Spectroscopic studies of lanthanides have been subjected to various workers. Lanthanides have no known inherent biological function but only trace amounts have been detected in whole body analysis.\(^1\) Lanthanide salts were first investigated in clinical trials for antimicrobial, anticoagulant and other pharmacological properties in the early part of the century.\(^2\) The scope of this review is to survey the biological activity and co-ordination phenomena of lanthanides.

Misra et al\(^5\) had proposed a modified method for the evaluation of spectral parameters (i.e., energy interaction, spin-orbital interaction, bonding, nephelauxetic, oscillator strength and Judd-Ofelt parameters) of 4f→4f transitions in Pr (III) and Nd (III) complexes. S.N. Misra and S.O. Somerer\(^6\) had studied the ligand mediated pseudohypersensitivity of the \(^3\)H\(_4\)→\(^3\)P\(_2\), \(^3\)H\(_4\)→\(^3\)P\(_1\), \(^3\)H\(_4\)→\(^3\)P\(_0\) and \(^3\)H\(_4\)→\(^1\)D\(_2\) transitions of Pr(III) complexes in solution media. They had reported that such transitions exhibit substantial intensification as well as a wide variation of oscillator strength by employing absorption difference, comparative absorption spectrophotometry and quantitative analysis of 4f-4f spectra of Pr(III) complexes with ligands possessing varying structural features and binding capabilities. These transitions

CHAPTER NO. II

REVIEW ON LANTHANIDES: BIOLOGICAL ACTIVITY AND COORDINATION PHENOMENA

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cannot be considered hypersensitive as they do not follow the selection rule. They had also considered the solution spectra of 173 species and reported the high sensitivity of the Pr (III) transitions, viz: $^3\text{H}_4 \rightarrow ^3\text{P}_2$, $^3\text{P}_1$, $^3\text{P}_0$ and $^1\text{D}_2$ and they had termed the unique sensitivity of such transitions as 'Ligand Mediated Pseudohypersensitivity'. K. Binnemans\textsuperscript{7} discussed the reliability and sensitivity of Judd-Ofelt intensity parameter $T_\lambda$ ($\lambda=2,4,6$) by comparing experimental absorption spectra with simulated spectra. S.N. Misra et al\textsuperscript{8} had studied about the preparation and characterization of some praseodymium haloacetates and investigation of their electronic spectra in different non-aqueous solvents (DMF, DMSO, MeOH and their equimolar mixtures). It has been reported that the absorption spectra of praseodymium monohaloacetates when recorded in non-aqueous polar solvents like methanol, DMF and DMSO and in their equimolar mixtures showed significant changes in the intensities of the absorption bands. The intensification of the bands had been interpreted in terms of increased interaction of the 4f-orbitals with ligand orbitals. They had also reported that praseodymium monohaloacetates form complexes with aprotic dipolar solvents DMF and DMSO and complex formation is responsible for intensification of the bands in these media. In general, they had found that the increase in the intensity was greatest with DMF and least for methanol. The intensity (oscillator strength, P) data with DMF and DMSO were quite similar which can be correlated with greater ligating strengths of DMF and DMSO as compared to that of Methanol.

S. Jerico et al\textsuperscript{9} had studied the behaviour of the phenomenological 4f-4f intensity parameters in compounds of the Nd\textsuperscript{3+} ion with Amino Acids (glycine, L-aspartic acid, L-glutamic acid, L-histidine, DL-malic acid and Aspartame) in aqueous solution, as a function of the P$^k$
values and partial charges on the oxygen of the carboxylate groups of these molecules. They had reported that the intensity of the hypersensitive $^4I_{9/2} \rightarrow ^4G_{5/2}, ^4G_{7/2}$ transitions increases as the pH increases up to approximately 5.4 value. For pH values above 5.5, the Nd$^{3+}$ ion hydrolyses. Among the $T_\lambda$ parameters, in general, $T_2$ is the most sensitive to the coordination geometry and the characteristics of the ligands. They had also examined the behaviour of $T_2$ with the ligands $P^k$ and found that $T_2$ has varied linearly with $P^k_1$ provided the monocarboxylic and dicarboxylic species were considered separately. They had also examined the behaviour of $T_2$ with the average value $<P^k>= (P^k_1 + P^k_2)/2$, since at $pH \sim 5$ both carboxylic groups are expected to be equally deprotonated. In this case, $T_2$ has increased with $<P^k>$, but not linearly.

