CHAPTER - 4

SUMMARY AND CONCLUSIONS

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Results obtained from various electronic spectral investigations made on the interactions between the titled metals and ligands (seven metals, one primary and four secondary] and the seven $4f^n$ configurations [four from pre Gd series and three from post-Gd series] and their possible interpretations based on the metal and ligand characteristics, the following conclusions may be drawn :

- The substitution of ligand /drug causes a significant change in the electronic spectral parameters:

- As regards the behaviours of 4f-shells in [Ln(III)-L] bond formation, the studies reveal that the interactions are in general predominantly ionic bonding.

- Though the effective shielding and substantial screening effects in these orbitals though restrict their direct involvement in bonding, yet, the deformation of the normalised 4f - electron wave function under the effect of ligand field is evident.

- The varied responses of the seven electronic configurations to different ligand environments are due mainly to the extrastabilisation or extra destabilization of their 4f-configuration under the effect of ligand / crystal field which on its turn get reflected in their electronic spectral parameters and the variations in their inter electronic repulsion Racah parameter values.

- The electronic spectral parameters and the radiative properties in general show a direct dependence on the ligand environment and the solution characteristics.

- The observed sequence in the oscillator strength values for the HST transitions with respect to the different $4f^n$ configurations in different ligand environments in general showed a sequence

Er(III) > Nd(III) > Tm(III) > Pr(III) > Sm(III) > Eu(III)

- The observed sequence in the oscillator strength values with respect to the different ligand environments in general showed a sequence

Sar > Pyrznmd > Lycn > Hist

which are in accordance with the ligand basicities or more precisely with the ligand softness values.

- The observed sequence in the oscillator strength values for binary and corresponding mixed ligand complexes show a general sequence **MAL > ML** which is expected on the basis of operative electrostatic effect.

- The observed sequence in the oscillator strength values for various assignments in different ligands in general followed a sequence

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) $^5L_6 > {}^5H_6 > {}^5L_7 > {}^5G_6 > {}^5D_2$

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

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

Tm(III) $^3F_3, {}^3F_2 > {}^1P_2 > {}^3H_4 > {}^1G_4$

- The variations in the ligands softness values of the complexes in gernal show a sequence

Sarco < Pyrznmd < Lyce < Hist

- The matching constant values have shown a periodic behaviour showing higher magnitutes for the pre-Gd elements than the post-Gd elements.This has been explained on the basis of relative reactivities of the bases with different acid.

- The matching constant values exhibit a steeper plots for the pre- Gd element than for the post- Gd elements which has been serve as an evidence to the observation of change in bonding pattern from electrostatic to covaloelectrostatic from the pre Gd element to post Gd elements.

- The T_λ values composing the oscillator strength show a sequence

$$\mathbf{T_2 < T_4 < T_6}$$

the show the significance of these parameters in the [Ln(III)-L] bonding.

- The covalency denoting parameters T_2 have shown lesser values than T_4 and T_6 which has been discussed in the light of core like nature of 4f- shells.

- The higher values of symmetry indicating parameters T_6 have been discussed in the light of the large cationic sizes and the rapture of hydration zone on complexation. 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 ratio of T_2/T_6 is used to examine the selective roles of covalency and symmetry in the susceptibility of particular electronic transition. This has been used as additional evidence to the change in bonding pattern from the pre Gd element to post Gd elements. The result has been discussed in the light of lanthanide contraction and the rupture of hydration zones.

- The inter-electronic repulsion (RACAH) parameters and the nephelauxetic ratio values lie within the theoretical ranges of (i) $\delta E^1, \delta E^3 \sim$ **1 % of E^1 and E^3** and (ii) **$-0.091 < \delta E^3/\delta E^1 > 0.214$** which justified the validity of present calculation.

- The nephelauxetic ratio values showed a direct dependance on the partial charge on the ligand donor atoms which has been

discussed as additional evidence to the delocalization of 4f orbitals under the ligand field.

- The energy values for the HST and pseudo- HST translation showed a sequence

Er < Nd < Tm < Pr < Sm < Dy < Eu

The trend has been discussed in light of the variation in S, L and J quantum numbers, the increasing order of S quantum numbers and decreasing order of L and J quantum numbers.

- The radiative properties of the metal in a revealed a dependence of the electric dipole line strength on the ligand characteristic and/or the partial charge on ligand donor atoms.

- The transition probabilities A and A_T and the branching ratio values showed a dependance on the ligand characteristic.

- The T_R values were utlised to evaluate the valuation in the T_R values for other inter mediated levels.

- The relaxation timing evaluated for the intermediate assingment levels showed a sequence

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) $^5L_6 > {}^5H_6 > {}^5L_7 > {}^5G_6 > {}^5D_2$

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

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

Tm(III) $^3F_3, {}^3F_2 > {}^1P_2 > {}^3H_4 > {}^1G_4$

which has been discussed in the light of relative allowances of the specific electronic transition.

- The variation in the HST trinsition for Pr (III) and Nd(III) has been used to evaluate the Ln-O bond distance for the present set of complexes. The variations in the bond distance with respect to ligand have been discussed in light of Ln(III) contraction and increased electrostatic nature of [Ln - L] interaction.

- The electronic spectral properties such as oscillator strength, Judd Ofelt , the electric dipole line strength, the T_R values have been correlated with the partial charge on ligand donor atoms which rebuild depedance.

- The variations in the various spectral parameters have been correlated with the J quantum number of the metal ions.

- The J plot exhibits semi - sigmoid nature with varied responses for different ligand systems.

○ The magnitude of semi sigmoid nature of the J plot also exhibited variation from pre Gd element to post Gd element which reassemble with the theoretical plots for U2 and E average values the nature of which have been discussed in the light of preserved core like feature of the 4f shell even after complexation.

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