CHAPTER IV
SUMMARY AND CONCLUSION
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From the various observations and their interpretation made in the thesis some prominent conclusions may be drawn as follows:

- The electronic spectral assignments in general exhibit a red shift with varied magnitudes which is observed to depend upon the ligand characteristics.

- The intensity of excitation of specific electronic transitions have been found to be dependent on the ligand characteristics as well as the pH value of the medium.

- The pH profile of the oscillator strength values exhibited a systematic variation which attributes to an increase in the population of complex specie with increased pH values.

- The variation in the oscillator strength values with respect to ligands within the series, in general follows a sequence of their ligand basicity.

- A significant effect of the ligand donor atom type such as O-O or
O-N, has been observed on the oscillator strength values, which suggests a probable dependence of the donor atom type on the lanthanoid nephelauxetic phenomenon.

An increase in the oscillator strength values due to a possible cooperative role played by the substituted moieties of the ligands has been discussed in light of the steric situations.

The symmetry indicating parameter ($\tau_\lambda$) composing the oscillator strength values have also been evaluated and their variation profiles examined with respect to metals and ligands. The values in general exhibit a sequence $T_2 < T_4 < T_6$ which are in agreement with the deep seated, highly screened $f$-orbitals and the large hydration zones associated with these ions in solution.

The variation profiles of the $\Omega_\lambda$ parameters evaluated using the refractive indices of the medium have also been discussed in light of the [Ln(III).L] interaction.

The partial charges on ligand donor atoms have also been evaluated which shows a direct effect on the Ln(III)-O bond distances (evaluated for Pr(III) and Nd(III)) indicating electrostatic mode of Ln(III)-L interactions.
The covalency indicating Judd Ofelt parameters \( (T_2) \) showed a marked dependence on the partial charge on ligand donor atoms, as ligand donor atom vis-a-vis \( \text{Ln(III)-O} \) bond distances also furnished an additional proof towards involvement of partial covalency.

The oscillator strength values have shown a dependence on the metal ligand bond distances vis-a-vis the partial charge on ligand donor atoms.

The variation in the \( T_2 \) parameters that are indicative of the partial covalency in the \([\text{Ln(III).L}]\) bond has been observed to follow the sequence of ligand basicities, within the series.

The variation in the \( T_6 \) parameters indicative of changes in the symmetry around the cation polyhedra as a result of complexation has been observed to depend upon the ionic potential or the lanthanoid metal ion characteristics, within the series. These parameters have also shown dependence on the chelate ring sizes and the donor atom types.

The symmetry indicating parameters \( (T_6) \) also showed a marked dependence on the partial charges on the ligand donor atoms vis-a-vis \( \text{Ln(III)-O} \) bond distances which also furnished a proof towards greater symmetry perturbations than the covalency.
The $\tau_\lambda$ values for the O-N donor ligand complexes have been found to be smaller than the corresponding O-O donor ligand complexes which has been discussed in the light of relative softness values of the donor atoms and ligands.

Higher $T_6$ values for the post-Gd elements as compared to those of the pre-Gd elements have been observed to be due to larger hydration zones and the concomitant greater symmetry perturbations in the case of higher lanthanoids.

An interesting sequence in the $T_\lambda$ parameters with respect to ligand characteristics suggest the effect of ligand polarizability in the [Ln(III)-L] bonding pattern. The correlation in the $T_2$ parameters vs partial charge on ligand donor atoms has shown a linear profile indicating a direct dependence of Judd's covalency parameters on the electrostatic characteristics of the ligand.

The inter electronic repulsion (RACAH) parameters $\delta E^k$ (where $k = 0,1,2,3$) and the nephelauxetic ratio values ($\delta E^3/\delta E^1$) lie well within the theoretically calculated ranges of $\delta E^k \approx 1\%$ of $E^k$ and $-0.0913 < \delta E^3/\delta E^1 > 0.214$, which justifies the validity of the present calculations,
The variation in the nephelauxetic ratio values with respect to the ligands within the series showed a marked dependence on the ligand characteristics. A linear correlation between the nephelauxetic ratio and the partial charge on the ligand donor atoms indicate an effective de-localisation of the 4f - shells under the ligand fields.

The nephelauxetic ratio values have been observed to be in general smaller for Er(III) than for Nd(III) which has been discussed in light of their relative positions in the lanthanide series. The greater magnitude for the post - Gd elements than for the pre - Gd elements within the lanthanoid series point towards a change in the bonding pattern from electrostatic to covalo-electrostatic from pre - Gd elements to the post - Gd elements.

The change in the electrostatic to covalo-electrostatic pattern from pre - Gd elements to the post - Gd elements has been attributed to lanthanoid contraction,

Amongst radiative properties, the $S_{ed}$ values have been found to be depend on the ligand characteristics and their substitutions.

Relaxation timings for the intermediate fluorescent levels have also been found to be dependent of the ligand characteristics.
(as examined under the influence of partial charge on ligand donor atoms). This may be attributed to the released inter-electronic repulsion due to greater partial charge and decreased degeneracy of the p-electron clouds over the donor atom moieties.

The branching ratios indicative of the relative relaxation life times of the intermediate flourescent levels have been found to be in general larger in magnitude for the lower energy levels than their corresponding higher levels.

The radiative properties for the titled ligand of the series, in general, show a sequence with respect to transition level.

Pr(III) : \(^3P_1 < ^3P_2 < ^1D_2\);

Nd(III) : \(^4G_{9/2} < ^4G_{7/2} < ^4G_{5/2} < ^2H_{11/2} < ^4F_{9/2} < ^4F_{7/2} < ^4F_{5/2}\);

Er(III) : \(^4S_{3/2} > ^4F_{9/2} > ^4F_{7/2} > ^4G_{9/2} > ^4F_{7/2} > ^4G_{11/2}\);

Similar observation in the case of branching ratios for the Nd(III) and Er(III) may be attributed to general lanthanide character and the concomitant lanthanoid contraction.

Overall comparison of the oscillator strength values and the nephelauxetic ratios for different ligands under study reveal a change in the bonding pattern from electrostatic to covalent-electrostatic from pre-Gd elements to the post-Gd elements. Also
a marked dependence of these parameters on the partial charge on the ligand donor atoms indicate the effective delocalisation of the 4f-orbitals under the ligand field.

Thus on the basis of all the above observations it may be stated that the 4f-orbitals show an effective delocalisation in the ligand field, where a quantitative correlation of the parameters on the ligand / metal characteristics is evident. As regards the behaviour of the 4f-shell they appear to behave predominantly as core like giving rise to ionic nature of the bond. However, the involvement of partial covalentcy is no more probable and its direct dependence on ligand characteristics is made evident through this work. The effective shielding and substantial screening of the 4f-shells though force them (4f-shell) to behave like a core; yet the deformation of their normal electronic wave function is quite clear.

As a word of caution, it may be stated that the changes in the electronic spectral parameters have shown a marked dependence on the metal ligand characteristics, however, an exact mechanism of the Ln(III)-L interaction, may be drawn taking into consideration, the theoretical approaches based on solution dielectrics,
the polarizability, the matrix (or the environment) and the matrix
characteristics and these parameters as a whole or individually and
their effects.