Tater et al.$^{10}$ had studied electronic spectral studies on Nd$^{3+}$ doped sulphoanilide system. It also provides useful information regarding metal-ligand interaction and change in symmetry around lanthanide ion. S.N. Misra et al.$^{11}$ had studied about the interactions of praseodymium and neodymium with nucleosides and nucleotides in different stoichiometry in water and water-DMF mixtures by employing absorption difference and comparative absorption spectrophotometry. These studies indicated that the binding of the nucleotide is through phosphate oxygen in a bidentate manner and the complexes undergo substantial ionisation in aqueous medium, thereby supporting the observed weak 4f-4f bands and lower values for nephelauxetic effect ($\beta$), bonding (b) and covalency ($\delta$) parameters derived from coulombic and spin-orbit interaction parameters.

J.L. Ryan and C.K. Jorgensen$^{12}$ had studied the absorption spectra of octahedral lanthanide hexalides particularly about Ce (IV), Sm (III), Eu (III), Tm (III) and Yb (III) hexalides. They
had found that the apparent optical electronegativities are somewhat higher than for the analogous halide complexes in ethanolic solution. S.N. Misra et al.\textsuperscript{13} had investigated about the synthesis and electronic spectral studies of mixed soaps, chloride mixed soaps and alkoxide mixed soaps of Pr (III) and Nd (III). As expected the values of $F_k$ and $\xi_{fr}$ for the Pr (III) and Nd (III) complexes are lower than the corresponding parameters of free ions. It is quite evident that ternary mixed trisoaps of the type $M(OOCR)(OOCR')(OOCR'')$ exhibit maximum nephelauxetic effect and lowest $F_2$ value. The chloride mixed disoaps have lowest nephelauxetic effect which is quite understandable in the presence of electronegative Cl\textsuperscript{-} ion bonded strongly to hard lanthanide metal ion. The isopropoxide mixed disoaps and t-butoxide mixed disoaps have the values of nephelauxetic effect (1-$\beta$) and mixing coefficient ($b^{1/2}$) which are intermediate between those of the comparatively covalent ternary mixed trisoaps $M(OOCR)(OOCR')(OOCR'')$ and comparatively ionic chloride mixed disoaps. In case of Pr (III) compounds, the negative values of $T_2$ parameter are of little significance while in case of Nd (III) compounds, the $T_2$ parameters are of great significance.

Misra\textsuperscript{14} had done studies on Pr (III) and fluorouracil, fluorocystosine, fluoroadine, fluorothymine, fluorouridine, fluorocytidine, fluoroadenosine and fluorothymididene systems at pH $\sim$ 5.5 and in different stoichiometries in 80% DMF by employing absorption difference and comparative absorption spectrophotometric technique. Magnitudes of spectral parameters and their variation have provided information on the binding mode of these biomolecules in terms of outer and inner sphere complexation, degree of covalency and extent of 4f-orbital involvement. The analysis of the isolated solid complexes had suggested octa- and nona-coordination for Pr(III) in fluorinated nucleic bases and fluorinated
nucleoside complexes. Joseph and his co-workers\textsuperscript{15} had reported about the absorption spectral studies on the interaction of adenine, adenosine, adenosine 5'-mono-adenosine 5'-di- and adenosine 5'-triphosphates with Pr(III) in different stoichiometries and at varying hydrogen ion concentrations. The sharp bands in the spectra had been analysed by Gaussian Curve analysis and various spectral parameters have been computed using partial and multiple regression methods. The studies of the crystalline complexes of the type: Pr (nucleotide)$_2$ (H$_2$O) (where nucleotide = AMP, ADP & ATP) indicate that the binding of the nucleotide is through phosphoric oxygen. Henrie and co-workers\textsuperscript{16} had shown that the low magnitudes of oscillator strengths indicate outer sphere complexation while high values indicate inner sphere complexation. For the present complexes T$_2$, T$_4$ and T$_6$ parameters have low values, indicating thereby the predominance of outer sphere complexation.

