

## ACKNOWLEDGEMENTS

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## PREFACE

A systematic analysis of the electronic spectral parameters has been utilised as a tool to investigate the structural modification in [Lanthanide-Aromatic ligand] complexes for the two sets of elements, Pr(III), Nd(III), Sm(III) and Eu(III) representing pre-Gd elements and Dy(III), Er(III) and Tm(III) representing the post-Gd elements of the lanthanoid series. Binary and ternary systems have been chosen for the present study. In all ~four ligands with seven lanthanoids comprising overall ~56 systems carried out at five different pH values making a total of ~ 240 spectral data measurements, have been carried out. The present thesis focusses upon the electronic spectral studies of a set of pre-Gd Pr(III), Nd(III), Sm(III) and Eu(III) post-Gd Dy(III), Er(III) and Tm(III) elements of lanthanide (rare earth) series in aqueous mediums with three aromatic amino acids and an antituberculosis drug Pyrazinamide. However, the ligands *show similarity in their bonding patterns, however, they differ in their donor atom characteristics*. A detailed spectral analysis of lanthanoids in these aromatic and aliphatic ligands environments has been undertaken.

The spectral studies include the evaluation of electronic spectral parameters such as **i.** oscillator strength values, **ii.** Judd-Ofelt parameters, **iii.** inter electronic repulsion (RACAH) parameters and **iv.** the nephelauxetic ratio values. The radiative properties like the following **i.** induced electric dipole transition strengths, **ii.** relaxation timings and **iii.** branching ratio have also been taken into account. The contents of the work have been divided into four chapters.

**Chapter-I INTRODUCTION AND SURVEY OF LITERATURE** incorporates **THE SURVEY OF LITERATURE** a brief description of general features of lanthanoid elements, their class A character, coordination number variation, structural adaptations ex-

hibited by pre- and post-Gd elements, have been incorporated in the beginning as **INTRODUCTION**. The chemical consequence of the lanthanoid contraction, concomitant nephelauxetic effects and their thermal consequences in both solid as well as solution complexes extracted from the literature have also been reported. A detailed survey of solution complexes especially with respect to spectral parameters has been made. A statement on the definition of *hypersensitivity* and theoretical models to explain the phenomenon including experimental evidences have also been incorporated. The chapter ends with a note on the aim and scope of the present work.

*Chapter - II* **METHODS, METHODOLOGY AND EXPERIMENTATION** has been divided into three parts. **Part A** briefly states the theory of electronic transitions in lanthanoids, their origin and possible characteristics. **Part B** in this part we have discuss in detail the method of evaluating electronic spectral parameters, the oscillator strength, and Judd - Ofelt theory. The specified electronic parameters with their definitions and units, radiative properties viz., induced electric dipole transition strengths, relaxation timings and branching ratio have also been discussed. **Part C** describes the preparation of stock solutions of lanthanoids and ligands ( amino acids / Pyrazinamide), sets for their comparative studies in complex mediums, the details of recording of electronic spectra, the required instrumental setup and the evaluation of spectral parameters. Details of the computer software used in the present study have also been given. The variations in the oscillator strengths, Judd Ofelt parameters, radiative properties for the individual systems have been incorporated in sets of four tables respectively.

*Chapter III* the **RESULTS AND DISCUSSION** incorporates a serieswise discussion on the observed electronic and radiative parameters with respect to lanthanide and / or ligand environment characteristics.

The Discussion follows observations on the variation

profiles of the oscillator strength values with respect to pH of the medium. A comparison of the oscillator strength values with respect to the ligands within the series has also been attempted and interpreted. The variation in the Judd - Ofelt parameters ( $T_{\lambda}$ ) and the corresponding ( $\Omega_{\lambda}$ ) parameters for a metal ion with respect to ligands or the metal ions within the series have been discussed in terms of the metal and ligand characteristics. A diagrammatic representation of these variation profiles using 3D Excel bar plots has also been incorporated. The variations in the oscillator strengths and the Judd Ofelt parameters have been discussed in the light of relative hardness of Ln(III) ions and the softness values of ligands. The radiative properties have been discussed in terms of the ligand characteristics. Few variation profiles between spectral parameters viz., oscillator strengths, Judd Ofelt parameters, nephelauxetic ratio values, the electric dipole line strengths and the relaxation timings and the matching constant values with the partial charge (evaluated using Pearson's Hard Soft acid base theory and the MOPAC7 PM1/AM3 level calculations) on the ligand donor atoms have also been discussed.

*Chapter IV* constitutes the **SUMMARY AND CONCLUSIONS** and summarises some of the prominent observations made in the thesis. Few fundamental properties viz., electronic configurations, S, L and J quantum numbers, structures of the ligands, the output of PM1/AM3 ab initio level calculations etc. alongwith a list of publications, have been presented at the end of the thesis as **APPENDIXES**.