

**SPECTRAL ANALYSIS OF SIMULTANEOUS COMPLEXATION OF
TWO OR THREE CHEMICALLY DISSIMILAR METAL IONS
Pr(III)/Nd(III)/Er(III) AND Ca(II)/Zn(II) WITH GLUTATHIONE
USING 4f-4f TRANSITION SPECTRA AS PROBE**

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By

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6 SUMMARY AND CONCLUSION

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A	Probability for spontaneous emission
A_{sp}	Crossed term co-efficient
A_{21}	Spontaneous parameter
A_{12}	Spontaneous parameter
c	Speed of light
C	Concentration
S	Slater-Condon parameter
L	Laporte factor
T	Intensity parameters (Judd-Ofelt parameter)
U^N	S-pure reduced matrix element
β	Hephaelguxetic parameter
δ	Covalency parameter
ϵ	Molar absorptivity
Q_i	Intensity parameter
U_i	Laporte spin orbit interaction parameter
ψ	Wave function
$\int \psi(x) \psi(x)$	Rudlal integral
I	Correction factor for medium effects

ABBREVIATIONS:

DC	Dynamic coupling
GSH	Glutathione reduced
GSSG	Glutathione oxidized
MeCN	Acetonitrile
DMF	Dimethyl formamide
MeOH	Methanol
NMR	Nuclear magnetic resonance
RMS	Root mean square
UV	Ultraviolet
LFSE	Ligand Field Stabilization Energy
SC	Static Coupling
IR	Infra red
l.e.	That is

SYMBOLS AND ABBREVIATIONS

Symbols :

A	Absorbance
$A(\Psi J, \Psi' J')$	Probability for spontaneous emission
A_{kp}	Crystal field co-efficient
A_{tp}^{λ}	Intensity parameter
$b^{1/2}$	Bonding parameter
c	Speed of light
C	Concentration
F_k	Slator-Condon parameter
g	Lande factor
T_{λ}	Intensity parameters (Judd-Ofelt parameter)
$U^{(\lambda)}$	Square reduced matrix element
β	Nephelauxetic parameter
δ	Covalency parameter
ϵ	Molar absorptivity
Ω_{λ}	Intensity parameter
ξ_{4f}	Lande spin orbit interaction parameter
Ψ	Wave function
$\Xi(k, \lambda)$	Radial integral
χ	Correction factor for medium effects

ABBREVIATIONS :

DC	Dynamic coupling
GSH	Glutathione reduced
GSSG	Glutathione oxidize
MeCN	Acetonitrile
DMF	Dimethyl formamide
MeOH	Methanol
NMR	Nuclear magnetic resonance
RMS	Root mean square
UV	Ultraviolet
LFSE	Ligand Filed Stabilization Energy
SC	Static Coupling
IR	Infra red
i.e.	That is

CHAPTER NO. I

INTRODUCTION

In 1794, Johann Gadolin, a French chemists, while investigating a rare Swedish mineral, discovered a new element in impure form, which he believed to be a new element and to which he gave the name Ytterbia, from Ytterby, the village where the ore was found. The name, however, was soon shortened to Ytria. Owing to the close chemical similarities between the members of the lanthanide series, they resisted easy purification and separation from one another. Numerous misidentifications, false claims and counter claims are scattered through the pages of lanthanide chemical history. The following Table 1.01 gives a picture about the history of lanthanides.

Table 1.01 : Discovery of the lanthanides

Lanthanide	Year of identification	Discoverer	Origin of name
Lanthanum	1839	Mosander	Lanthanum: Greek for "to lie hidden"
Cerium	1803	1. Berzelius and Hisinger 2. Klaproth	Ceres, an asteroid discovered in 1801
Praseodymium	1885	Von Welsbach	From Greek : prasio=green; dymium=twin
Neodymium	1885	Von Welsbach	From Greek : Neo= new; Dymium=twin
Promethium	1947	1. Marinsky 2. Glendenin 3. Coryell	Prometheus, the Greek God who stole fire from heaven for men's use
Samarium	1879	De Boisbaudran	From its ore, Samarskite, named after the Russian engineer Samarski

Europium	1889	Crookes	Europe
Gadolinium	1880	Marignac	After the Finnish chemist Gadolin
Terbium	1843	Mosander	After the town of Ytterby in Sweden
Dysprosium	1886	De Boisbaudran	From Greek: Dysprositors=hard to get at
Holmium	1879	1. Cleve 2. Soret	Holmia, Latinized version of Stockholm
Erbium	1843	Mosander	After the town of Ytterby in Sweden
Ytterbium	1878	Marignac	After the town of Ytterby in Sweden
Lutetium	1908	1. Von Welsbach	Lutetia, Latin for Paris
	1907	2. Urbain	
Ytterium	1794	Gadolin	After the town of Ytterby in Sweden.

*Biochemistry of the Lanthanides by C.H. Evans, Plenum Press (New York and London) (1990), Chapter 1

1.1 : General Feature of Lanthanides

The term lanthanides refer to the very similar fourteen elements following lanthanum (La, At. No. 57) to Lutetium (Lu, At. No. 71), which resemble each other in their physical and chemical properties and are characterized by gradual filling up of electrons in the inner lying 4f-shell. The general electron configuration of lanthanides is $(n-2)f^{1-14}(n-1)d^{0-1}ns^2$. Since 4f-electrons are relatively less involved in binding, these highly electropositive elements have their prime oxidation number +3.

Table 1.02 : Some properties of lanthanide atoms and ions

Atomic number	Name	Symbol	Electronic configuration		$E^0(V)$	Radius M^{3+}_0 (Å)
			Atom	M^{3+}		
57	Lanthanum	La	$5d^16s^2$	[Xe]	-2.37	1.17
58	Cerium	Ce	$4f^15d^16s^2$	$4f^1$	-2.34	1.15
59	Praseodymium	Pr	$4f^36s^2$	$4f^2$	-2.35	1.13
60	Neodymium	Nd	$4f^46s^2$	$4f^3$	-2.32	1.12

61	Promethium	Pm	$4f^5 6s^2$	$4f^4$	-2.29	1.11
62	Samarium	Sm	$4f^6 6s^2$	$4f^5$	-2.30	1.10
63	Europium	Eu	$4f^7 6s^2$	$4f^6$	-1.99	1.09
64	Gadolinium	Gd	$4f^7 5d^1 6s^2$	$4f^7$	-2.29	1.08
65	Terbium	Tb	$4f^9 6s^2$	$4f^8$	-2.30	1.06
66	Dysprosium	Dy	$4f^{10} 6s^2$	$4f^9$	-2.29	1.05
67	Holmium	Ho	$4f^{11} 6s^2$	$4f^{10}$	-2.33	1.04
68	Erbium	Er	$4f^{12} 6s^2$	$4f^{11}$	-2.31	1.03
69	Thulium	Tm	$4f^{13} 6s^2$	$4f^{12}$	-2.31	1.02
70	Ytterbium	Yb	$4f^{14} 6s^2$	$4f^{13}$	-2.22	1.01
71	Lutetium	Lu	$4f^{14} 5d^1 6s^2$	$4f^{14}$	-2.30	1.00

An important feature of lanthanide elements is the occurrence of "Lanthanide Contraction", a steady decrease in ionic and atomic size with increasing atomic number. The major cause of lanthanide contraction is the screening effect of the increasing nuclear charge by inner sphere 4f-electrons.