Misra et al\textsuperscript{17} had recorded absorption spectral intensity data in a series of structurally related Pr (III) and Nd (III) complexes with nitrogen, phosphorous, arsenic, bismuth and oxygen donor ligands (L) [L-being triphenylamine (TPA), triphenylphosphine (TPP), triphenylphosphineoxide (TPPO), triphenylarsine (TPAs) and triphenyl bismuthine (TPBi)] in DMF, methanol and acetonitrile. The significant variation in the intensities of certain absorption bands and perturbation on f-f transition intensities which are clearly apparent in Judd-Ofelt. (T$_3$) parameters computed for the different complexes under different experimental conditions are caused by the different ligands and solvents. The relative sensitivities of the 4f-4f transitions and (T$_3$) parameters and the specific correlation between relative intensities, ligand structures and nature of Ln(III)-ligand interaction are shown by the variation of oscillator strengths of different 4f-4f transitions and the computed values of
Judd-Ofelt electric dipole intensity (T\textsubscript{A}) parameters. Indira\textsuperscript{18} had one studies involving 4f-4f transition of Nd (III) and different diols (butane1, 4-diol, butene1, 4-diol and butyne1, 4diol) by employing intensity difference and comparative absorption spectrophotometric technique in DMF and Methanol as well as in equimolar mixtures of DMF+CH\textsubscript{3}N, DMF+CH\textsubscript{3}OH, DMF+dioxane, CH\textsubscript{3}OH+CH\textsubscript{3}CN and CH\textsubscript{3}CN+dioxane. The involvement of \pi-electron density of diols in complexation with Nd (III) are revealed from the correlations made from the plot of Oscillator strength (Pobs) against T\textsubscript{A} parameters. The absorption spectral bands of Nd (III)-diols in DMF solvent clearly show that the presence of single, double and triple bonds in diols affect the energies and oscillator strength of these 4f-4f bands. It has been found that the sequence of the three diols in complexation is butane diol <butene diol <butyne diol.

Lakshman and Buddhudu\textsuperscript{19} had calculated the values of the Slater-Condon (F\textsubscript{2}, F\textsubscript{4}, F\textsubscript{6}), Racah (E\textsuperscript{1}, E\textsuperscript{2}, E\textsuperscript{3}) and Lande (\xi\textsubscript{d}) coefficients, the nephelauxetic ratio (\beta), the bonding parameter (\beta) and the Judd-Ofelt Intensity (T\textsubscript{A}) parameters from the reported absorption spectra of Pr\textsuperscript{3+}, Nd\textsuperscript{3+} and Er\textsuperscript{3+} ions in an aprotic solvent SeOCl\textsubscript{2} acidified with antimony pentachloride. They had suggested that the nature of bonding is covalent in the laser liquid (for Pr\textsuperscript{3+}, Nd\textsuperscript{3+} and Er\textsuperscript{3+} ions). Peacock\textsuperscript{20} had studied the sensitivity of completed Judd-Ofelt parameters to the particular transitions used. It appears to be necessary to associate a separate value of T\textsubscript{2} with each hypersensitive transition. Hussain et al \textsuperscript{21} had reported about the optical absorption and NMR studies of trivalent lanthanide complexes with 2,2'-bipyridine (bpy). The paramagnetic and intramolecular shift ratio have been recorded and analysed and suggested that the paramagnetic shift is predominantly dipolar in origin. They had also studied the electronic
spectra Pr, Nd, Ho, Er and Dy complexes in different solvents viz, MeOH, pyridine, DMSO and DMF) and revealed that the chemical environment around the lanthanide ion has great impact on f-f transitions and any change in the environment results in modifications of the spectra. They had also determined the oscillator strength for the hypersensitive and non-hypersensitive transitions. It has been found that the largest increase in the oscillator strength is found in pyridine and this could be related to the ligand polarization effect and the smallest increase in the oscillator strength in DMSO. It has been found that the values of $b^{1/2}$ and $\delta$ are highest for pyridine, which follows that it is the strongest ligand in a nephelauxetic sense and the complexes in this solvent show largest covalency.

Khan and Iftikhar\textsuperscript{22} had studied the interaction of trivalent lanthanide thiocynates and 2, 2'-bipyridyl in ethanol and this results in the formation of the complexes viz; [Ln (bpy)$_n$ (SCN)$_3$ (H$_2$O)]$_y$ where Ln stands for La ($n=3$, $x=1$, $y=0$), Pr ($n=3$, $x=y=0$), Nd ($n=3$, $x=0$, $y=1$), Sm, Eu ($n=2$, $x=1$, $y=0$), Dy, Er ($n=2$, $x=2$, $y=1$), Ho and Yb ($n=2$, $x=2$, $y=0$). It has been found that the complexes are non-electrolyte in methanol and the three triocynates are inside the first co-ordination sphere, the La-complex is ten-coordinate, the Sm and the Eu complexes are eight-coordinate while others are nine-coordinate. They had also analysed the chemical shifts and the paramagnetic shifts are found to be predominantly dipolar in nature. The Pr, Nd, Sm and Eu are isostructural in methanol.

