^3H_4 > ^1G_4 \)

The sequences are in agreement with the theoretical
Fig. 3.1.1
Variation in the Oscillator strength values with pH of the mediums
values of tensor operators reported by Carnall and Devlin. The deviation from the theoretical trend may be due to ligand mediated excitation of transition level which has been observed and reported by Mishra et al [24]. Similar studies have also been reported from our laboratory for same binary and mixed ligand complexes of amino acids.

The observed sequence in the oscillator strength values with respect to the ligands given as follows is the expected sequence on the basis of their ligand basacities.

\[
\begin{align*}
\text{Pr(III)} & : {^3P_2} > {^3P_1} > {^1I_6} > {^1D_2} > {^3P_0} \\
\text{Nd(III)} & : {^4G_{5/2}} > {^4D_{7/2}} > {^4F_{5/2}} > {^4F_{7/2}} > {^2G_{5/2}} > {^4F_{3/2}} > {^2G_{9/2}} > {^4F_{9/2}} > {^2P_{1/2}} \\
\text{Sm(III)} & : {^6P_{3/2}} > {^4I_{13/2}} > {^4I_{13/2}}({^6P_{5/2}}) > {^4M_{15/2}}({^4I_{11/2}}) \\
\text{Eu(III)} & : {^5L_{6}} > {^5H_{6}} > {^5L_{7}} > {^5G_{6}} > {^5D_{2}} \\
\text{Dy(III)} & : {^6P_{7}} > {^4K_{17/2}} > {^4I_{15/2}} > {^6F_{5/2}} > {^4F_{9/2}} > {^4G_{11/2}} > {^6P_{5/2}} \\
\text{Er(III)} & : {^4G_{11/2}} > {^2H_{11/2}} > {^4F_{7/2}} > {^4F_{9/2}} > {^4G_{9/2}} > {^4F_{5/2}} > {^2K_{15/2}} > {^2G_{9/5}} \\
\text{Tm(III)} & : {^3F_{3}} > {^3F_{2}} > {^1P_{2}} > {^3H_{4}} > {^1G_{4}}
\end{align*}
\]

There are, however, deviations from the general trend for pre-Gd elements to post-Gd elements perhaps due to nephelauxetic consequences of the lanthanoid contraction (8). The smaller cationic sizes with increased ionic potentials are expected to get more polarized under the ligand field there by increasing the extent of metal-ligand interaction. This in turn may influence the nephelauxetic parameters there by increasing the oscillator strength values. Similarly in case of mixed ligand complexes, the varied responses of the secondary ligands, might be due to residual acid character on the metal and the effective softness of primary ligand combinations.

An attempt has made to evaluate the matching constants for the binary and the mixed ligand complexes of the present series. Table 3.1. gives the variation in the metal ion hardness and the ligand softness values along
<table>
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<tr>
<th>S.NO</th>
<th>Ln(III)</th>
<th>HARDNESS $H_A$</th>
<th>SOFTNESS $H_S$</th>
<th>Matching Constant $C_{L1}$</th>
<th>Matching Constant $C_{L2}$</th>
<th>Matching Constant $C_{L3}$</th>
<th>Matching Constant $C_{L4}$</th>
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<td>2.</td>
<td>Nd(III)</td>
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<td>32.059</td>
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<td>3.</td>
<td>Sm(III)</td>
<td>10.252</td>
<td>32.362</td>
<td>32.125</td>
<td>32.0634</td>
<td>31.922</td>
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<tr>
<td>4.</td>
<td>Eu(III)</td>
<td>10.223</td>
<td>32.333</td>
<td>32.096</td>
<td>32.0344</td>
<td>31.859</td>
<td>31.859</td>
</tr>
<tr>
<td>5.</td>
<td>Dy(III)</td>
<td>10.16</td>
<td>32.27</td>
<td>32.033</td>
<td>31.971</td>
<td>31.818</td>
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<td>7.</td>
<td>Tm(III)</td>
<td>10.088</td>
<td>32.234</td>
<td>31.961</td>
<td>31.899</td>
<td>31.787</td>
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</tbody>
</table>

Table 3.1. Variation in the Metal Hardness and Ligand softness Values along with the calculated values of Matching constants.
Chapter 3: Results And Discussion

with their matching constant values.

As regards the organic reactivity of the lanthanoid ions various reasons have been given [25] based on varied responses of lanthanide cations. The observations are based on assumptions that these interactions occur through a coordination of substrata to the metal ion. Thus the different reactivity between the various Ln(III) cations can be ascribed to a first approximation, to their different affinity (hard soft acid base reactivity) for a given substrate. Consequently a better knowledge of a lanthanoid selectivity for the ligands may be allowed from the deeper insight of the reactivities between various Ln(III) cations. An evaluation of the relative matching constant values for the given set of complexes has been done in order to observe the relative responses of these ligands to the Ln(III) ions; at the same time to examine the relative responses of the Ln(III) cations to the complex bases. The present studies are based on the concept of charge and frontier orbital control method [26,27]. Fig. 3.1. A-B records the variations in the hardness values of the titled Ln(III) cations and also the matching constants for the binary complexes under study. The plots indicate a periodicity with decreasing hardness values from pre-Gd elements to post-Gd elements which may be on account of decreased electrostatic Ln(III)-L interaction or an increased covalency factor in the Ln(III)-L bond. It is however, evident that the magnitudes of the semisigmoid heaps decrease with complexation showing a dominant role played by the ligands in the matching constant values. This points towards the robust characteristics of the titled ligands and the role of steric parameters in the Ln(III)-L interactions. Fig. 3.1. C-D shows the variations in the matching constant values with the relative softness values of the ligands. The plots represent the two members of the pre-Gd series, however, it may be observed that the variation for-pre-Gd elements is almost similar to that
Fig - 3.1.2

Variation in the Metal Softness Values (A) and the matching constant values for the complexes (B) for the Ln(III) ions of the present series and for Pr(III),Nd(III) with respect to ligands.
observed for the post-Gd elements. An almost linear nature of the plots is indicative of the dependence of the matching constant values on the ligand characteristics.

The observed sequence within oscillator strength values for binary and corresponding mixed ligand complexes shows a general sequence **MAL > ML** which is expected on the basis of operative electrostatic effect. In binary complexes the L combines with the bare (aquated) metal ion forming a complex, therefore, the coulombic attraction between the Ln\(^{3+}\) and L\(^{n-}\) (n = -1 or -2) facilitates the binary complexation, however, in case of mixed ligand complexes where the secondary ligand L\(^{n-}\) combines with the primary complex [MA]\(^n\) (where n = (Q\(_{Ln}^{3+}\); Q\(_{L}^{n-}\); n is in general -1 for lanthanoids) experiences electronic repulsion. On account of these electrostatic interactions the [ML] binary interactions are expected to be more facile than the corresponding ternary complexation thereby influencing the nephelauxetic parameters and, in turn, the oscillator strength values for the cited systems. The deviation from the trend may be attributed to the involvement of factors other than electrostatic viz., steric, thermodynamic and other astatistical factors[28].

The oscillator strength (P) values that are composed of three parameters termed as Judd-Ofelt parameters, may be expressed by the following expression given by Judd.

\[
P = T_{\lambda} E \{ f^n \psi J | | U^{\lambda} | f^n \psi J' \}^2 \quad \ldots(4)
\]

where \(\lambda = 2, 4, 6; P\) is the oscillator strength corresponding to the induced electric dipole transition \(\psi J \rightarrow \psi'J'\) at energy \(E\) (in cm\(^{-1}\)) and \(U^{\lambda}\) is a Tensor operator of rank \(\lambda\). The values of matrix elements of \(U^{\lambda}\) were taken from literature[19,20]. The three quantities \(T_{\lambda}\) (\(\lambda=2,4,6\)) are
related to the radial part of the wave function \(4f^n\), which the nearest is \(4f^{n-1} 5d\), the refractive index of the medium and the ligand field parameters which characterise the environment of the medium. In principle, values of \(T_\lambda\) may be calculated from the experimental values of the oscillator strength.