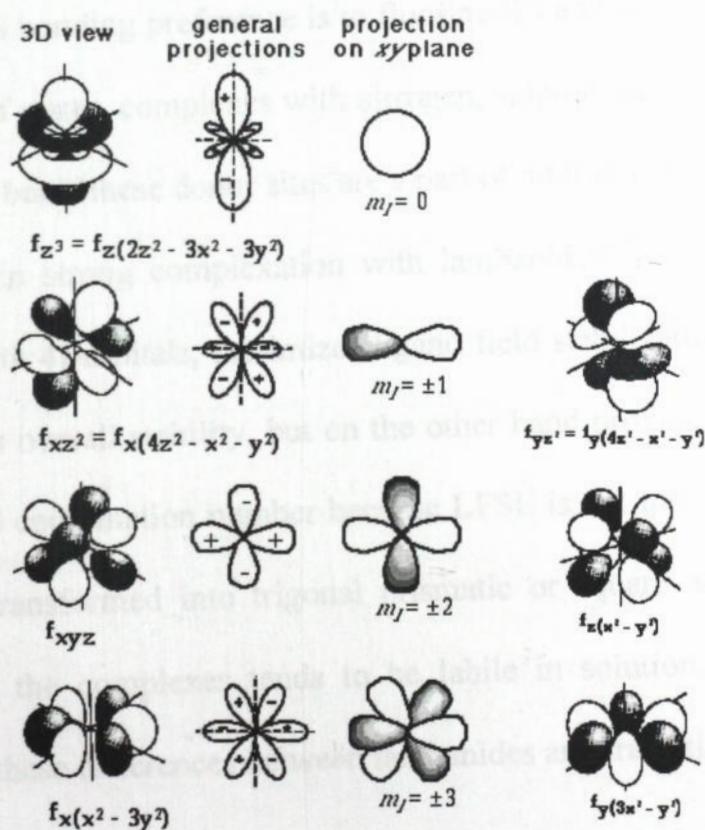


Figure 1.01 Shapes of 4f-orbitals

The reduction in size from one lanthanide to the next makes their separation possible but the smallness and regularity of the reduction in size makes the separation difficult. By the time Ho^{3+} is reached, the radius has been sufficiently reduced to be almost identical with that of Y^{3+} , that is why with much lighter element is associated with heavier lanthanide. The total lanthanide contraction is of the similar magnitude to the expansion found in passing from the first to the second transition series, which might therefore have been expected to occur from passing from second to third. This interaction of lanthanides in fact almost cancel this anticipated increase with the result, i.e. in each group of transition elements the second and third member have almost similar sizes and properties¹⁻³.

According to Hard and Soft Acid Bases concept, lanthanides behave as typical hard acids and so its bonding preference is to fluorine (F) and oxygen (O) donor ligands. In the presence of water, complexes with nitrogen, sulphur and halogen (except fluorine) are not stable, but if these donor sites are a part of multidonor ligands these donor sites are involved in strong complexation with lanthanides^{4,5}. The absence of extensive interaction with 4f-orbitals, minimizes ligand field stabilization energy (LFSE). Low LFSE reduces overall stability, but on the other hand provides a greater flexibility in geometry and coordination number because LFSE is not lost e.g. when an octahedral complex is transformed into trigonal prismatic or square anti prismatic geometry. Furthermore, the complexes tends to be labile in solution. Table 1.03 presents a summary of these differences between lanthanides and transition metal ions.

Table 1.03 : Comparison of transition metal ions and lanthanide ions

Property	Lanthanide ions	First series transition metal ions
Metal orbitals	4f	3d
Ionic radii	106-85 pm	75-60 pm
Common coordination no.	6,7,8,9	4,6
Typical coord. Polyhedra	Trigonal prism, square antiprism, dodecahedron	Square planar, tetrahedron, octahedron
Bonding	Little metal-ligand orbital interaction	Strong metal-ligand orbital interaction
Bond direction	Little preference in bond direction	Strong preference in bond direction
Bond strengths	Bond strengths correlate with electronegativity, decreasing in the order : F ⁻ , OH ⁻ , H ₂ O, NO ₃ ⁻ , Cl ⁻	Bond strengths determined by orbital interaction normally decreasing in the following order: CN ₂ , NH ₃ , H ₂ O, OH ⁻ , F ⁻
Solution complexes	Ionic; rapid ligand exchange	Often covalent; covalent complexes may exchange slowly

1.2 : The Biochemistry of Lanthanides and Actinides

In spite of the fact that *f*-block elements, the members of lanthanide and actinide transition series, have no known essential role in life processes⁶, they no doubt pose some of the most fascinating, challenging and important chemical and biochemical problems of all inorganic elements of the periodic table. The reasons for this, primarily stem from the properties conferred by their outer electron configuration and associated

energy levels coupled with their chemical toxicity which are low for lanthanides and with their radio toxicities which are a major problem for actinides.

The paramagnetic nature of lanthanides is responsible for higher magnetic moment due to number of unpaired electrons in $4f$ orbitals. This makes them of great practical value for their application in Nuclear Magnetic Resonance Spectroscopy (NMR) as well Nuclear Magnetic Resonance Imaging (MRI).

Gadolinium(III) complexes especially with polyamino-polycarboxylic acids, make good contrast enhancing agent because of their high magnetic moment coupled with good relaxation efficiencies. Dysprosium and Thulium chelates have been proved excellent SHIFT REAGENTS in following compartmentalization of sodium during onslaught of *Ischaemia*. Other important biological and biochemical applications are as follows:

- (i) Lanthanides can be used as heavy atom 'STAINS' in electron microscopy or x-ray diffractions studies.
- (ii) Thermodynamic properties of metal ion binding site, e.g. for Calcium(II) can be elucidated through competition or exchange reactions with lanthanide ions. This is most important because calcium, one of the most important and ubiquitous of essential elements, has very few properties, which can be used to PROBE its Biochemistry *in situ*. The lanthanide(III) ions, make almost BIOMIMETIC agent for Ca(II) [Table 1 .04]

Table 1.04 : Comparison of Calcium and Lanthanide Ion Characteristics

Property	Ca(II)	Ln(II)
Coordination number	6 - 12 reported	6 - 12 reported
	6 or 7 favored	8 or 9 observed
Coordination geometry	Highly flexible	Highly flexible
Preference for donor sites	O > N > S	O > N > S
Ionic radii (A ⁰)	1.00 - 1.18	0.86 - 1.22
	(CN 6-9)	(CN 6-9)
Type of Bonding	Electrostatic	Electrostatic
Hydration number	Six	8 or 9
Water exchange rate constant (s ⁻¹)	~ 5 x 10 ⁸	~5 x 10 ⁷
Crystal field stabilization	None	Negligible
Spectroscopic behavior	Spectroscopic	Abundance of
	silence	spectroscopic signals both optical and magnetic
Stability of complexes	Weak complexes	Strong complexes

(iii) Kinetic properties of biochemical react involving metal ions, can likewise be investigated and mechanistic information gained.