Khan et al\textsuperscript{23} had done absorption spectroscopic studies on the mixed ligand complexes of Pr (III) and Nd (III) with 2,2'-bipyridyl and thiocyanate in pyridine, DMSO, DMF and methanol. They had calculated the oscillator strengths for the hypersensitive and non-hypersensitive transitions and had compared with 1,10-phenanthroline complexes and shown
that bipyridyl is a weaker ligand than phenanthroline for these ions. It has also been found that pyridine is the most effective ligand in promoting 4f-4f intensity. M. Indira\textsuperscript{24} carried out Comparison of electric-dipole intensity parameters for a series of structurally related Nd(III) complexes with ureas and thioureas in non-aqueous media. Fields and Rajnak\textsuperscript{25} had correlated the experimentally determined band intensities in the solution absorption spectra of the trivalent lanthanides with a theoretical expression derived by Judd. The spectra were measured in a single medium, dilute acid solution, and, in most cases, in the range \( \approx 6000-50,000 \text{ cm}^{-1} \). They had also discovered the variation of the intensity parameters.

Gunnlaugsson et al\textsuperscript{26} had reported about the synthesis, structural and biological evaluation of Gly, Ala based lanthanide macrocyclic conjugates as supramolecular ribonuclease mimics. Zhang et al\textsuperscript{27} had done hydrothermal synthesis and crystal structures of three novel lanthanide coordination polymers with glutarate and 1, 10-phenanthroline. They had prepared the first series of lanthanide coordination polymers with glutarate (glu) and 1, 10-phenanthroline (phen), \([\text{Nd}_2 \text{(glu)}_3 \text{(phen)}\text{Cl}]_n\)\textsubscript{1}, \([\text{Tb (glu)} \text{(phen)}\text{Cl}]_n\textsubscript{2}\) and \([\text{Ho (glu)} \text{(phen)}\text{Cl}]_n\textsubscript{3}\) by hydrothermal reaction and they are two different conformations for glutarate ligands, the gauche- and anti-forms. Nd (III) ions are bridged by glutarate ligands in three modes to form 2D layer structure. Phen ligand coordinate to Nd (III) ions in chelating mode and protrude from the polymeric layer in two different directions. There exists two types of \( \pi-\pi \) interactions between two adjacent layers. In complex 2, Tb (III) ions are connected by glutarate ligands into 1D chain structure. Phen ligands coordinate to Tb (III) ions in chelating mode and locate at both sides of the chain. It has been found that the C-H...O, C-H...Cl weak hydrogen bonds and \( \pi-\pi \) slacking interactions between chains result in 3D
supramolecular structure. They have found that complex 3 is isostructural with complex 2 by single-crystal x-ray diffraction analysis. Subhan et al\textsuperscript{28} had reported the simultaneous observation of low temperature 4f-4f and 3d-3d emission spectra in a series of Cr (III) (ox) Ln (III) assembly.

Wang et al\textsuperscript{29} had studied the complexation of trivalent lanthanides with aromatic (mellitic, pyromellitic, hemimellitic, trimellitic, trimesic, phtalic, isopthalic, terephthalic and benzoic) carboxylic acids by employing luminescence and absorption spectroscopic methods. They had also found that both the luminescence spectra and decay constants under the conditions of this study, mellitate, pyromellitate, hemimellitate, trimellitate, trimesate and terephthalate form 1:1 complexes while phthalate, isophthalate, benzoate form 1:1 and 1:2 complexes. The carboxylate ligands with adjacent carboxylates group are bidentate and replace two water molecules upon complexation. It has also found that benzoate and terephthalate are unindented while isophthalate and trimesate replace approximately 1.5 H\textsubscript{2}O molecules, suggesting greater binding capability of these ligands due to the contribution from the non-binding carboxylate groups. They had also proposed that ligand polarisability along with other factors are responsible for the variation in oscillator strength in these complexes. Wang and Xie\textsuperscript{30} had reported about synthesis and crystal structure of a novel praseodymium complex with β-alanine: \{[Pr\textsubscript{2}(alanine)\textsubscript{6} (H\textsubscript{2}O)\textsubscript{4}] [(ClO\textsubscript{4})\textsubscript{6} H\textsubscript{2}O]\}. The structure of this complex comprises of two kinds of polymer chains, both with dimeric repeat units. In each dimeric unit, two praseodymium ions are connected by four carboxyl groups from β-alanine, two using simple bridges and two using tridentate bridges. A symmetry centre exists in each dimeric unit. The other two carboxyl groups link the units to each other by simple bridges.
With two coordination water molecules for each central ion, the praseodymium ions are nine-coordinated, forming distorted, monocapped, square antiprism polyhedrons. They had also reported that \( \beta \)-alanine-praseodymium complex exhibits significant differences in both composition and structure than \( \alpha \)-alanine lanthanide complex, usually with the core formula \([\text{Ln}(\alpha\text{-alanine})_4(\text{H}_2\text{O})_8]^{6+}\). Since the \( \beta \)-alanine ligand is more slender than \( \alpha \)-alanine, it is expected that \( \beta \)-alanine forms more compact structural complexes than \( \alpha \)-alanine.