Carnall [19] has pointed out the proportionality of the \(T_\lambda\) parameters, using a crystal field model which may be expressed as

\[
T_\lambda \sim <r^{\lambda+1}>^2 R^{-2t-2} \quad \ldots (5)
\]

where for \(\lambda = 2, t = 1 \) and \( 3 \); for \( \lambda = 4, t = 3 \) and \( 5 \) and for \( \lambda = 6, t = 5 \) and \( 7 \). This expects an order of decreasing sensitivity of the \(T_\lambda\) parameter to the environment giving rise to a theoretical sequence of \(T_2 < T_4 < T_6\) to the \(T_\lambda\) parameters.

The values of Judd Ofelt parameters \((T_\lambda\) and \(\Omega_\lambda\)) for the present series are recorded in the subsequent Table TL-2.1 to TL-2.7, where a comparative variation of their values has been demonstrated through 3D Excel bar diagrams. These are recorded in figure 3.1.1A,B to 3.1 7A,B for various metal ions respectively. Figures A and B represent the Binary and ternary systems where rows 1,2,3 and 4 record the four ligands respectively and S1,S2 and S3 represent the \(T_2\), \(T_4\) and \(T_6\) respectively.

The observed values of \(T_\lambda\) in general exhibit a sequence \(T_2 < T_4 < T_6\). As mentioned above, among the \(T_\lambda\) value \(T_2\) is indicative of the covalency or the orbital interaction part of a near-LCAO model for the Ln-L interaction where as the \(T_4\) and \(T_6\) parts exhibit the symmetry perturbations associated with the metal ligand interaction. It may be stated that the parameter \(T_2\) which is covalency denoting parameter is expected to be small in case of \(4f\)-shell. In lanthanides the bare metal ion \(Ln^{3+}\) is nothing but the \(4f\)-shell core which is exposed directly to the ligand field. However, these deeply seated \(4f\)-shells being strongly shielded
Variation in the Judd-Olfelt ($T_i$) values for the titled Ln(III) ions with respect to ligand for Binary and Ternary systems.
Variation in the Judd Ofelt ($T_\alpha$ values) parameters for the titled Ln(III) ions with respect to Ligand for Binary and Ternary systems

![Bar graph for Binary Systems](image)

**Figure 3.1.4A**

![Bar graph for Ternary Systems](image)

**Figure 3.1.4 B**
Variation in the Judd Ofelt ($T_{\alpha}$ values) parameters for the titled Ln(III) ions with respect to Ligand for Binary and Ternary systems.

**Figure 3.1. 5 A**

**Figure 3.1. 5 B**

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Variation in the Judd Ofelt ($T_i$ values) parameters for the titled Ln(III) ions with respect to Ligand for Binary and Ternary systems.
Variation in the Judd Ofelt ($T_{\alpha}$ values) parameters for the titled Ln(III) ions with respect to Ligand for Binary and Ternary systems.

Figure 3.1. 7 A

Figure 3.1. 7 B
Variation in the Judd Ofelt ($T_x$ values) parameters for the titled Ln(III) ions with respect to Ligand for Binary and Ternary systems.

**Figure 3.1.8 A**

**Figure 3.1.8 B**
Variation in the Judd Ofelt ($T_\alpha$ values) parameters for the titled Ln(III) ions with respect to Ligand for Binary and Ternary systems.

**Figure 3.1.9 A**

**Figure 3.1.9 B**
<table>
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<tr>
<th>Ln(III)</th>
<th>SYSTEM</th>
<th>Ratio (%)</th>
<th>SARCOCINE</th>
<th>PYRAZINAMIDE</th>
<th>LYSINE</th>
<th>HISTIDINE</th>
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<td>Pr(III)</td>
<td>ML</td>
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<td></td>
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<td>--</td>
<td>30.07</td>
<td>52.77</td>
<td>--</td>
</tr>
<tr>
<td></td>
<td></td>
<td>T6</td>
<td>--</td>
<td>69.93</td>
<td>47.23</td>
<td>--</td>
</tr>
<tr>
<td></td>
<td>MAL</td>
<td>T2</td>
<td>--</td>
<td>55.81</td>
<td>41.57</td>
<td>--</td>
</tr>
<tr>
<td></td>
<td></td>
<td>T6</td>
<td>--</td>
<td>44.19</td>
<td>58.43</td>
<td>--</td>
</tr>
</tbody>
</table>
and with high screening effects are expected to be less available for bonding thereby decreasing the covalency part in the Ln(III).L interaction. Thus the Ln-L bonds are expected to be predominantly ionic (with probable partial covalency). Therefore, smaller value of parameter $T_2$ among the $T_{\kappa}$ parameter becomes an expected feature.

Large cationic radii of lanthanoids [Ln(III)] with large three concentric hydration zones, on the other hand, may lead to greater change in symmetry as a result of viscinal [Ln(III).L] interaction. This in its turn, is expected to increase the symmetry perturbations parameters, indicated by $T_4$ and $T_6$ amongst the $T_{\kappa}$ parameters. Thus the values of $T_4$ and $T_6$ are expected to be larger. This justifies the observed sequence of $T_2 < T_4 < T_6$ for $T_{\kappa}$ values. The observed sequence for the $T_{\kappa}$ parameters is in general in good agreement with the theoretical explanation. Deviations from theoretical trend may be on account of sterio parameters associated both with metal and ligand.

An evaluation of relative involvement of $T_2$ and $T_6$ parameters [Table 3.1] may be expressed by the ratio (or percentage) of $[T_2/T_6]$ for various metal ions in different ligand environment. The $T_2$ values interestingly show smaller magnitude for pre-Gd elements than the post-Gd elements. This smaller magnitude may be on account of the intimate/viscinal interaction in the metal-ligand by increased lanthanoid contraction. Also the increase polarizability with concomitant lanthanoid contraction may also add to increase in the extent of metal-ligand interaction. The $T_6$ parameters have, however, shown higher values for the pre-Gd element than the post-Gd element which may attributed to symmetry perturbation originated by the rupture of the associated concentric hydration zones on metal ligand interaction. The values, however, show a gradual decrease in the $T_6$ parameters for post-Gd elements which is significantly small as re-
gards the lanthanoid contraction. The lanthanoid ion contracts ~17% of
its radius from La(III) to Lu(III), thereby increasing the ionic potential and
thus the size of the concentric hydration zone for the post Gd element. In
comparison to this expansion in the hydration zone (by ~20%) the symme-
try parameters said to be associated with the cation environment also
change. It is due to the rapture of this thowed hydration zone. This may
lead us to a conclusion that the lanthanoid interactions are predominately
ionic with minimal covalent interaction and the bonding pattern shows a
gradual change from a predominately ionic (electrostatic) form to a par-
tial ionic (partial covalent (or covalo electrostatic)) from pre Gd ele-
ments to post Gd elements.

The studies also reveal an interesting pattern with respect to sec-
ondary ligand and the corresponding ternary complexes. Amongst all the
ligand studied in the present case histidine and pyrazinamide being aro-
matic ligands lack conformational freedom and exhibit great changes in
symmetry and covalency than the lysine and sarcosine. These being small
appear to have a more close metal ligand interaction and thus add to a
greater symmetry perturbation. Lysine, however, has shown both favoured
and unfavoured steric condition which may be attributed to the long
subordinated side change. It has been reported [29-31] that the long side-
chain in amino acids has a tendency to coil around the metal centre by
virtue of the hydrophobicity. This phenomenan appears to take place in
the present series of complexes, there by showing irregular values of sym-
metry and covalency parameter. A probable / possible cooperative role of
the substituted side-chain may extend to favoured structural modifica-
tion thereby causing a change in the Tₚ parameter.