(iv) Fine structural features of biological systems may be researched and defined using NMR, ESR and 4f-4f transition spectra and energy transfer leading to fluorescence.

- (v) Further applications include *in vivo* targeting and localization in tumors using appropriate lanthanide ion complexes.⁷

1.2.1 : Biochemistry in Body Compartments

After entry into the body by whatever route, transport of lanthanide or actinides, secondary disposition sites is mainly via the plasma in blood stream. Within body compartment it is convenient to consider the f-element as being placed between the three (or perhaps four) fractions which are in equilibrium with one another and which are responsible for transport and intracellular uptake. We take iron as important essential elements to illustrate this concept. Iron is partitioned between fractions, which exist in a labile and thermodynamic equilibrium with one another. There a fourth fraction in which the metal is bound inertly and which is also exchangeable with the other three fractions. This latter fraction can be thought as storage compartment.

<i>Inert and or Thermodynamically</i>	<i>Labile</i>	<i>and</i>
<i>Non-reversible</i>	<i>Thermodynamically Reversible</i>	

<i>Hemoglobin</i>		<i>Low molecular mass</i>
<i>Myoglobin</i>	\rightleftharpoons	<i>Fe³⁺ Complexes with</i>
	<i>Transferrin</i>	<i>free aquo ion and</i>
<i>Ferritin</i>	\rightleftharpoons	<i>[Fe(H₂O)₆]³⁺ and</i>
		<i>citrate</i>

Inert and labile forms of metal ions *in vivo*

With respect to metal transport, it is the three labile compartments, which are of interest. Transferrin, the protein which is responsible for transporting iron in and out of cells via receptor mediated endocytosis, appears to play a major role in f-element transport within the blood stream.⁷⁻⁸ Transferrin is a glycoprotein (molecular mass 80k Da) containing 800 amino acid residues. The protein is bilobular with one metal binding site in each lobe. These metal bindings are designated as N- and C- terminal sites. In addition to binding and transporting Fe^{3+} ions, transferrin is also responsible for binding lanthanides and actinides *in vivo*.

The protein also binds to both lanthanide and actinides. Comparative Studies *in vitro* and *in vivo* have shown the binding of lanthanides.⁹⁻¹¹ UV difference spectroscopy and other studies *in vitro* with Pu(IV), Th(IV) and a number of trivalent lanthanides have very clearly demonstrated that, like iron, two lanthanide or actinide metal atoms are bound per transferrin molecule.¹²

Data on the formation constants for actinide and lanthanide complexes with transferrin is very sparse. Harris¹³ however reported conditional values of equilibrium formation constants of Nd(III) and Sm(III) transferrin complexes, using absorption difference and comparative absorption spectra. However the data published on conditional stability constants of human serum transferrin with lanthanides and actinides have important implications with regard to actinide/lanthanide distribution within the human body. It has been shown that in binding to human serum transferrin, the *f* elements are participating in certain aspects of iron transport pathways *in vivo*. However, no plutonium e.g. is found within RBC following incorporation and there is no unequivocal evidence that plutonium and the other actinides or lanthanides are

transported into the cell via "Transferrin-Receptor Mediated Endocytosis", This is the PUZZLING aspect of *f*-element transferrin chemistry and biochemistry and it requires much more study. A number of explanations can be advanced which may explain the apparent dichotomy of *f* elements binding to transferrin and the imperfect participation in the iron metabolic pathway. Duffied and Taylor¹⁴ investigated absorption spectral studies and shown the line details of Pu(IV) and Th(IV) binding to transferrin very similar to that of Fe(III). One molecule of transferrin bind two moles of Pu(IV) in a specific fashion implying that Pu(IV) binds at same sites as Fe(III). The same is true for Th(IV). Fe(III) binding to transferrin requires stabilization with a synergistic anion, carbonate or bicarbonate. Binding of Pu(IV) and Th(IV) also requires synergistic anion.

Differences in Fe(III)-transferrin and lanthanide/actinide transferrin may be due to changes in the conformation upon metal ion binding and the conformational changes are very critical regarding subsequent binding of metal transferrin complexes to cell surface receptor, prior to internatization by Receptor Mediated Endocytosis.¹⁵

The interactions of various lanthanides with a very wide range of proteins have been reviewed in depth by Evans (1990). The range of proteins which have been investigated is large and includes enzymes such as *Trypsins*, *Elastase*, *Collagenase*, *Amylase*, *Nuclease*, *ATPase*, *Phospholipase—A₂* and *Acetylcholinesterase*, the contractile proteins *Actins*, *Myosin* and molecular oxygen carriers such as *Haemocyanin*. These studies have shown that the major ligand for Ln(III) ion is the carboxyl group with additional coordination through carboxyl or hydroxylic oxygen. Often lanthanides occupy Ca²⁺ binding sites. However, Ln³⁺ ions may also bind to sites

of proteins, which are not known to bind Ca^{2+} or any other metal. Because of their higher charge to volume ratio, Ln^{3+} ions usually have higher affinity for proteins than Ca^{2+} . The affinities of different lanthanides vary widely but in general they increase with decreasing hydration of sequestered lanthanide ion and with increasing cationic charge of binding site. In addition to protein study the Ln^{3+} binding to other types of biomolecules *in vitro* can also provide valuable structural and other information. The biomolecules include *Nucleic acid, Phospholipids, Phospholipid membrane, Porphyrins, Vitamin B₁₂ and high-density Lipoproteins.*

The most important aspect of lanthanide binding to biomolecule is the fact that these MIMIC interaction of these biomolecules with radioactive actinides. Increasing use of nuclear reactor, radioactive isotopes, nuclear medicines, the medicinally compatible Ln(III) interaction has been extremely useful in exploring biochemistry and biological chemistry of actinides.¹⁶⁻¹⁸

1.2.2 : Similarities and Differences in Trivalent Lanthanide and Actinide-ions:

While comparing the absorption spectra of lanthanides and actinide ions having same number of f-electron the most evident difference lies in the absolute values for molar absorptivities. Actinide ion molar absorptivities, generally decrease across actinide series to Am^{3+} . For Cm^{3+} and heavier actinides the molar absorptivity becomes more or less constant but continue to be significantly larger than the lanthanide having similar number of f-electrons,

The entire energy range of calculated "free ion" f-states is shown in Figure 1.02 for trivalent lanthanide ions and in Figure 1.03 for trivalent actinide ions. Several features are evident in comparing Figure 1.02 and 1.03 Actinide ions tend to have a somewhat

more open energy-level structure near their ground state, but a less open energy-level structure for higher-lying states. This arises from larger spin-orbit coupling parameters, but reduced Slater parameter values in the actinide series when parameter values for actinide and lanthanide ions having the same number of f -electrons are compared. For mid-series and actinide ions, it is evident that many or even most f states occur at energies corresponding to vacuum-ultraviolet or shorter wave length light (i.e. at energies where little observed data on f -state energies exist). The fingerprinting character of f -state successfully used for analytical purposes as characteristics. Birnbaum et al¹⁹ by using absorption difference and comparative absorption spectra could demonstrate the binding sites of Transferrin, Albumin and Trypsin, which were given sound support by other studies. The changes in the f -state energies are large enough for the observed spectra to permit the determination of complexation, but not so large enough as to make assignments of complexed metal ion bands. What we think the emphasis should be given more on intensity data, which definitely yields better and more useful findings. With sophistication and better understanding of solution absorption spectroscopy will definitely prove boon for lanthanide/actinide coordination and biochemistry.

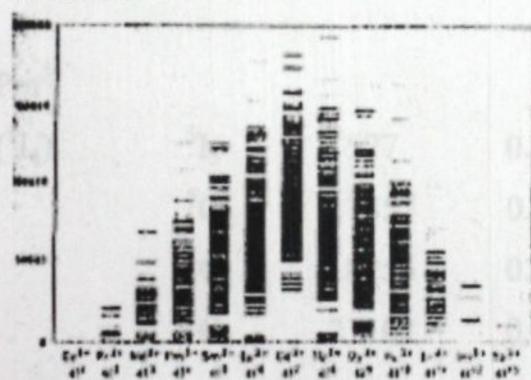


Figure 1.02 Calculated free ion energy-level structure of $4f$ states of trivalent lanthanide ions

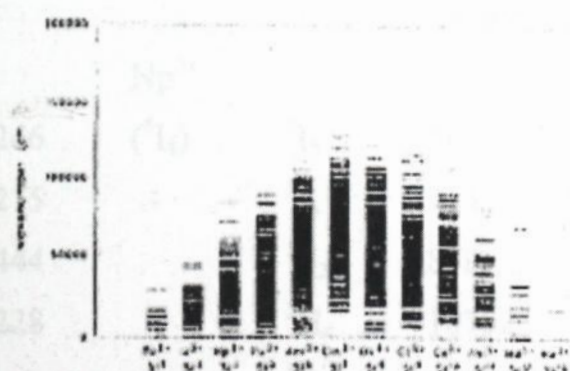


Figure 1.03 Calculated free ion energy-level structure of $5f$ states of trivalent actinide ions

Table 1.05 : Listing of absorption bands with calculated $U^{(2)} > 0.01$ for aquated trivalent lanthanide ions to 50000 cm^{-1} and trivalent actinides to 31000 cm^{-1} .

Lanthanide ion	Excited state	Transition energy (cm^{-1})	Calculated $U^{(2)}$	Actinide ion	Excited state	Transition energy (cm^{-1})	Calculated $U^{(2)}$
Pr^{3+}				Pa^{3+}			
$(^3\text{H}_4)$	$^3\text{H}_4$	2322	0.1095				
	$^3\text{H}_4$	5149	0.5089				
	$^3\text{H}_4$	6540	0.0654				
	$^3\text{H}_4$	6973	0.0187				
	$^3\text{H}_4$	16840	0.0026				
	$^3\text{H}_4$	22535	~0				
Nd^{3+}				U^{3+}			
$(^4\text{I}_{9/2})$	$^4\text{I}_{11/2}$	2007	0.0194	$(^4\text{I}_{9/2})$	$^4\text{I}_{11/2}$	4563	0.0214
	$^4\text{G}_{5/2}$	17167	0.8979		$^2\text{H}_{9/2}$	9631	0.0544
	$^2\text{G}_{7/2}$	17333	0.0757		$^4\text{F}_{5/2}$	9921	0.2016
	$^4\text{G}_{7/2}$	19103	0.0550		$^4\text{G}_{5/2}$	11220	0.7029
					$^4\text{F}_{7/2}$	11518	0.0392
					$^4\text{G}_{7/2}$	13297	0.0884
					$^2\text{K}_{13/2}$	16133	0.0346
					$^2\text{I}_{11/2}$	21585	0.0134
Pm^{3+}				Np^{3+}			
$(^5\text{I}_4)$	$^5\text{I}_5$	1577	0.0246	$(^5\text{I}_4)$	$^5\text{I}_5$	3954	0.0192
	$^5\text{G}_2$	17857	0.7215		$^5\text{I}_6$	7231	0.0134
	$^5\text{G}_3$	18256	0.1444		$^5\text{F}_2$	8197	0.2275
	$^3\text{G}_3$	21102	0.0228		$^3\text{H}_4$	10752	0.0215
					$^5\text{F}_3$	11588	0.0114
					$^5\text{G}_2$	11853	0.4629
					$^5\text{G}_3$	12732	0.1493

					5K_6	15087	0.0150
					3D_2	18424	0.0141
					3H_5	21809	0.0184
					3F_2	22595	0.0145
Sm ³⁺				Pu ³⁺			
($^6H_{5/2}$)	$^6H_{7/2}$	1080	0.2062	($^6H_{5/2}$)	$^6H_{7/2}$	3327	0.1312
	$^6H_{9/2}$	2290	0.0256		$^6H_{9/2}$	6254	0.0541
	$^6F_{1/2}$	6397	0.1939		$^6F_{3/2}$	6745	0.1481
	$^6F_{3/2}$	6641	0.1444		$^6F_{5/2}$	6751	0.0144
	$^6F_{5/2}$	7131	0.0332		$^6F_{1/2}$	6925	0.1513
	$^6D_{1/2}$	26573	0.0001		$^4I_{4/2}$	17471	0.0222
Eu ³⁺	7F_2	1018	0.1375	Am ³⁺			
(7F_0)	5D_2	21499	0.0008	(7F_0)	7F_2	5350	0.0961
					5D_2	21709	0.0065
					5G_2	21961	0.0112
Gd ³⁺				Cm ³⁺			
				($^8S_{7/2}$)	$^6D_{5/2}$	20208	0.0108
					$^6I_{9/2}$	22949	0.0115
					$^6D_{7/2}$	28078	0.0191
					$^6D_{5/2}$	30644	0.0137
Tb ³⁺				Bk ³⁺			
(7F_6)	7F_5	2112	0.5376	(7F_6)	7F_5	4566	0.1373
	7F_4	3370	0.0889		7F_4	5156	0.4901
					5H_5	21020	0.0121
					5H_7	21036	0.0429
					5I_6	26071	0.0164
					5F_4	26529	0.0155
					5L_7	26858	0.0103
Dy ³⁺				Cr ³⁺			
($^6H_{15/2}$)	$^6H_{13/2}$	3506	0.2457	($^6H_{15/2}$)	$^6F_{11/2}$	6453	0.8901
	$^6H_{11/2}$	5833	0.0923		$^6H_{13/2}$	5103	0.2098