Misra \(^{31}\) had studied the absorption spectral intensity data for multiplet to multiplet electronic transitions in a series of structurally related Nd (III) complexes of the type, \( \text{Nd(diket)}_2(\text{N})_2 \) (where diket is 1-phenyl-1,3-butanedione benzoylacetonate, \( \text{bzac} \), 1,3- diphenyl- 1,3-propanedione (dibenzoylmethane, \( \text{dbm} \)) and 4,4,4-trifluoro-L-(2-thienyl)-1,3-butenedione(thenyltrifluoroacetone, \( \text{ttfa} \)) and \( \text{(N)}_2 \) stands for two molecules of unidentate nitrogen ligands: pyridine, 2-chloro-, 2-bromo-, 2-acetyl-, 3-acetyl-, 4-acetyl-pyridine or one mole of bidentate 2,2'-bipyridine or O-phenanthroline) which have been recorded in MeOH, DMF, acetonitrile and isopropanol. They had also suggested specific correlations between the relative intensities, ligand structure and nature of Nd (III) -ligand interaction by studying the variation of oscillator strengths of different 4f-4f transitions and computed values of electric dipole intensity and Judd-Ofelt parameters(\( T_\lambda \)). Zhao et al \(^{32}\) had reported the synthesis of lanthanide complexes with L-isoleucine: X-ray crystal structure of \([\text{Nd}_2(1\text{-leu})_4(\text{H}_2\text{O})_8][\text{ClO}_4]_6\). They had synthesized two lanthanide complexes, \( \text{Ln}_2(1\text{-leu})_4(\text{ClO}_4).8\text{H}_2\text{O} \) in aqueous solution (where \( \text{Ln} = \text{Nd or Er}, 1\text{-leu} = \text{L-isoleucine} \)). They had determined the crystal structure of the Nd – complex by X-ray diffraction. The complex is a
binuclear complex, each neodymium ion is coordinated by four carboxylic oxygen atoms from four L-isoleucine and four oxygen atoms from water, forming a square antiprism coordination polyhedron. They had also reported that the crystal structure of the isoleucine complex has some similarities with those of alanine and phenylalanine complexes. For example, they are all dimeric molecules, eight-coordinated and have a $C_2$ symmetry axis.

Inomata et al.\textsuperscript{33} had reported the synthesis and crystal structure of lanthanide metal complexes with N,N-bis(2-hydroxyethyl)glycine and they are characterized by means of IR spectra, magnetic susceptibility, thermal analysis and powder X-ray analysis. They had reported that this complexes appear as two types: $[M(\text{bheg})_2]\text{Cl.}3\text{H}_2\text{O}$ and $M(\text{bheg})_2(\text{CH}_3\text{COO})(\text{H}_2\text{O})_4$ ($M$: La, Ce, Nd). They had determined the crystal and molecular structure of $[\text{La(}\text{bheg})_2]\text{Cl.}3\text{H}_2\text{O}$ by a single crystal X-ray diffraction method. The central lanthanum atom is nine-coordinated with a face-centered trigonal prism geometry. The structure of this complex consists of a one-dimensional polymer bridged by carboxylato oxygen atoms. This complex has two types of carboxyl groups: one works as a bidentate ligand and bridges to two lanthanum atoms in anti-anti type. There are six intramolecular and twelve intermolecular hydrogen bond. The complex molecules are connected to each other in three dimensions by these intermolecular H-bonds. Zou et al.\textsuperscript{34} had studied the synthesis and structure of carboxylate-bridged polynuclear Copper (II):Lanthanum(III) ring: $[\text{La(}\text{H}_2\text{O})_5(\text{CuL})_2][\text{CuL}].8\text{H}_2\text{O}$. They had prepared the complex, $[\text{La(}\text{H}_2\text{O})_5(\text{CuL})_2][\text{CuL}].8\text{H}_2\text{O}$ by the reaction of the Na[CuL] (where $L$ = Schiff base derived from 5-bromosalicylaldehyde and glycylglycine) with LaCl$_3$.nH$_2$O. The structure of the title complex is such that it contains ring like hexanuclear $[\text{La}_2(\text{H}_2\text{O})_{10}(\text{CuL})_4]^{2+}$ cation.
Gheorghe and his co-workers\textsuperscript{35} had reported new binuclear model compounds for the study of the 4f-4f exchange interaction. Zhang and Wang\textsuperscript{36} had studied and investigated and measured the absorption spectrum of Neodymium (III) (Nd\textsuperscript{3+}) doped in poly(methylmethacrylate). They had found that the nephelauxetic effect in the spectrum had been compared to other spectra of Nd\textsuperscript{3+} doped in various matrices. By using the Taylor series expansion which is based on the assumption that the energy separation between J levels of the 4f\textsuperscript{n} configuration is a function of F\textsubscript{2}, F\textsubscript{4}, F\textsubscript{6} and \( \xi_{4f} \), they had calculated the Slater-Condor parameters (F\textsubscript{2}, F\textsubscript{4}, F\textsubscript{6}) and Lande parameter. They had reported that the nephelauxetic parameter can be related to the covalency factor by