A better insight of the mode of bonding pattern may be
visualised from the analysis of inter-electronic repulsion Racah para...
eters and nephelauxetic ratio values. Table- 3.2 states the IERP Racah parameters and the nephelauxetic ratio values for various binary and mixed ligand environment for Pr(III), Nd(III) and Er(III).

The variations in the inter electronic repulsion Racah parameters suggest that the Racah notations [32] are more suitable for explanation as the E⁰ values which state the variation in the energy from baricentre are negligible as compared to the ground energy of the core and E² is = 0 (zero). The E¹ and E³ represent the effect of external field on the 4f electron wave function. The E¹ corresponds to the radial elongation of the wave function where as E³ correspond to the orbital distortion. A bare lanthanoid [ Ln³⁺] ion (6s²;5d¹ electrons ionised) when exposed to ligand field, the outerlyng 4f-shell core faces the ligand field. The 6s²,5d¹ electron may add to extend predominantly ionic character to [Ln- L ] bond, however, the incoming ligand field is expected to influence the 4f-shell core, though marginally, causing a change in the IERP Racah parameters and the related nephelauxetic ratio. Thus the possible/probable role of the incoming ligand may be estimated to [6];

(i) Radially elongate the 4f- wave function causing a change in E¹,
(ii) Radially distort the 4f- wave function causing a change in E³ parameters or
(iii) Changing the nephelauxetic ratio (covalency factor |δE³/δE¹|.

The δE¹ and δE³ values for the present case lie with in 1% of E¹ and E³ which is in agreement with the theoretically observed range, and δE³/δE¹ ratio values lie within the range - 0.091< E³/E¹ > 0.214. This justifies the validity of the present calculation. A perusal of E³/E¹ values show a marked dependence on the ligand characteristics. This dependancy may be attributed to the effective influence of the ligand field on the radial elongation and orbital distortion of the 4f electron wave functions. This
### Table 3.1.3

Variations in the Inter electronic Repulsion Racah parameters (δE¹, δE³) and the Nephelauxetic ratio (δE⁵/δE¹) Values

<table>
<thead>
<tr>
<th>Ligand</th>
<th>Ln(III)</th>
<th>Partial</th>
<th>δE¹</th>
<th>δE³</th>
<th>δE⁵/δE¹</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td></td>
<td>(in esu)</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>1. Sar</td>
<td>Pr(III)</td>
<td>0.3461</td>
<td>-1.638</td>
<td>0.319</td>
<td>0.195</td>
</tr>
<tr>
<td></td>
<td>Nd(III)</td>
<td>16.12</td>
<td>3.11</td>
<td>0.193</td>
<td></td>
</tr>
<tr>
<td></td>
<td>Er(III)</td>
<td>98.2</td>
<td>18.46</td>
<td>0.188</td>
<td></td>
</tr>
<tr>
<td>1. Sar</td>
<td>Pr(III)</td>
<td>0.6031</td>
<td>-1.235</td>
<td>0.202</td>
<td>0.164</td>
</tr>
<tr>
<td></td>
<td>Nd(III)</td>
<td>12.538</td>
<td>1.078</td>
<td>0.086</td>
<td></td>
</tr>
<tr>
<td></td>
<td>Er(III)</td>
<td>11.11</td>
<td>1.067</td>
<td>0.096</td>
<td></td>
</tr>
<tr>
<td>2. Pyrzmd</td>
<td>Pr(III)</td>
<td>0.4379</td>
<td>5.36</td>
<td>0.981*</td>
<td>0.183</td>
</tr>
<tr>
<td></td>
<td>Nd(III)</td>
<td>-12.35</td>
<td>-2.013</td>
<td>0.163</td>
<td></td>
</tr>
<tr>
<td></td>
<td>Er(III)</td>
<td>-6.3</td>
<td>1.1088</td>
<td>0.176</td>
<td></td>
</tr>
<tr>
<td>2. Pyrzmd</td>
<td>Pr(III)</td>
<td>0.6949</td>
<td>14.3</td>
<td>2.022</td>
<td>0.154</td>
</tr>
<tr>
<td></td>
<td>Nd(III)</td>
<td>3.144</td>
<td>0.295</td>
<td>0.094</td>
<td></td>
</tr>
<tr>
<td></td>
<td>Er(III)</td>
<td>6.54</td>
<td>0.5625</td>
<td>0.086</td>
<td></td>
</tr>
<tr>
<td>3. Lycn</td>
<td>Pr(III)</td>
<td>0.4772</td>
<td>-3.54</td>
<td>-0.613</td>
<td>0.173</td>
</tr>
<tr>
<td></td>
<td>Nd(III)</td>
<td>8.54</td>
<td>1.221</td>
<td>0.143</td>
<td></td>
</tr>
<tr>
<td></td>
<td>Er(III)</td>
<td>-1.23</td>
<td>0.1945</td>
<td>0.158</td>
<td></td>
</tr>
<tr>
<td>3. Lycn</td>
<td>Pr(III)</td>
<td>0.7342</td>
<td>8.25</td>
<td>0.7672</td>
<td>0.093</td>
</tr>
<tr>
<td></td>
<td>Nd(III)</td>
<td>6.32</td>
<td>0.436</td>
<td>0.069</td>
<td></td>
</tr>
<tr>
<td></td>
<td>Er(III)</td>
<td>-1.23</td>
<td>-0.078</td>
<td>0.063</td>
<td></td>
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<tr>
<td>4. Hist</td>
<td>Pr(III)</td>
<td>0.4881</td>
<td>12.3</td>
<td>1.243</td>
<td>0.101</td>
</tr>
<tr>
<td></td>
<td>Nd(III)</td>
<td>10.6</td>
<td>1.049</td>
<td>0.099</td>
<td></td>
</tr>
<tr>
<td></td>
<td>Er(III)</td>
<td>0.91</td>
<td>0.0664</td>
<td>0.073</td>
<td></td>
</tr>
<tr>
<td>4. Hist</td>
<td>Pr(III)</td>
<td>0.7451</td>
<td>21.8</td>
<td>1.853</td>
<td>0.085</td>
</tr>
<tr>
<td></td>
<td>Nd(III)</td>
<td>14.3</td>
<td>0.958</td>
<td>0.067</td>
<td></td>
</tr>
<tr>
<td></td>
<td>Er(III)</td>
<td>1.36</td>
<td>-0.0318</td>
<td>-0.023</td>
<td></td>
</tr>
</tbody>
</table>
also serves as an evidence to 4f-delocalization under the ligand field. A more quantitative correlation with the ligand characteristic have been made in part B of this chapter.