	${}^6F_{11/2}$	7730	0.9387		${}^2H_{11/2}$	11585	0.1648
	${}^4I_{15/2}$	22293	0.0073		${}^6H_{15/2}$	16172	0.0258
	${}^4G_{11/2}$	23321	0.0004		${}^4K_{17/2}$	20869	0.0798
	${}^4K_{17/2}$	26365	0.0109		${}^4I_{13/2}$	23176	0.0616
					${}^4K_{15/2}$	27614	0.0143
					${}^4I_{15/2}$	29135	0.0176
					${}^4H_{11/2}$	29517	0.0398
					${}^4H_{13/2}$	30306	0.0178
Ho^{3+}				Es^{3+}			
(5I_8)	5I_7	5116	0.0250	(5I_8)	5I_7	11039	0.0188
	3K_8	21308	0.0208		5I_6	13009	0.5686
	5G_6	22094	1.5201		3K_8	19904	0.0779
	3H_6	27675	0.2155		5G_6	19933	1.0614
	3L_9	29020	0.0185				
	3I_7	38470	0.0157				
Er^{3+}				Fm^{3+}			
(${}^4I_{15/2}$)	${}^4I_{13/2}$	6610	0.0195	(${}^4I_{15/2}$)	${}^2H_{11/2}$	10037	0.7517
	${}^4I_{11/2}$	9256	0.7125		${}^4I_{11/2}$	21365	0.7534
	${}^4G_{11/2}$	26496	0.9183				
	${}^2K_{15/2}$	27801	0.0219				
Tm^{3+}				Md^{3+}			
(3H_6)	3F_4	5811	0.5375	(3H_6)	3F_4	3500	0.5828
	3H_5	8390	0.1074		3H_5	15487	0.1048
	3H_4	12720	0.2373		3H_4	19088	0.2177
	1G_4	21374	0.0483				
	1I_6	34886	0.0106				

1.2.3 :Clinical Applications of Lanthanides

Radioactivity and radioactive species of various lanthanides formed significant use in localizing tumors and exposing the high potential of lanthanide compounds as

antitumor drugs and tumor scanning agents. Much serious research was devoted to attempting to harness the anticoagulant properties of the lanthanides for clinical use. However, lanthanides are presently finding medicinal use as contrast-enhancing agents in NMR imaging.²⁰ Their applications in scintigraphy imaging for localizing of abscesses and sites of inflammation and the detection of cartilaginous lesions in arthritic joints and in following the degree of osteoarthritic degeneration. Lanthanides applications in computed tomography, Radio synovectomy, in regulation of atherosclerosis and also in diagnosing and following the progress of arthritic diseases are also known.

The main idea behind this present work is to explore the potential of these fascinating lanthanides as spectral and structural probe in biochemical reaction of immense importance in human metabolism.

1.3 : Spectroscopic Features of Lanthanides

The trivalent lanthanide ions have unique spectroscopic properties. Since $4f$ shell is effectively shielded by closed $5s$ and $5p$ shells, the ligand environment has only a weak influence on the electronic cloud of lanthanide ion. Although weak, this perturbation is responsible for the spectral fine structure. The line width of the bands is small and its peak position reveals the electronic structure (of a part) of the $4f^n$ configuration. The crystal field splitting gives information about the symmetry of the rare earth site and about the shape of the coordination polyhedron.²¹

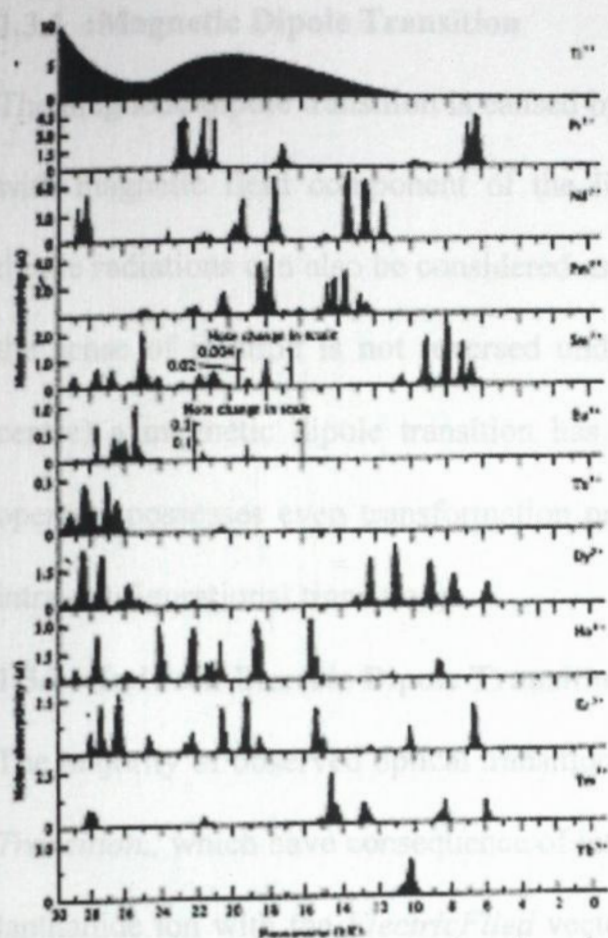


Figure 1.04 Absorption spectra of Pr^{3+} , Nd^{3+} , Pm^{3+} , Sm^{3+} , Eu^{3+} , Dy^{3+} , Ho^{3+} , Er^{3+} , Tm^{3+} and Yb^{3+} in dilute acid solution. Each group or band corresponds to the transition between $^{2S+1}L_J$ free ion levels (or J-manifolds). They are not accompanied by a change in configuration and hence named as Intra-configurationally Transition. Three mechanisms must be considered for the interpretation of the observed transitions²².

- (i) Magnetic-Dipole Transitions
- (ii) Induced Electric Dipole Transitions
- (iii) Electric Quadrupole Transition.