\[ b^{1/2} = \left[ \frac{1 - \beta}{2} \right]^{1/2} \]

indicating that as \( \beta \) decreases, \( b^{1/2} \) increases, the 4f–ligands mixing increases, the degree of covalency increases and the nephelauxetic effect exhibits a corresponding increase. Costes, Novitchi, Lebrun\textsuperscript{37} had reported the synthesis and characterization of new heterodinuclear (4f, 4f') lanthanide complexes. They had synthesized heterodinuclear complex from the reaction of 3-ethoxysalicylaldehyde and tris (2-amino ethyl) amine in which the La ions are coordinated in the inner N\textsubscript{4}O\textsubscript{3} and the outer sites. Introduction of the second lanthanide ion as a trifluoroacetate salt yields heterodinuclear entities which are soluble enough to be characterized by electrospray mass spectrometry techniques. Bukietynska and Choppin\textsuperscript{38} had investigated the environmental effects of nitrate, sulfate and \( \alpha \)-picolinate anions on f-f transitions of lanthanide ions in aqueous solution.
Zinner and Brito\textsuperscript{39} had reported about the synthesis and properties of complexes between lanthanide trifluoroacetates and 2-picolline-N-oxide (2-PicNO)\textsuperscript{+}. They had described the complexes of lanthanide trifluoroacetates with 2-picoline-N-oxide (2-PicNO) with composition Ln (CF\textsubscript{3}COO\textsubscript{3}. 2 (2-Pic-NO). They were characterized by elemental analysis, electrolytic conductance measurements, x-ray powder patterns, IR and absorption (neodymium) and emission (europium) spectra. They had grouped the compounds in 3 isomorphous series: (a) La, Pr (b) Nd, Sm and (c) Eu, Lu, Y. They behave as non-electrolytes in CH\textsubscript{3}CN. They had suggested two types of coordination of the anion and coordination of 2-PicNO through the oxygen. Electrostatic interaction has been indicated from the absorption spectra. Benetollo et al\textsuperscript{40} had reported about the coordination chemistry of lanthanides with Cryptands: An x-ray and spectroscopic study of the complex, Nd\textsubscript{2} (NO\textsubscript{3})\textsubscript{6} [C\textsubscript{18}H\textsubscript{36}O\textsubscript{6}N\textsubscript{2}.H\textsubscript{2}O. They had synthesized the complex Nd\textsubscript{2} (NO\textsubscript{3})\textsubscript{6} [C\textsubscript{18}H\textsubscript{36}O\textsubscript{6}N\textsubscript{2}.H\textsubscript{2}O by reacting neodymium nitrate hexahydrate with the cryptand <222> in methanol. They were analysed by single crystal x-ray diffraction. They had reported that the compound contains the cations [Nd<222>(NO\textsubscript{3})\textsubscript{2}]\textsuperscript{2+} and the anions [Nd(NO\textsubscript{3})\textsubscript{6}.H\textsubscript{2}O]\textsuperscript{2-} and is isostructural with the samarium analogue.