An overall comparison in the electronic spectral parameters for lanthanoid, specifically, with respect to the oscillator strength values for the hypersensitive and ligand mediated pseudo-hypersensitive transitions show the following sequence

Table 3.1.4

<table>
<thead>
<tr>
<th></th>
<th>Ln(III)</th>
<th>Er(III)</th>
<th>Nd(III)</th>
<th>Tm(III)</th>
<th>Pr(III)</th>
<th>Sm(III)</th>
<th>Dy(III)</th>
<th>Eu(III)</th>
</tr>
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<tbody>
<tr>
<td>Assign.</td>
<td>4G 1/2</td>
<td>4G 5/2</td>
<td>3F 3</td>
<td>3P 2</td>
<td>6P 3/2</td>
<td>6P 7/2</td>
<td>5L 6</td>
<td></td>
</tr>
<tr>
<td>E cm⁻¹</td>
<td>26400</td>
<td>17300</td>
<td>14500</td>
<td>22600</td>
<td>24950</td>
<td>28500</td>
<td>25400</td>
<td></td>
</tr>
<tr>
<td>S</td>
<td>3/2</td>
<td>3/2</td>
<td>2/2</td>
<td>2/2</td>
<td>5/2</td>
<td>5/2</td>
<td>6/2</td>
<td></td>
</tr>
<tr>
<td>L</td>
<td>6</td>
<td>6</td>
<td>5</td>
<td>5</td>
<td>5</td>
<td>5</td>
<td>3</td>
<td></td>
</tr>
<tr>
<td>J</td>
<td>5 3/2</td>
<td>9/2</td>
<td>12 5/2</td>
<td>8 5/2</td>
<td>5 5/2</td>
<td>15 1/2</td>
<td>0</td>
<td></td>
</tr>
</tbody>
</table>

The trend in the energy of the HST (and pseudo HST) assignment with respect to S, L and J quantum numbers shows a very interesting feature (cf. above table). Cations having S = 3/2 and L = 6 have expressed greater susceptibility to the hypersensitive transitions as compared with other cations. The cations having S = 2/2 and J = 12/2, 8/2 have shown lesser stability whereas the cation with S = 6/2 and J = 0 have shown least sensitivity of the peaks. Also a perusal of the E values shows that most of the peaks lie a in near UV (higher energy) region.

A more quantitative correlation with the ligand characteristics has been made in part B of this chapter.
Radiative Properties:

Radiative properties evaluated for the present set of complexes (Record in tables -RAD2.1.1 to RAD2.7.2) have been used to examine the effect of ligand environments on the 4f-shell delocalisations. The radiative parameter includes the electric dipole moment of specific electronic transition under the ligand field. These parameters have been evaluated for possible transition of intermediate fluorescent levels. This gives a measure of the electric component associated with the excitation of specific electronic transition under the ligand field. A perusal of these values shows a general sequence with respect to the prominent electronic transition which is a sequence of their relative allowance.

Pr(III) $^3P_2 > ^3P_1, ^1I_6 > ^1D_2 > ^3P_0$
Nd(III) $^4G_{5/2}, ^2G_{7/2} > ^4D_{5/2} > ^4F_{7/2} > ^4F_{5/2} > ^2G_{7/2} > ^4F_{3/2} > ^2G_{9/2} > ^4F_{9/2} > ^2P_{1/2}$
Sm(III) $^6P_{3/2} > ^4I_{13/2}, ^4I_{13/2} > ^6P_{5/2} > ^4M_{15/2} ( ^4I_{11/2} )$
Eu(III) $^5L_6 > ^5H_6 > ^5L_7 > ^5G_6 > ^5D_4$
Dy(III) $^6P_7 > ^4K_{17/2} > ^4I_{15/2} > ^6F_{5/2} > ^4F_{9/2} > ^4G_{11/2} > ^6P_{5/2}$
Er(III) $^4G_{11/2} > ^2H_{11/2} > ^4P_{7/2} > ^4G_{9/2} > ^4G_{5/2} > ^2K_{15/2} > ^2G_{9/2}$
Tm(III) $^3F_3 > ^3F_2 > ^1P_2 > ^3H_4 > ^1G_4$

Since the excitation has been considered to be on account of electric dipole (magnetic dipole either not calculated or considered to be negligible for the present series) moment values are expected to show a dependence on the ligand basicity. A better quantitative analysis of this dependence has been attempted in the part B of this chapter.

The radiative life time and the branching ratio for the intermediate transition levels show a marked dependence on the ligand basicity and the type of metal ligand interaction. The radiative life time $\lambda_T$ gives a measure of the probability factor of resting or residing of an electron in a specific electronic transition from ground level to the intermediate
Fig. 3.1.10 A,B

Evaluation of the relaxation timings for the intermediate fluorescent transition levels for Pr(III) complexes

\[ ^3H_4 \]
\[ ^3P_1 \]
\[ ^3P_2 \]
\[ ^1D_2 \] [Pr (III).Sarcocine]

\[ ^3H_4 \]
\[ ^3P_1 \]
\[ ^3P_2 \]
\[ ^1D_2 \] [Pr (III).A.Sarcocen]
Evaluation of the relaxation timings for the intermediate fluorescent Transition levels for Nd(III) complexes

\[ \text{Tm(III).Sarco} \]

\[ \text{Tm(III).EDTA.Sarco} \]

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Fig.: 3.1.12 A,B:

Evaluation of the relaxation timings for the intermediate fluorescent transition levels for Er (III) complexes

\( ^4I_{15/2} \)

\( ^4G_{11/2} \)

\( ^4F_{7/2} \)

\( ^4F_{5/2} \)

\( ^2G_{(1)9/2} \)

\( ^4F_{9/2} \)

\( ^4S_{3/2} \)

\( ^4I_{15/2} \)

[Er(III).Sarcoen]

\( [\text{Er(III).EDTA.Sarcoen}] \)

\( 152 \)
Evaluation of the relaxation timings for the intermediate fluorescent Transition levels for Tm(III) complexes
allowed levels. The transition, however, shows an increase for the high energy level transitions than the lower energy levels. In other words an electron prefer to stay for a lesser time in the high energy transition levels than the lower energy transitions. This may be attributed to the interference between the vibronic transitions associated with the low energy levels. It is, however, expected to vary from matrix to matrix and host to host.

Figures 3.1.10 A,B to 3.1.13A,B record the ray diagrams for the $A_r$ values for some representative binary and ternary cases for Pr(III), Nd(III), Er(III) and Tm(III). The ray diagrams indicate the calculated relaxation timings for the various intermediate levels along with the derived values for the relaxation timings for other intermediate levels not used in the calculations. (Marked with dotted lines in figures).

The $A_r$ and $T_R$ values, however, show a different trend for sarcosine than the three ligand which may possibly be on account of restricted electronic transition with increased vicinity of the ligand. The correlation has been examined in greater detail in part B of this chapter. $A$, $A_r$ and $T_R$ values, however, follow same trend with respect to other transition levels.

On the basis of all these values and the possible interpretation, it may be stated that these different ligand environments exhibit a significant compositional effect on the electronic spectral parameters and the radiative properties. It also supports the observation of effective 4f-delocalization under the ligand field.
3.2 PART B: SOME PROPERTY CORRELATIONS

General Discussion

Part A describes an account of the observed result and probable interpretation in the light of the metal ion and the ligand characteristic. To have a better insight into the metal ligand interaction and the role of fundamental characteristics of Ln(III) correlations between the spectral parameters and the fundamental properties of lanthanoids and the ligand under study, have been sought.

In lanthanoids the f-f level transitions are said to be operated by the transition from J to J+1 levels. Since the J values are composed of S and L their values for pre-Gd elements are equal to L - S, for post Gd elements are equal to L + S. A direct correlation is expected in the electronic spectral parameters and the fundamental quantum numbers of the lanthanoid elements. An attempt has been made to examine such correlation in the coming part of this chapter.

