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PREFACE

Electronic spectral parameters have been utilised as a tool, to investigate the structural modifications developed in the binary and mixed ligand complexes of lanthanoids, involving amino acids. The lanthanoid elements chosen for the studies are: Nd(III), Sm(III) and Eu(III) (representing pre-Gd elements) and Er(III) (representing the post-Gd elements). Amino acids chosen for the present study include eight Aliphatic / Aromatic amino acids viz., include- α-alanine, valine, leucine, serine, cystine, aspartic acid, histidine and tryptophane and a primary ligand diaminocyclohexane N,N,N′,N′-Tetra Acetic acid (CDTA). Eight ligands with four lanthanoids, comprising of ~64 systems were carried out at three different pH values (in higher and lower buffer regions) making in all ~192 spectral data measurements. The present thesis emphasises upon a comparison of electronic spectral studies of a set of pre- and post-Gd elements in aqueous medium. The ligands show similarity in their bonding patterns, but, they differ in their side chains, length or bulk or the aliphatic and/or aromatic substitutions.

An effect of these side chains (their bulk and lengths) and their aliphatic/aromatic substitutions on the spectral parameter and the spectral stabilisation of the ground terms have been examined. The effect has been observed in light of variations in the symmetry indicating parameters and parameters indicating 4f-shell deformation under the ligand field. A detailed spectral analysis of lanthanoids in these aromatic and aliphatic ligands environments has been undertaken. The spectral parameters include: i. oscillator strengths, ii. Judd-Ofelt parameters, iii. inter electronic repulsion (RACA) parameters and iv. the nephelauxetic ratio values and the radiative properties such as 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 five 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 (exhibited 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 and also the extrastabilisation of the mixed ligand complexes due to possible cooperative inter ligand interactions have been taken from the literature. A detailed survey of solution complexes especially with respect to spectral parameters have been made. Stabilites of amino acids and their extra stabilization caused due to inter-ligand interactions and the concomitant structural modification in the complexes have also been made. The chapter ends with a note on the aim and scope of the present work.

Relevant references on the subject have been incorporated at the end of the chapter.

Chapter II METHODS, METHODOLOGY AND EXPERIMEN-
TATION 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 a detailed discussion on the method of evaluating electronic spectral parameters, the oscillator strength, and Judd - Ofelt theory has been attempted. 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), 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 and the computer softwares used in the present study etc. The variations in the oscillator strengths, Judd-Ofelt parameters, radiative properties for the individual systems have been incorporated in sets of four tables respectively.

Relevant references on the subject have also been incorporated at the end of the chapter.

Chapter III incorporates the PRELIMINARY DATA as observations made on electronic spectral parameters and their radiative properties. Representative electric spectral variation for the
four Ln(III) from in different ligand environments different pH values have been recorded as electric spectral plots in the beginning of spectral variations. A diagrammatic representation of Judd Ofelt parameters using 3D Excel bar plots have also been incorporated.

Chapter IV the **RESULTS AND DISCUSSION** incorporates a metal wise discussion on the observed electronic and radiative parameters with respect to different ligand environment.

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 have also been attempted and interpreted. The variation in the Judd - Ofelt parameters (T_a) and the corresponding (\( \Omega_a \)) 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. 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, and the matching constant values with the partial charge (evaluated using Pearson’s Hard Soft acid base theory) have also been attempted.

Chapter V constitutes the **SUMMARY AND CONCLUSIONS** and summarises some of the prominent observations made in the thesis.

Fundamental ligand structures and a list of publications have been presented at the end of the thesis as **APPENDIXES**.