Bukietynska and Mondry\textsuperscript{41} had investigated the spectral properties of Nd\textsuperscript{3+} - EDTA solutions at different Nd\textsuperscript{3+} EDTA concentrations within a broad pH region. In order to investigate the formation and the type of bonding in the Nd\textsuperscript{3+} - EDTA species, the analysis of the oscillator strength values of the 'hypersensitive' \textsuperscript{4}G\textsubscript{7/2}, \textsuperscript{4}G\textsubscript{5/2} \leftrightarrow \textsuperscript{4}I\textsubscript{9/2} transition and of the Judd-Ofelt intensity parameters. They had suggested a relatively complete model of the Nd\textsuperscript{3+} - EDTA coordination by the correlation of these results with NMR and kinetic data. Kamenskaya and Mikheev\textsuperscript{42} had also investigated about the coordination compounds of divalent lanthanides.
with crown ethers. Santos et al\textsuperscript{43} had reported about the crystal structures of Neodymium and Holmium Trifluoromethane sulfonate Enneahydrated. Fox et al\textsuperscript{44} had studied about praseodymium nitrate and neodymium nitrate complexation with organophosphorus reagents in supercritical carbon-dioxide solvent. Mehta et al\textsuperscript{45} had explored heterobimetallic complexation of lysozyme (HEW) with hard metal ions Pr (III)/Nd (III) and soft metal ion Zn (II) using absorption difference and comparative absorption spectroscopy involving 4f-4f transitions in aquated organic solvents. They had correlated the changes in the oscillator strengths of different 4f-4f bands and experimentally determined Judd-Ofelt (T\text(_j\text) parameters with the binding of lysozyme with the two chemically different metal ions Pr (III)/Nd (III) and Zn (II) in different aquated organic solvent. They had recorded the comparative absorption spectra of Pr (III)/Nd (III) in aqueous and aquated organic solvents at pH 0.6, 1.4, 2.0, 4.0 and 6.0 and they had calculated intensity parameters from the observed 4f-4f bands using partial and multiple regression analysis (Misra et al, 1980, 1992, 1993, 1994 and 1997). They had investigated and reported that the binding of lysozyme and Pr (III)/Nd (III) is stronger in acidic medium i.e, pH less than one, but no significant change is observed upto pH 6.0. When pH increases from 0.6 to 6.0, the intensity data shows some hypochromacity in the observed 4f-4f bands of Pr (III) and Nd (III). They had also reported that in 50 : 50 DMF – water, the change in the oscillator strength values were meager while noticeable effect was seen when solvent solvent was 70 : 30 DMF – water. Not only this they had also reported that similar observations were found in aquated acetonitrile, aquated methanol and aquated dioxane. From these, they had concluded that solvent effect are more marked on the complexation as compared to the effect of pH (0.6 to 6.0).
Issa et al\textsuperscript{46} had described the synthesis and structural elucidation of some lanthanide–thioschiff base complexes. The structures of the complexes had been characterized by elemental analysis, IR, $^1$NMR and thermal analysis. The results indicate the formation of 1 : 2 (M : L) complexes with the general formula $(ML_2H_2O.X)2H_2O$ where $M = \text{trivalent Y, La, Ce, Pr, Nd, Sm, Gd, Dy, Ho, Er and Yb; HL (or H}_2L) = \text{thioschiff base and X = ClO}_4^{-}$ or Cl$^{-}$ ion. They had proposed C.N’s 6 and 8 for the lanthanides in these complexes. Takahashi and Ishiguro\textsuperscript{47} had reported about the inner-sphere and outer-sphere complexes of Yttrium (III), Lanthanum (III), Neodymium (III), Terbium (III) and Thulium (III) with halide ions in N, N-dimethylformamide. Habenschuss and Spedding\textsuperscript{48} had studied about the coordination (hydration) of rare earth ions in aqueous chloride solutions from X-ray diffraction in SmCl$_3$, EuCl$_3$ and series behavior. They had investigated and reported that inner sphere water coordination of the ions in aqueous solutions decreases from 9 to 8 due to the decreasing rare earth ionic radii. The ions La$^{3+}$ through Nd$^{3+}$ are nine coordinated, those between Nd$^{3+}$ and Tb$^{3+}$ are transitional between nine and eight, and those from Tb$^{3+}$ to Lu$^{3+}$ are eight coordinated.

Kumar and Rao\textsuperscript{49} had reported studies on some rare-earth metal complexes: Ten- and six-coordinated complexes of an unsymmetrical amino acid derivative. They had synthesized and characterized 2, 4-Dihydroxy benzaldehyde (N-benzoyl) glycy1 hydrazone, $H_2$dhbbgh. They had also synthesized rare earth metal complexes of the empirical formulae, [Ln ($H_2$dhbbgh)$_2$Cl$_2$]Cl.nH$_2$O and [Ln (dhbbgh) (H$_2$O)$_2$], where $Ln = \text{La (III), Pr (III), Nd (III), Sm (III), Eu (III), Gd (III), Tb (III), Dy (III) and Y (III) and they are characterized by elemental analyses, molar conductances, magnetic susceptibilities, electronicx, IR and NMR.
spectral studies. They had calculated various bonding parameters ($\beta$, $b^{1/2}$, $\delta^\%$ and $\eta$) from the electronic spectra of Pr (III), Nd (III), Sm (III) and Dy (III) complexes had suggested that there is a weak covalent bond between the metal and ligand. The experimental values and the theoretical values of the oscillator strength and the Judd-Ofelt Intensity parameters ($T_\alpha = 2, 4, 6$) are in good agreement. They had proposed C.N’s ten and six for the Ln (III) ions in the adduct and deprotonated complexes respectively on the basis of the spectral profiles of the hypersensitive transitions ($^4I_{9/2} \rightarrow ^4G_{3/2}$, $^4G_{7/2}$). Srivastava et al$^{50}$ had studied about the lanthanide complexes of 4-(N-Acetyl)-amino antipyrine. They had synthesized a series of new complexes of lanthanide (III) chlorides and bromides with 4-(N-acetyl) amine antipyrine (NAAA) and they are characterized by various physicochemical techniques. They had reported that the C.N. of lanthanide (III) in these complexes is seven.