Yatsimirskii and Devidenko [30] attempted a correlation between the energy of some J-J transition (E cm⁻¹) with the metal ligand donor atom bond distance [Ln (III) - O] in Å. With a view to estimate the coordination number of the lanthanoid ion similar coordination has been attempted for the present series of O-O and O-N donor ligand for Pr(III) and Nd(III). The transition \(^{3P_0} \leftarrow \^{3P_4}(20700\) cm) for Pr(III) \(^{2P_{1\_2}} \leftarrow \^{4H_{9\_2}}\) transition (23410) for Nd(III) were selected.
3.2.1 VARIATIONS IN THE ENERGY OF THE BONDS AND THE Ln-O BOND DISTANCE:

Table 3.2.1 records the variations in $E \text{ cm}^{-1}$ values for $3P_0 \leftrightarrow 3H_4$ (Pr(III)) and the $3P_{1/2} \leftrightarrow 4H_{9/2}$ (Nd(III)) level transition and the reported [Ln-O] bond distances reported by Yatsimirski and Dovidenko (33). Figures 3.2.1A-D represent the original plot for $E$ and [Ln-O] bond distances for Pr(III) and Nd (III) which was used to evaluate the Ln-O bond distance. The values of the [Ln(III)-O] bond distances (in Å) obtained for Pr(III) and Nd(III) for the present ligand of the series are:

Binary:

<table>
<thead>
<tr>
<th>Systems</th>
<th>Ln(III)-O</th>
<th>Systems</th>
<th>Ln(III)-O</th>
</tr>
</thead>
<tbody>
<tr>
<td>[Pr(III)-Sar]</td>
<td>2.672 ;</td>
<td>[Pr(III)-Pyrzmd]</td>
<td>2.621 ;</td>
</tr>
<tr>
<td>[Pr(III)-Lycn]</td>
<td>2.581 ;</td>
<td>[Pr(III)-Hist]</td>
<td>2.551 ;</td>
</tr>
<tr>
<td>[Nd(III)-Sar]</td>
<td>2.652 ;</td>
<td>[Nd(III)-Pyrzmd]</td>
<td>2.566 ;</td>
</tr>
<tr>
<td>[Nd(III)-Lycn]</td>
<td>2.523 ;</td>
<td>[Nd(III)-Hist]</td>
<td>2.469 ;</td>
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</tbody>
</table>

Ternary:

<table>
<thead>
<tr>
<th>Systems</th>
<th>Ln(III)-O</th>
<th>Systems</th>
<th>Ln(III)-O</th>
</tr>
</thead>
<tbody>
<tr>
<td>[Pr(III)-A-Sar]</td>
<td>2.668 ;</td>
<td>[Pr(III)-A-Pyrzmd]</td>
<td>2.616 ;</td>
</tr>
<tr>
<td>[Nd(III)-A-Sar]</td>
<td>2.632 ;</td>
<td>[Nd(III)-A-Pyrzmd]</td>
<td>2.542 ;</td>
</tr>
</tbody>
</table>

The plots are allmost linear showing a decrease in the [Ln-O] bond distances with an increase in the energy of the assignment. This indicates an effective delocalisation of the 4f- electron wave function by intimate approach of the lanthanide ion with the ligand. The calculate values of
[Ln–O] bond distances have been utilized to evaluate the approximate coordination number of the Ln(III) ion; The values of coordination numbers for Pr(III) and Nd (III) (binary and ternary) as given below. The two cations show a coordination number almost equal to 10 which is derived by virtue of their large cationic sizes.

<table>
<thead>
<tr>
<th>SYSTEMS</th>
<th>C.N.</th>
<th>SYSTEMS</th>
<th>C.N.</th>
</tr>
</thead>
<tbody>
<tr>
<td>Binary :</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>[Pr(III)-Sar] :</td>
<td>10.6 ;</td>
<td>[Pr(III)-Pyrzmd] :</td>
<td>10.2 ;</td>
</tr>
<tr>
<td>[Pr(III)-Lycn] :</td>
<td>10.9 ;</td>
<td>[Pr(III)-Hist] :</td>
<td>9.7 ;</td>
</tr>
<tr>
<td>Ternary :</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>[Pr(III)-A-Sar] :</td>
<td>10.6 ;</td>
<td>[Pr(III)-A-Pyrzmd] :</td>
<td>10.2 ;</td>
</tr>
</tbody>
</table>

An insight into the interaction may be better visualized from correlation between the coordination in the energy and/or Ln–O bond distances and the partial charge in the ligand donor atoms as expressed in the correlation. Fig. 3.2.1A-D.
Variation in the Ln(III)-O Bond distance and the Energy (in eV/cell)

Variation in the La(III)-O Bond distances and the Energy (in cm$^{-1}$)

values for the [Pr(III)-O] systems (Coord. Chem. Rev. 1979, 47, 225.)
Fig. 3.2.1 C

Variation in the Ln(III)–O bond distance versus energy (in cm⁻¹) for the Nd(III)–O systems (Coord. Chem. Rev. 1974, 27, 223.)
Fig. 3.2.1 D

Table 3.2.1 A

Ln(III) - O bond distance in Pr(III) and Nd (III) (oxydiacetate complexe systems and their Energy values [3])

<table>
<thead>
<tr>
<th>Complex</th>
<th>E Value (^{3}H_{4} \rightarrow {^{3}P_{0}})</th>
<th>Pr - O</th>
<th>E Value</th>
<th>Nd - O</th>
</tr>
</thead>
<tbody>
<tr>
<td>Ln(III). aq</td>
<td>20750</td>
<td>2.590</td>
<td>23393</td>
<td>2.500</td>
</tr>
<tr>
<td>Ln(OOCCH(\text{OCH}_{2}\text{COO}))</td>
<td>20719</td>
<td>2.584</td>
<td>23348</td>
<td>2.486</td>
</tr>
<tr>
<td>Ln(OOCCH(\text{OCH}_{2}\text{COO}))(^{2-})</td>
<td>20689</td>
<td>2.572</td>
<td>23313</td>
<td>2.476</td>
</tr>
<tr>
<td>Ln(OOCCH(\text{OCH}_{2}\text{COO}))(^{3-})</td>
<td>20621</td>
<td>2.552</td>
<td>23279</td>
<td>2.468</td>
</tr>
<tr>
<td>N(\text{aLn(OOCCH}<em>{2}\text{OCH}</em>{2}\text{COO})\cdot\text{O}<em>{2})(\cdot\text{NdCl}</em>{6}\text{H}_{2}\text{O})</td>
<td>20582</td>
<td>2.540</td>
<td>23262</td>
<td>2.462</td>
</tr>
</tbody>
</table>

Table 3.2.1 B

Ln(III) - O bond distance in Pr(III) and Nd (III) acetylacetone complex systems and their Energy values [ ]

<table>
<thead>
<tr>
<th>Complex</th>
<th>E Value (^{3}H_{4} \rightarrow {^{3}P_{0}})</th>
<th>Ln - o</th>
<th>E Value</th>
<th>Ln - o</th>
</tr>
</thead>
<tbody>
<tr>
<td>Ln(III). aq</td>
<td>20750</td>
<td>2.590</td>
<td>23385</td>
<td>2.498</td>
</tr>
<tr>
<td>Ln (C(\text{H}<em>{2}\text{COCHCOCH}</em>{2}))(^{2+})</td>
<td>20741</td>
<td>2.588</td>
<td>23320</td>
<td>2.482</td>
</tr>
<tr>
<td>Ln (C(\text{H}<em>{2}\text{COCHCOCH}</em>{2}))(^{3+})</td>
<td>20681</td>
<td>2.570</td>
<td>23298</td>
<td>2.473</td>
</tr>
<tr>
<td>Ln (C(\text{H}<em>{2}\text{COCHCOCH}</em>{2}))(^{4+})</td>
<td>20664</td>
<td>2.565</td>
<td>23244</td>
<td>2.457</td>
</tr>
<tr>
<td>Ln (C(\text{H}<em>{2}\text{COCHCOCH}</em>{2}))(^{5+})</td>
<td>20596</td>
<td>2.542</td>
<td>23217</td>
<td>2.450</td>
</tr>
</tbody>
</table>
3.2.2 VARIATIONS IN THE $Ln-O$ BOND DISTANCE AND THE PARTIAL CHARGE ON LIGAND DONER ATOMS:

The partial charge on ligand donor atoms have been evaluated using Pearson's Hard and Soft Acid Base (HSAB) theory [using the equation given in Appendix] the stability ratio values for ligand were evaluated using standard values of atoms as reported by Alfred Rachow (34). The values evaluated using Person's equation have been used for correlation.

