CHAPTER - V

SUMMARY AND CONCLUSIONS
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Results obtained from various electronic spectral investigations made on the interactions between the metals and ligands (Four metals, one primary and Eight secondary) and four 4f^11 configurations and their possible interpretations based on the metal and ligand characteristics, the following conclusions may be drawn:

A perusal of the oscillator strength values and their variations with respect to fundamental properties of lanthanoids exhibit that the substitution of ligand causes a significant change in this parameters.

The oscillator strength values showed a direct dependance on pH values of the medium indicating that the spectral parameter specially the degree of allowance of specific electronic transition is a function of concentration of the absorbing species. The values also showed a dependance on the nature of the ligand and their substitution.

The effect of the ligand substitution on the spectral parameters has been successfully used as a tool to examine the co-operative inter ligand interaction and the extra stabilisation of mixed ligand complexes.

This extra stabilisation of the mixed ligand complexes has been
observed from the magnitude of the oscillator strength values, with increased length/bulk or substitution on the ligand side chains. The extra stabilisation has been observed to be higher in magnitudes for larger ligand than corresponding smaller ligands (a-Alanine complexes) in the present case. This has been discussed in light of co-operative inter ligand interaction leading to possible aromatic ring stacking in the ligands.

The long side chains of the amino acid viz valene and leucine have shown a extra stabilisation due to interligand interaction.

The imadazole and benzimidazole moities of the tryptophan and histidine has shown possible stacking mechanism with CDTA moities leading to a extra stabilisation of the mixed ligand complexes.

Among serine, cystine and aspartic acid, serine and histidine have shown exceptional stabilities due to a change in doner atom or possibly due to chelate formation.

The use of Judd ofelt parameters and their variation have been further sought to examine the possible change in symmetry, due to the possible inter ligand interaction. The parameters have been found to vary in sequence: covalency < dielectrics of the medium < Symmetry perturbations as indicated by

\[ T_2 < T_4 < T_6 \]
The variations in the $T_2$ and $T_6$ parameters are also in accordance with the general 4f-shell features where the 4f shells are deeply seated decreasing the direct metal ligand interaction where as their large cationic sizes increasing the symmetry perturbations in the system.

The relative variation in the $T_2$ and $T_6$ parameters have been examined to furnish as additional evidence to the inter ligand interaction and the consequential changes in symmetry. The ratio $T_2/T_6$ have also been utilized in support of these observations.

The use of parameters $T_2$, $T_6$ the ratio $T_2/T_6$ and their relative variations for Nd(III) and Er(III) have also been used to examine the mode of the binding pattern.

As regards the 4f-shells in bond formation the parameters reveal a change in the bonding pattern from predominantly (ionic) electrostatic to partly (ionic) covalent electric from pre-Gd elements to post-Gd elements.

Nd(III) and Er(III) are the suitable examples to study the role of J- and other quantum numbers (spin and orbital angular quantum numbers) on extrastabilising the electronic states and a probable effect of the ligand field.

The two members are aptly suited for comparison as they possess almost equal number of unpaired electrons, similar spin quantum numbers and orbital an-
gular quantum number, but differ only in their J-quantum states. In lanthanoids the origin of spectral transitions is expected to be from one J-state to another J+1. Thus the comparison indicate a J-dependency of the ground level terms.

The variations in the Racah parameters and nephelauxetic ratio values observed are well within the theoretically calculated ranges which justify the validity of the present calculation.

The dependence of Racah parameters and nephelauxetic ratio \( \frac{E^3}{\delta E^1} \) on the ligand nature and the partial charge on the secondary ligand also furnish additional evidence in favour of effective 4f shell delocalisation under the ligand field.

The \( T_2 \) value show a direct dependence on partial charge on ligand donor atoms showing increasing covalent interaction due to increased ligand field.

The radiative properties also exhibited direct dependence on the ligand characteristics, where the sed value have been found to show the sequences (with respect to their assignment which is an agreement with their relative population of these levels):
\( \text{Nd(III)} - 4G_{9/3} < 4G_{7/2} < 4G_{5/2} < 2H_{11/2} < 4F_{9/2} < 4F_{5/2} < 4F_{3/2} \)

\( \text{Sm(III)} - 6P_{3/2} > 4I_{3/2} > 6P_{1/2} > 4M_{13/2} > 4I_{11/2} \)

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

The total transition probabilities \( A_T \) and the branching ratio \( \{ \beta_R \} \) value also showed a depandence on the ligand characteristics.

Where the relaxation timings cause the intermediate florescence level have been utilized to evaluate the relaxation timings for the other interme-
diate level for which the transitions probabilities are not mentioned.

Thus it may be stated that the electronic spectral parameters, the radiative properties and their variation profiles though do not seem to be di-
rectly linked with the chemical bonding, however, their variations have shown a dependance on metal characteristics, their ground term values, fundamen-
tal levels, the ligand characteristics and their properties.

The nephelauxetic values showed a direct dependance on partial charge on ligand doner atoms showing a significant deformation of radial wave function under the ligand influence than the orbital distortion.

As regards the behaviour of 4f shells in bond formation the studies reveal that the bonds are predominantly ionic. As substantial screening effect
in these orbital, though restrict their direct involvement, the deformation of the
normalised 4f- wave function is evident.

The studies however furnish ample proof to utilize oscillator strength
value as a tool to examine the co-operative interligand interaction.

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