Wong$^{51}$ had reported about the configuration interaction of the Pr$^{3+}$ ion. Misra et al$^{52}$ had studied about the neodymium (III)-substituted bismuth titanate thin film generation using metal alkoxo, acyloxo and $\beta$-diketonato precursors employing a sol-gel route and using 4f-4f transition spectra as probes to explore kinetic performance. Lebret et al$^{53}$ had reported about single crystal and for IR analysis of some lanthanide thiophosphates. Binnemans et al$^{54}$ had investigated about the relabilility of Judd-Ofelt Intensity parameters by graphical simulation of the absorption spectrum. Malta et al$^{55}$ had studied the intensity parameters of 4f-4f transitions in the Eu (dipivaloylmethanate)$_3$ 1, 10-phenanthroline complex. Chen and his co-workers$^{56}$ had investigated about the spectroscopic properties of Nd$^{3+}$ ions in La$_2$ (WO$_4$)$_3$ crystal. Devlin et al$^{57}$ had reported model calculations of 4f-4f intensity parameters for a series of tris (terdentate) Er (III) complexes. They had calculated the intensity which are
based on an electrostatic intensity model for lanthanide 4f-4f electric-dipole transitions by considering the static coupling (point-charge crystal field) and dynamic coupling (ligand polarization) intensity mechanisms. They had compared the intensity parameters obtained from the model calculations to those derived from empirical intensity data and correlations are made between the relative intensity properties exhibited by the various systems and their respective structural features. They had drawn conclusions regarding the relative contributions made by the static coupling Vs. dynamic coupling mechanisms to the $T_\lambda (\lambda = 2, 4, 6)$ intensity parameters.

Verma et al.\(^{58}\) had studied and calculated electronic spectral parameters, viz, Judd-Ofelt ($T_\lambda$), Racah ($E_k$), Slater Condon ($F_k$), Lande ($\xi_{\text{el}}$) and bonding parameters ($\beta$, $b^{1/2}$, $\delta$ and $\eta$) for the saturated solution of fifteen ligands having N and O donor atom, doped with Nd (III) ion. They had also observed the change in symmetry around Nd (III) ion and covalency in M-L interaction.

Wang et al.\(^{59}\) had reported the lanthanide coordination with $\alpha$-Amino Acids under near physiological pH conditions: Polymetallic complexes containing the cube-like [Ln₄($\mu_5$-OH)₄]⁺⁺ cluster core. Wang et al.\(^{60}\) had reported about spectroscopic study of lanthanide (III) complexes with aliphatic dicarboxylic acids. Tang et al.\(^{61}\) had studied about the synthesis and characterization of mixed-ligand 1, 3-dithiole-2-thione-4, 5-dithiole and 1, 10-phenanthroline complexes of lanthanide chloride and their iodinated materials. Gelinsky et al.\(^{62}\) had studied zinc complexation of glutathione and glutathione-derived peptides. Khan, Saxena and Iftikhar\(^{63}\) had reported mixed ligand lanthanide complexes. Interaction of trivalent lanthanides with 1,10-phenanathroline and thiocyanate in alcohol. Khan and Iftikhar\(^{64}\) had
studied mixed-ligand lanthanide complexes. Absorption spectra and hypersensitivity in the complexes of Pr$^{3+}$, Nd$^{3+}$, Ho$^{3+}$, Er$^{3+}$ in non-aqueous solvents (pyridine, DMSO, DMF and methanol). They had determined the oscillator strengths for the hypersensitive and non-hypersensitive transitions and variations in the oscillator strengths and band shapes with respect to solvent type is rationalized in terms of ligand (solvent) structures and ligand coordination properties. Pyridine has been found to be most effective in promoting 4f-4f intensity and is the strongest ligand in a nephelauxetic sense among the solvents studied.
REFERENCES