Table 3.2.2A and 3.2.2B reported the variations in $Ln-O$ bond distance (for the binary and ternary system for Pr(III) and Nd(III)) with the partial charge on ligand donor atoms. The following figures exhibit almost close to linear correlation showing a gradual decrease in the $Ln-O$ bond distance with increase in the partial charge on ligand donor atoms. This may be attributed to increase coulombic attraction leading to closer metal ligand interaction Fig 3.2.2 A-B. The ternary complexes have, however, shown more close interaction as compared to corresponding binary complexes (as seen from the $Ln-O$ bond distances) which may be due to greater partial charges associated with the ternary systems. A direct effect of this coulombic interaction on the oscillator strength values is expected, as the oscillator strength values are electric dipole fields where the susceptibility of the specific electronic transitions has operative electric and magnetic dipoles. An insight into this has been worked out in the next correlation.
### Table 3.2.2
Variation in the Ln(III)-O bond distance with partial charge on the ligand donor atoms

| S. No. | A. Binary | | A. Binary | | | | B. Ternary | | B. Ternary |
|--------|----------| | | | | | | | |
| 1 | 0.3461 | 2.668 | 0.3461 | 2.652 |
| 2 | 0.4379 | 2.616 | 0.4379 | 2.566 |
| 3 | 0.4772 | 2.555 | 0.4772 | 2.523 |
| 4 | 0.4881 | 2.49 | 0.4881 | 2.46 |
| 1 | 0.6031 | 2.672 | 0.6031 | 2.632 |
| 2 | 0.6949 | 2.621 | 0.6949 | 2.542 |
| 3 | 0.7342 | 2.581 | 0.7342 | 2.503 |
| 4 | 0.7451 | 2.551 | 0.7451 | 2.491 |

### Diagrams

**Binary**
- Ln-O Bond Dist vs Partial Charge
- Curve shapes indicate decreasing bond distance with increasing partial charge.

**Ternary**
- Ln-O Bond Dist vs Partial Charge
- Similar trend as binary, but with different data points and possibly different molar compositions.

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3.2 III THE VARIATION IN THE OSCILLATOR STRENGTH VALUES WITH THE PARTIAL CHARGE ON LIGAND DONER ATOMS

Tables 3.2.3 give the variation in the oscillator strength values for the hypersensitive and pseudo hypersensitive transitions and the total partial charge on the ligand donor atoms for the binary and mixed ligand system. Table 3.2.3 records the oscillator strength values. Figure 3.2.3 A-E record the variation profile for the oscillator strength values for binary and ternary system. The values in general show a gradual increase in oscillator strength values with the partial charge on ligand donor atoms. This may be attributed to an increased component of the electric dipole in the oscillator strength values. This, in turn, influences the oscillator strength values thereby increasing these values. There are, however, deviations which may be attributed to either the significant involvement of the magnetic dipole or the nonhomogenous ligand field.

Since the oscillator strength values are composed of $T_\lambda$ parameters where $T_2$ corresponds to direct metal ligand interaction and $T_6$ corresponds to the symmetry change associated with the cation symmetry. There individual dependence on the partial charge may be visualized from studying their individual correlation with the partial charge.
<table>
<thead>
<tr>
<th>BINARY</th>
<th>pc</th>
<th>Pr(III)</th>
<th>Nd(III)</th>
<th>Sm(III)</th>
<th>Eu(III)</th>
<th>Dy(III)</th>
<th>Er(III)</th>
<th>Tm(III)</th>
</tr>
</thead>
<tbody>
<tr>
<td>sarco</td>
<td>0.3461</td>
<td>1320</td>
<td>2050</td>
<td>743</td>
<td>133</td>
<td>43</td>
<td>-1190</td>
<td>--</td>
</tr>
<tr>
<td>pyrznmd</td>
<td>0.4379</td>
<td>1498</td>
<td>2230</td>
<td>782</td>
<td>226</td>
<td>81</td>
<td>1340</td>
<td>429</td>
</tr>
<tr>
<td>lycine</td>
<td>0.4772</td>
<td>1572</td>
<td>2320</td>
<td>833</td>
<td>138</td>
<td>68</td>
<td>1420</td>
<td>386</td>
</tr>
<tr>
<td>hist</td>
<td>0.4881</td>
<td>1598</td>
<td>3260</td>
<td>894</td>
<td>145</td>
<td>71</td>
<td>1960</td>
<td>--</td>
</tr>
<tr>
<td>TERNARY</td>
<td>pc</td>
<td>Pr(III)</td>
<td>Nd(III)</td>
<td>Sm(III)</td>
<td>Eu(III)</td>
<td>Dy(III)</td>
<td>Er(III)</td>
<td>Tm(III)</td>
</tr>
<tr>
<td>sarco</td>
<td>0.6031</td>
<td>1322</td>
<td>2160</td>
<td>753</td>
<td>150</td>
<td>71</td>
<td>1190</td>
<td>--</td>
</tr>
<tr>
<td>pyrznmd</td>
<td>0.6949</td>
<td>1432</td>
<td>2250</td>
<td>762</td>
<td>320</td>
<td>71</td>
<td>1260</td>
<td>429</td>
</tr>
<tr>
<td>lycine</td>
<td>0.7342</td>
<td>1572</td>
<td>2350</td>
<td>762</td>
<td>149</td>
<td>68</td>
<td>1260</td>
<td>386</td>
</tr>
<tr>
<td>hist</td>
<td>0.7451</td>
<td>1569</td>
<td>2420</td>
<td>843</td>
<td>150</td>
<td>76</td>
<td>1260</td>
<td>--</td>
</tr>
</tbody>
</table>
Fig. 3.2.3 A-F

Variation in the Oscillator Strength values with Partial Charge on the Ligand Donor Atoms

**BINARY SYSTEMS**
Fig. 3.2.3 A-E

Variation in the Oscillator Strength values with Partial Charge on the Ligand Donor Atoms

BINARY SYSTEMS
3.2.IV The variations in the $T_2$ and $T_6$ values with the partial charge on ligand donor atoms:

Figure 3.2.4A,B and 3.2.4C,D record the variation in the $T_2$ and $T_6$ values for corresponding binary and ternary complexes with partial charge on ligand donor atoms respectively. These values individually show a dependence, however any generalized correlation could not be sought from these plots. This may attributed to the changes in symmetry or the coordination phases during complexes. The studies, however, are in agreement with the discussion conducted in this chapter part A (Page No 145).
Fig. 3.2.4 B

Variation in the Judd Ofoelt ($T_6$ values) parameters with the Partial Charge on Ligand Donor Atoms

**BINARY SYSTEMS**
Fig. 3.2.4 C
Variation in the Judd-Oelfelt ($T_2$ values) parameters with the Partial Charge on Ligand Donor Atoms

TERNARY SYSTEMS

[Pr(III).A.L]

[Nd(III).A.L]

[Dy(III).A.L]

[Er(III).A.L]
Fig. 3.2.4 D

Variation in the Judd Ofelt ($T_6$ values) parameters with the Partial Charge on Ligand Donor Atoms

TERNARY SYSTEMS
3.2.V VARIATIONS IN THE INTER ELECTRONIC REPULSION RACAH PARAMETERS AND THE NEPHELAXETIC RATIO VALUES WITH THE PARTIAL CHARGE ON LIGAND DONER ATOMS:

Table 3.1.3 (page 147) records the variation in the inter electronic repulsion Racah parameters $\delta E^1$ and $\delta E^3$ and the nephelaxetic ratio $(\delta E^3/\delta E^1)$ values. Figs 3.2.5 A-F record the variation profiles for the nephelaxetic ratio values and the partial charge on the ligand donor atoms. The plots in general show a decrease in the nephelaxetic ratio values with the increase in the partial charge on the ligand donor atoms. As expected from the $(\delta E^3/\delta E^1)$ from these ratios, it are expected to show smaller values under the condition when i. $\delta E^3$ is small or ii. $\delta E^1$ is large. On the contrary the higher values of the ratio will correspond to i. $\delta E^1$ is small and ii. $\delta E^3$ as large. $\delta E^1$ indicate radial elongation of the 4f wave function under the ligand fields whereas the $\delta E^3$ towards angular distortions. Under the framework of LCAO, the effective charges on ligands are expected to affect directly $\delta E^1$ more than $\delta E^3$. As evident from the figures, an increase in total partial charge results in a general decrease in the nephelaxetic ratio. Since the smaller values of $(\delta E^3/\delta E^1)$ are expected on account of smaller $\delta E^3$ and/or large $\delta E^1$ values, it may be stated that the higher charge on the donor atom has been able to affect the $\delta E^1$ function, thereby, increasing the $\delta E^1$ and consequently causing a change in $(\delta E^3/\delta E^1)$. Similarly the smaller charge values being less effective cause lesser change in $\delta E^1$ increasing the ratio $(\delta E^3/\delta E^1)$. This dependence of the nephelaxetic ratio values on the partial charges on ligand donor atoms may further serve as additional evidence to effective 4f-delocalisation.
Fig. 3.2.5

VARIATIONS IN THE INTER ELECTRONIC REPULSION RACAH PARAMETERS AND THE NEPHELAUXETIC RATIO VALUES WITH THE PARTIAL CHARGE ON LIGAND DONER ATOMS
3.2.VI VARIATIONS IN THE TOTAL TRANSITION PROBABILITY / RELAXATION TIMINGS AND THE PARTIAL CHARGE ON LIGAND DONER ATOMS:

Tables (Chapter 2) record the variations in the $A_T$ and $T_R$ values for the lanthanoid ions in different binary and mixed ligand environments whereas figures 3.2.6 A, B record the variations in the $A_T$ vs partial charge on ligand donor atoms. These profiles are expected to be identical with the $T_R$ plots as the $T_R$ values are numerically equal to $1/A_T$. The plots show a dependence on the partial charge showing a gradual increase in $A_T$ (reciprocal change expected for $T_R$) from sarcosine to lysine via pyrazynamide. This may be attributed to the changes in the symmetry around metal ion with this ligand. The histidine is the aromatic ligand where the primary ligand EDTA cause a constraint in the combination of histidine as in coming ligand with the metal ions. The dependence on the partial charge on the extra-stabilisation of the serine or lysine system may be on account of increased stabilization with increased hydrophobicity of the substituted side chain. This in its turn increases the oscillator strength values.
Table 3.2.6 A
Variations in the Relaxation Timings (\(\tau_R\)) parameters with the Partial Charge on Ligand Donor Atoms

BINARY SYSTEMS

![Graphs showing variations in Relaxation Timings (\(\tau_R\)) with Partial Charge for different binary systems.](image)
Table 3.2.6 B

Variation in the Relaxation Timings ($A_T$) parameters with the Partial Charge on Ligand Donor Atoms

TERNARY SYSTEMS
3.2.VII: VARIATIONS IN THE TOTAL METAL HARDNESS VALUES AND
THE MATCHING CONSTANTS OF THE COMPLEXES WITH
LIGAND CHARACTERISTICS:

Tables given in the Section 3.1 (of this chapter) record the metal hardness
and ligand softness values along with the matching constants for the binary com-
plex species under studies. To investigate the exact dependence of the matching
constants on the ligand characteristics, the values have been plotted against ligand
characteristics and/or the partial charges on the ligand donor atoms. Figs 3.2.7A-
G record the variations for Pr(III), Nd(III), Sm(III), Dy(III), Er(III) and Tm(III) with
respect to ligand characteristics. The graphs are almost linear which may be attrib-
uted to the similarity in the ligational behaviour of this ligand. The deviations
around pyrazinamide may be due to changes in the steric situations in case of
these ligands. Though the plots appear to be same for all the metals, they are
expected to exhibit varied slopes for pre-Gd elements then for post-Gd elements.
The slope values obtained for the Ln(III) ions of the present complexes show a steeper
variation for the pre-Gd elements than for the post-Gd elements. This trend is ex-
pected on account of the lanthanoid contraction. The studies may serve as an ad-
tional evidence to our earlier observation of a change in the bonding pattern from
electrostatic to covalo-electrostatic from pre-Gd elements to post-Gd elements.
Fig. 3.2.7: Variation in the Matching constants with the Ligands for the titled Ln(III) atoms of the present series
3.3 PART C:

VARIATIONS IN THE SPECTRAL PARAMETERS ALONG THE LANTHANOID SERIES:

The electronic configuration taken under present studies is typically identical as the three members of the present series resemble the other three members in both electronic configuration, the total spin quantum number and the orbital angular momentum values, however, the cations differ in their ionic sizes and the total (J) quantum number values. The symmetry may be observed as follows:

<table>
<thead>
<tr>
<th></th>
<th></th>
<th></th>
<th></th>
<th></th>
<th></th>
<th></th>
<th></th>
<th></th>
<th></th>
<th></th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>8/2</td>
<td>Pr 59</td>
<td>[Xe]6s^2,5d^1,4f^1</td>
<td>2</td>
<td>2/2</td>
<td>5</td>
<td>2</td>
<td>[Xe]6s^2,5d^1,4f^2</td>
<td>12/2</td>
<td>Tm 69</td>
</tr>
<tr>
<td>2</td>
<td>9/2</td>
<td>Nd 60</td>
<td>[Xe]6s^2,5d^1,4f^1</td>
<td>3</td>
<td>3/2</td>
<td>6</td>
<td>3</td>
<td>[Xe]6s^2,5d^1,4f^1</td>
<td>15/2</td>
<td>Er 68</td>
</tr>
<tr>
<td>3</td>
<td>5/2</td>
<td>Sm 62</td>
<td>[Xe]6s^2,5d^1,4f^1</td>
<td>5</td>
<td>5/2</td>
<td>5</td>
<td>5</td>
<td>[Xe]6s^2,5d^1,4f^1</td>
<td>15/2</td>
<td>Dy 66</td>
</tr>
</tbody>
</table>

Since in lanthanoid the 4f- shells are deeply seated and the interaction are predominately ionic the CFSE are negligible. Under these conditions the variations across the series are either governed by the spin quantum number S or the total orbital angular momentum L or total quantum number value J. There has been considerable discussion on considering either of these parameters as fundamental properties for correlation along the series. It has been observed that the variations in the spectral energies transition originate from the extrastabilisation energy composed of inter electronic repulsion Racah parameters and their coefficient denoted by the S and L quantum numbers. It has also been reported that the ground levels of the lanthanoid are purely L
states with very minimal (above ~2%) coupling interaction.

Poluektov and others have tried to correlate the variations in the exprimantal properties of lanthanoid with the fundamental properties of the lanthanoid [35]. Attempts have also been made to correlate the spectral parameters with the fundamental quantum number of lanthanoid; however have failed to reach any consolidated statement. Some attempts to correlate the electronic spectral parameters with the J quantum number values have been made from our laboratory [36-37].