Absorption and luminescence spectroscopy are important techniques in the study of lanthanide system as they allow determining the natural frequencies of lanthanide. The absorption spectra of lanthanide doped single crystals of lanthanide compounds show group of narrow lines in solution or in glasses, however the lines within group broaden to one absorption band, these bands have to be ascribed to

1.3.1 :Magnetic Dipole Transition

The magnetic dipole transition is caused by the interaction of spectroscopic active ion with magnetic field component of the light through a magnetic dipole. Magnetic dipole radiations can also be considered as rotational displacement of charge. Because the sense of rotation is not reversed under inversion through a point (or inversion centre) a magnetic dipole transition has even parity. Therefore a magnetic dipole operator possesses even transformation properties between states of equal parity (or intra-configurational transition).

1.3.2 :Induced Electric Dipole Transition

The majority of observed optical transition of lanthanides are *Induced Electric Dipole Transition*, which have consequence of interaction of spectroscopically active ion/ the lanthanide ion with the *Electric Filed* vector through an electric dipole. The creations of electric dipole suppose a linear movement of charge, and such transition has odd parity. The electric dipole operator has therefore odd transformation properties under inversion with respect to an inversion centre. Intra configurational electric dipole transitions are forbidden by the Laporte Selection rules. The induced electric dipole transitions are described in details in Judd²³-Ofelt²⁴ theory.

1.3.3 :Electric Quadrupole Transition

The electric quadrupole transition arises from the displacement that has a quadrupole nature. An electric quadrupole consists of four point charges with overall zero charge and zero dipole moment. It may visualized as two dipoles arranges in a way to annul each other's dipole moment. An electric quadrupole has even parity. Electric quadrupole transitions are much weaker than magnetic dipole, which in turn are

weaker than induced electric dipole transitions. However *hypersensitive transitions* are considered as pseudoquadrupole transitions as these transitions obey the selection rules of quadrupole transitions.

1.3.4 : Selection Rules

Selection rules are only valid in strict conditions and can be relaxed under circumstances. The selection rules for ΔL and ΔS are only applicable for Russell Saunders Coupling Scheme. These selection rules are relaxed in intermediate coupling scheme, because in this scheme L and S are not good numbers. Since J remains a good quantum number in the intermediate coupling scheme, the selection rules on ΔJ are harder to break down; it can be relaxed only by J -mixing, which is a weak effect. The selection rules on ΔM depend on point group symmetry of the rare earth site.²⁵ The selection rules for magnetic dipole and induced electric dipole transitions are given in Table 1.06

Table 1.06 : Selection rules for magnetic dipole and induced electric dipole transitions:

Magnetic Dipole Transition (MD)	Induced Electric Dipole Transition (ED)
$\Delta\tau=\Delta S=\Delta L=0$	$\Delta L=\pm 1, \Delta\tau=0, \Delta S=0, \Delta L \leq 6$
$\Delta J=0, \pm 1$ but $0\leftrightarrow 0$ is forbidden	$ \Delta J \leq 6 ; \Delta L =2,4,6$ if $J = 0$ and $J' = 0$
$M' - M = -P$, where $P = \pm 1$	$M' - M = -(q+p)$

A well known example of the breakdown of selection rules of the Judd-Ofelt theory is determined by crystal field symmetry constraints and lies between 0 and 1 is the occurrence of ${}^7F_0 \rightarrow {}^5D_0$ and ${}^5D_0 \rightarrow {}^7F_0$ transitions in some Eu(III) complexes.²⁶⁻²⁹ The ${}^7F_0 \leftrightarrow {}^5D_0$ transitions are forbidden by the selection rules, as $\Delta J (0\leftrightarrow 0)$ is

forbidden. The breakdown of closure approximation in Judd-Ofelt can be explained to this exceptional behaviour was ascribed by Tanaka et al^{30,31}. Wybourne³² has shown that the second order matrix element $U^{(0)}$ is zero, so that no intensity can come from this mechanism. Wybourne proposed a mechanism in which spin selection rule is relaxed by scalar third order contribution involving spin-orbit interaction acting within higher lying perturbing states. This model was later developed further by Burdick.³³⁻³⁶

1.3.5 : Intensity Parameterization of Transition between Crystal Field Levels

1.3.5.1 : Static Coupling(SC) Model for Line Transition

The induced electric dipole matrix elements between two states B and B' of the f^n configuration can be written as :

$$\begin{aligned}
 \langle B | \hat{m}_p^{(1)} | B' \rangle &= \langle B | -e\hat{D}_p^{(1)} | B' \rangle \\
 &= -e \sum_M \sum_{M'} a_M a_{M'} \sum_{T,S,LT'SL'} h(TSL) h(T'S'L') \\
 &\times \sum_{k,q} \sum_{\lambda=\text{even}} A_{kq} \Xi(k,\lambda) (-1)^{(q+p)+(J-M)+(S+L'+J+\lambda)} \\
 &\times \begin{pmatrix} 1 & \lambda & k \\ p-q & -p & q \end{pmatrix} \begin{pmatrix} J & \lambda & J' \\ -M & q+p & M' \end{pmatrix} \begin{pmatrix} L & \lambda & L' \\ J' & S & J \end{pmatrix} \\
 &\times (2\lambda+1) [(2J+1)(2J'+1)]^{1/2} \langle f^N || \hat{U}^{(\lambda)} || f^N T'S'L' \rangle
 \end{aligned} \tag{1}$$

The matrix element in above equation (1) is valid for transitions between two crystal field levels. Because of the radial integrals, the calculation of matrix elements is very tedious and can in fact be done by using some approximations. Axe³⁷ treated the quantities $A_{kq} \equiv (k, \lambda)$ in equation in equation (1) as adjustable parameter with λ is equal to 2,4 and 6 and k is restricted to the values of $\lambda \pm 1$. the values of q are determined by crystal field symmetry constraints and lie between 0 and $\pm k$. Porchner and Caro³⁸ introduced notation $B_{\lambda kq}$ for the intensity parameters.

$$B_{\lambda kq} = A_{kq} \equiv (k, \lambda) \quad (2)$$

All the quantities of equation (1) are not included in $B_{\lambda kq}$ parameters and are taken together in a coefficient $\alpha_{\lambda kq}$. When the coefficient $\alpha_{\lambda kq}$ of intensity parameters $B_{\lambda kq}$ have been calculated and when the experimental dipole strength has been corrected for the magnetic dipole contribution, the $B_{\lambda kq}$ parameters can be determined by a fitting procedure. For a crystal field transition ($B \leftarrow \alpha$) a quadrate can be constructed.

$$\frac{1}{\chi_{ED}} [D_{\text{exp}} - \chi_{MD} D_{MD}] = \left[\sum_{\lambda kq} \alpha_{\lambda kq}^{p\alpha\alpha} B_{\lambda kq} \right] \quad (3)$$

or

$$D_{\text{exp}}^0 = \left[\sum_{\lambda kq} \alpha_{\lambda kq}^{p\alpha\beta} B_{\lambda kq} \right]^2 \quad (4)$$

Where D_{exp}^0 is the experimental dipole strength for the magnetic dipole contribution and p is the polarization number. The symbol α and β stands for ground and excited state respectively. In general one has to write down such an equation for each of the M transitions for which a value of the experimental dipole strength is available and $M \geq N$ (N is the number of intensity parameters). The parameters are determined by finding the minimum of a function, which consists of sum of M nonlinear quadratic functions in N variables. The equations to be solved are of the form :

$$\sum_M \left| \sum_{\lambda kq} \alpha_{\lambda kq}^{p\alpha\beta} B_{\lambda kq} \right|^2 - D_{\text{exp}}^0 = 0 \quad (5)$$

The optimised phenomenological intensity parameters depend to a large extent on starting values chosen for those parameters, because the minimisation procedure stops at the first local minimum.