In lanthanoid where the spectral transitions are marked nearly by J and (J+1) transition states, a direct correlation exists between the electronic spectral parameters and the S, L and J quantum number values for the hypersensitive or pseudo-hypersensitive transitions of lanthanoid. These correlations include the variations in the $T_2$, $T_4$, $T_6$ oscillator strength, $S_{ed}$ and $T_R$ values (for hypersensitive and pseudohypersensitive) only. Figure 3.3.1 A,B records the theoretical variations in the $U_2$ and the $E$ (in cm$^{-1}$) values for the aquo complexes as reported in literature [35]. The spectral parameters for the present member of lanthanoids [figures 3.3.2, 3.4,6 and 6 represent the variations in the $T_2$, $T_4$, $T_6$ and the oscillator strength values respectively with their S and J quantum numbers.

As seen from the plots, all the plots in general exhibit a semi-sigmoid type of pattern which varies in amplitude from the pre-Gd elements to post-Gd elements. These variations in amplitude have, however, been observed to be dependent of ligand characteristics. It may, however, be stated that the general trend of the plots resemble the variation-pattern of the total angular moment J values with the variation profile obtained for J values. This may be attributed to a preserved core like feature of the f shell besides complexation.
<table>
<thead>
<tr>
<th>Ln(III)</th>
<th>J</th>
<th>U2</th>
<th>E cm⁻¹</th>
</tr>
</thead>
<tbody>
<tr>
<td>Ce(III)</td>
<td>5/2</td>
<td>0</td>
<td>0</td>
</tr>
<tr>
<td>Pr(III)</td>
<td>8/2</td>
<td>0.509</td>
<td>5.200</td>
</tr>
<tr>
<td>Nd(III)</td>
<td>9/2</td>
<td>0.974</td>
<td>17.333</td>
</tr>
<tr>
<td>Pm(III)</td>
<td>8/2</td>
<td>0.886</td>
<td>17.950</td>
</tr>
<tr>
<td>Sm(III)</td>
<td>5/2</td>
<td>0.338</td>
<td>6.483</td>
</tr>
<tr>
<td>Eu(III)</td>
<td>0</td>
<td>0.004</td>
<td>1.940</td>
</tr>
<tr>
<td>Gd(III)</td>
<td>7/2</td>
<td>0</td>
<td>0</td>
</tr>
<tr>
<td>Tb(III)</td>
<td>12/2</td>
<td>0.538</td>
<td>2.100</td>
</tr>
<tr>
<td>Dy(III)</td>
<td>15/2</td>
<td>1.285</td>
<td>6.296</td>
</tr>
<tr>
<td>Ho(III)</td>
<td>16/2</td>
<td>1.736</td>
<td>22.793</td>
</tr>
<tr>
<td>Er(III)</td>
<td>15/2</td>
<td>1.631</td>
<td>23.418</td>
</tr>
<tr>
<td>Tm(III)</td>
<td>12/2</td>
<td>0.774</td>
<td>7.947</td>
</tr>
<tr>
<td>Yb(III)</td>
<td>7/2</td>
<td>0</td>
<td>0</td>
</tr>
</tbody>
</table>
Fig 3.3.1

Variations in the Theoretical values of $U_2$ and $E$ (in cm$^{-1}$) vs $J$ values of the Ln(III) series

![Graph of Largest Tensor Operator ($U_2$) to HST](image)

![Graph of $U_2$ or $E$ values](image)
Fig 3.3.2
Variations in the Judd–Ofelt Parameters with Lanthanoid Ions
Fig 3.3.3

Variations in the Judd - Ofelt Parameters with Lanthanoid Ions
Fig 3.3.4

Variation in the Oscillator Strength values of the HST bands with Ln(III) ions

BINARY SYSTEMS

TERNARY SYSTEMS
Figure 3.3.5

Variation in the Softness Values of Ln(III) ions of the present series and the Matching constants with the titled ligands of the present series.
CONCLUSIONS

A perusal of variation profiles of the electronic spectral parameters and the corresponding radiative properties for the seven lanthanoid ions in different ligand environments exhibits that the substitution of ligand/drug causes a significant change in these parameters.

As regards the behaviour of 4f-shells in [Ln(III)-L] bond formation, the study reveal that the interaction in general exhibits predominantly ionic bonding. However, there are evidences of its intermediate behaviours with certain degree of covalency associated with it. The effective shielding and substantial screening thus restrict the direct involvement of their orbitals from bonding, however, the deformation in their normal electronic wave function under the effect of ligand field is evident.

The varied responses of the seven electronic configurations to different ligand environments is due mainly to the extrastabilisation or extra destabilisation of their 4f-configuration under the effect of ligand / crystal field. The extra stabilisation gets demonstrated in their 4f-electronic wave functions, which in its turn gets reflected in their electronic spectral parameters and the variations in their inter electronic repulsion Racah parameter values.

The variations in these parameters follow the pattern based on the Ln(III) ion characteristics, the ligand characteristics and the astatistical factors viz., electrostatic, steric or thermodynamic parameters. In addition to that a possible correlation with the relative hardness values of the Ln(III) ions, the relative softness values of ligands and consequential matching constants of the complexing might have significant effect on the Ln(III)-L interactions. An attempt to evaluate the relative matching constant values for the given set of complexes has been made in order to
Chapter 3: Results And Discussion

Solution studies on Rare ....Amino acids observe the relative responses of these ligands to the metal ions and to examine the relative responses of the Ln(III) cations to the complexing bases.

The oscillator strength values in general follow the sequence of the basic strength of the secondary ligands, or more precisely the sequences of the relative softness values of the ligands. The dependence is almost identical and is expected on account of the similar ligational behaviour of the ligands. Certain deviations in case of some ligands may be on account of steric situations extended by the ligand and as availed by the Ln(III) cation.

The electrostatic factors that govern the stabilisation of the mixed ligand complexes show their significant effect on the electronic spectral parameters. The oscillator strength values have been found to follow a sequence EDTA > ML. The oscillator strength values are composed of three different parameters indicating covalency and the symmetry perturbations associated with the metal ligand interactions. The lanthanoids in which the 4f-shells are deeply shielded and are effectively screened, are less available for bonding. Under these conditions direct metal ligand interactions are expected to be small. Thus the covalency parameters are expected to be very small in case of lanthanoids. Simultaneously, the lanthanoid cations are associated with three large concentric hydration zones which rupture during close metal ligand interactions. Thus the Ln(III)-L interactions exhibit greater symmetry perturbations, and thus the magnitude of the symmetry indicating parameters in the electronic spectral parameters is expected to be more. The lanthanoid ion contracts to ~17% of its radius from La(III) to Lu(III), thereby increasing the ionic potential and thus the size of the concentric hydration zone for the post Gd element. In comparison to this expansion in the hydration zone by 20% the symmetry parameters said to be associated with the cation environment are due to the rupture of this thawed hydration zone. This leads us to a conclusion that the lanthanoid interactions are predomi-
nately ionic with minimal covalent interaction.

An evidence of 4f-delocalisation has also be drawn from variations in the inter electronic repulsion Racah parameters and the nephelauxetic ratio values. The nephelauxetic parameters, in general, indicate a predominantly ionic mode of Ln(III) - L interaction with partial covalency. In other words the bonding pattern shows a gradual change from a predominately ionic (electrostatic) form to a partial ionic (partial covalent or covalo electrostatic) form from pre Gd elements to post Gd elements.

It may be stated that the changes in the electronic parameters and the branching ratios are complex phenomenon collectively governed by the Ln(III) ions, their environments, their hardness values, the solution dielectrics, the polarizability, the matrix or the environment and the matrix characteristics. The variation profiles and the phenomenon though do not seem to be directly linked with chemical bonding, however, the variations in these parameters with the compositional variations of the complex ions and the matrix have expressed the dependence on both metal ion characteristics, S, L, and J quantum numbers, fundamental levels and the ligand properties. An exact explanation may be drawn with the theoretical approaches and a systematic investigation on the individual parameters and their effects.
References:

23. S.N. Limaye, Ph.D. Thesis, Dr. H.S. Gour University, Sagar (M.P.) India, 1983.