Intensity parameterisation of spectral transitions between crystal field levels for lanthanide doped single crystal have been reported for $\text{LaAlO}_3 : \text{Pr}^{3+}$ (Diricks), $\text{LaF}_3 : \text{Pr}^{3+}$, $\text{Pr}_2\text{Mg}_3(\text{NO}_3)_{12} \cdot 24\text{H}_2\text{O}$ (Gorller-Walrand et al)⁴¹, $\text{LiYF}_4 : \text{Nd}^{3+}$ (Gorller – Walrand et al)⁴², $\text{LiYF}_4 : \text{Eu}^{3+}$ (Fluyet et al)⁴³, $\text{Na}_5\text{Eu}(\text{MoO}_4)_3$ and $\text{Na}_5\text{Eu}(\text{WO}_4)_3$ (Holsa et al)⁴⁴. The parameterisation scheme given by Judd-Ofelt for J-multiplet transition intensities in terms of T_λ parameters is general and is limited by the assumption of one electron one photon interaction. The parameterisation scheme is independent of the nature of metal ligand interaction. The parameterisation scheme of Axe of describing the intensities of crystal field transition is not general in terms of its applicability. In addition to one electron and one photon assumption, the parameterisation scheme required that the superposition approximation is valid which requires all metal-ligand pair wise interactions to be cylindrically symmetric and independent.⁴⁵ The superposition approximation poses problems for lanthanide systems with polyatomic ligands with highly anisotropic charge distribution.

1.3.5.2 : Reid-Richardson Intensity Model

Reid – Richardson⁴⁶⁻⁵⁰ developed a parameterisation scheme, which is very similar to that given by Newman and Subramanian⁴⁵. They pointed out that the intensity parameters can be interpreted and calculated in terms of two intensity mechanism namely STATIC COUPLING (SC) and DYNAMIC COUPLING(DC). In both SC and DC models the interactions are considered purely electrostatic and thus an overlap between the charge distributions between the ligand and central metal ion is neglected. In SC coupling model the electronic configuration of the lanthanide ion is perturbed by the ligands and the ligands produced a static potential of odd parity

around lanthanide ion, so the 4f states of mixed parity are formed. Transitions between these states can be polarised isotropically by the Ln^{3+} ion. The basic assumption in the Static Coupling Model is however; that the ligands are not perturbed by the radiation field of the incident light. The intermediate perturbing wave functions are fully localized on the lanthanide ion. Judd-Ofelt theory is an example of Static Coupling Model.

1.3.5.3 : Dynamic Coupling (DC) Model

In DC model the change in the distribution of the ligand charges under the influence of radiation field of light is taken into account. The electric dipole component of the light induces transient dipoles on the ligands, which in turn induce 4f-4f transitions in lanthanide ions. These are two possibilities (1) isotropic polarisability and (2) anisotropic polarisability. In the former the ligands are isotropic and ligand-ligand polarisation is cylindrically symmetric and independent. In case of the anisotropic polarisability the ligand are anisotropic (BO_3^{-3} , NO_3^- , ODA, GSH) and thus lanthanide-ligands interactions cannot be considered cylindrically symmetric. The perturbing wave functions in DC mechanism are localised on ligands. Reid-Richardson used a combination of DC and SC mechanism and made 'ab initio' calculation of intensity parameters in such a way that an easy differentiation between SC and DC mechanism can be made. Their intensity parameters A_{tp}^{λ} , the $t=\lambda$ parameter reflect the lanthanide ligand pair wise interactions, which are not cylindrically ellipsoids. These extra parameters are symmetry allowed in all point groups except $C_{\infty v}$.

The static coupling scheme gives rise to A_{tp}^{λ} parameters with $\lambda = 2, 4, 6$ are with

$t = \lambda \pm 1$ and employing Reid-Richardson (SC) and (DC) models, parametric calculations were made successfully by Burdick et al.^{51,52} and Chertanov et al.⁵³

The agreement between the experimental and calculated oscillator strength (P) of transitions between the ground state and $2S+1L_j$ manifolds is good, but the relative intensities of crystal field transitions are still not well produced.

Placing the samples in a magnetic field induces optical activity. The differential absorption of left and right circularly polarised light in a longitudinal magnetic field can be measured. In the longitudinal magnetic field, the magnetic lines are parallel to the light beam. This technique is known as MCD (Magnetic Circular Dichroism), which is based upon Zeeman Effect. The simulation of MCD spectrum and calculation of MCD signals do not require more parameters than crystal field and intensity parameters extracted from absorption spectrum.^{54,55}

1.3.6 : Carnall's \mathfrak{S}_λ Intensity Parameters and Ω_λ Intensity Parameters

These are very commonly used in solution spectral analysis studies. Carnall et al used new parameter T_λ and thus described Oscillator Strength as :

$$P_{\text{exp}} = \sum_{\lambda=2,4,6} \mathfrak{S}_\lambda \frac{\bar{\nu}_0}{2J+1} \left| \langle f^N \Psi J \| f^N \Psi' J' \rangle \right|^2 \quad (6)$$

The parameter \mathfrak{S}_λ (Carnall et al) is related to Judd-Ofelt (T_λ) parameter through

$$\mathfrak{S}_\lambda = (2J+1)cT_\lambda \quad (7)$$

This is essentially only an extraction of $(2J+1)^{-1}$ weighing factor out of the T_λ parameter. The factor c (the speed of light) is used to convert frequency ν_0 into the wane number $\bar{\nu}_0$ ($\nu_0 = c \bar{\nu}_0$). Workers studying absorption spectra of lanthanide

complexes in solution⁵⁶⁻⁶⁰ still universally use these spectral parameters T_λ and \mathfrak{F}_λ .

The parameter Ω_λ is introduced by Axe which is related to \mathfrak{F}_λ by

$$\Omega_\lambda = \left(\frac{8\pi^2 mc}{3h} \chi_{ED} \right)^{-1} \mathfrak{F}_\lambda \quad (8)$$

$$\text{or } \Omega_\lambda = (1.085 \times 10^{11} \chi_{ED})^{-1} \mathfrak{F}_\lambda \quad (9)$$

The χ_{ED} is the correction factor included in the \mathfrak{F}_λ parameters but not in Ω_λ parameters. Similarly Ω_λ parameters are also related to $A_{t,p}^\lambda$ parameters as follows :

$$\Omega_\lambda = \frac{1}{2\lambda + 1} \sum_{t,p} |A_{t,p}^\lambda|^2 \quad (10)$$

1.3.6.1 : Standard Least Square Fit Procedure

The standard least square method minimizes the absolute differences between experimental and calculated values. This method is much simpler than Chi-square fit method, but has the disadvantage that a small discrepancy in a large experimental value has the same influence as a large error in small experimental value. Hence the magnitude of T_λ or Ω_λ parameters depend largely on the relative magnitude of the Oscillator Strength of transitions used in the fit. However, the parameter set is able to predict both small and large Oscillator Strength.

$$\Delta^{\text{exp}} = \frac{(2J+1)D_{\text{exp}}}{e^2 \chi_{ED}} \quad (11)$$

then,

$$\Delta^{\text{exp}} = \Omega_2 U^{(2)} + \Omega_4 U^{(4)} + \Omega_6 U^{(6)} \quad (12)$$

The same thing can be used for writing down such an equation for each spectral transition resulting in a system of equation for n transitions.

$$\begin{aligned}
 \Delta_1^{\text{exp}} &= \Omega_2 U_1^{(2)} + \Omega_4 U_1^{(4)} + \Omega_6 U_1^{(6)} \\
 \Delta_2^{\text{exp}} &= \Omega_2 U_2^{(2)} + \Omega_4 U_2^{(4)} + \Omega_6 U_2^{(6)} \\
 \Delta_3^{\text{exp}} &= \Omega_2 U_3^{(2)} + \Omega_4 U_3^{(4)} + \Omega_6 U_3^{(6)} \\
 &\dots\dots\dots \\
 &\dots\dots\dots \\
 \Delta_n^{\text{exp}} &= \Omega_2 U_n^{(2)} + \Omega_4 U_n^{(4)} + \Omega_6 U_n^{(6)}
 \end{aligned}
 \tag{13}$$

We want to find a good estimate for the parameter set $(\Omega_2', \Omega_4', \Omega_6')$ or (T_2', T_4', T_6')

The set of equation (13) is of form:

$$\begin{aligned}
 Y_1 &= a_1 X_{11} + a_2 X_{12} + a_3 X_{13} + \dots\dots\dots + a_k X_{1k} \\
 Y_2 &= a_1 X_{21} + a_2 X_{22} + a_3 X_{23} + \dots\dots\dots + a_k X_{2k} \\
 Y_3 &= a_1 X_{31} + a_2 X_{32} + a_3 X_{33} + \dots\dots\dots + a_k X_{3k} \\
 &\dots\dots\dots \\
 Y_n &= a_1 X_{n1} + a_2 X_{n2} + a_3 X_{n3} + \dots\dots\dots + a_k X_{nk}
 \end{aligned}
 \tag{14}$$

The Y_i is the values of the observations and X_{ik} is coefficients and a_i is the unknown parameters. The observational model is a general linear model, because the dependent variable Y_i , is described as a function of several independent variables X_{ik} . The function is a linear function (there are no terms of degree higher than 1). The matrix method is used to solve the problem. The equation (14) can be written in terms of the response random vector containing the response values of n observations:

The matrix representation for any set of observation $Y_1, Y_2, Y_3, \dots, Y_n$

$$Y = \begin{bmatrix} y_1 \\ y_2 \\ y_3 \\ \cdot \\ \cdot \\ y_n \end{bmatrix} \quad (15)$$

the model parameter vector

$$a = \begin{bmatrix} a_1 \\ a_2 \\ a_3 \\ \cdot \\ \cdot \\ a_n \end{bmatrix} \quad (16)$$

the vector of errors associated with n observations :

$$E = \begin{bmatrix} \varepsilon_1 \\ \varepsilon_2 \\ \varepsilon_3 \\ \cdot \\ \cdot \\ \varepsilon_n \end{bmatrix} \quad (17)$$

and the n X k design matrix

$$X = \begin{bmatrix} X_{11} & X_{12} & X_{13} & \dots & X_{1k} \\ X_{21} & X_{22} & X_{23} & \dots & X_{2k} \\ X_{31} & X_{32} & X_{33} & \dots & X_{3k} \\ \cdot & \cdot & \cdot & \dots & \cdot \\ \cdot & \cdot & \cdot & \dots & \cdot \\ X_{n1} & X_{n2} & X_{n3} & \dots & X_{nk} \end{bmatrix} \quad (18)$$

The matrix representation for any set of observation $Y_1, Y_2, Y_3, \dots, Y_n$ becomes

$$Y = Xa + E \quad (19)$$

Let the matrix *Chi-Square Method*

$$\hat{a} = \begin{bmatrix} \hat{a}_1 \\ \hat{a}_2 \\ \hat{a}_3 \\ \cdot \\ \cdot \\ \hat{a}_n \end{bmatrix} \quad (20)$$

Equation 20 represents the matrix of the least square estimates for the parameters of the general linear model. The matrix can be calculated as follows:

$$\hat{a} = (\chi^T X)^{-1} X^T Y \quad (21)$$

Where χ^T is the transpose of X. The matrix χ is an n X k matrix. X^T is a k x n matrix and $\chi^T X$ is a K x K matrix with $n \geq k$. The matrix solution gives the set of parameter estimates d_1, d_2, \dots, d_k in general linear model that minimizes $\sum_i (y_i - \bar{y}_i)^2$ for the data collected.

After the parameter estimates (T_2, T_4, T_6 or $\Omega_2, \Omega_4, \Omega_6$) have been obtained D'_{ED} or P'_{ED} can be calculated

$$P'_{ED} = e^2 (\Omega_2 U_i^{(2)} + \Omega_4 U_i^{(4)} + \Omega_6 U_i^{(6)}) \quad (22)$$

$$RMS = \left[\frac{\text{Sum of square of deviation}}{\text{Number of observation} - \text{Number of parameters}} \right]^{1/2} \quad (23)$$

1.3.6.2 : Chi-Square Method

If one wants to weigh each value of dipole strength or Oscillator Strength by its own uncertainty, the Chi-Square method has to be chosen as the minimizing quantity. Caird et al⁶¹, Seeber et al⁶² and Goidner and Auzel⁶³

This method minimizes the relative difference between the experimental and calculated values rather than their absolute differences. The uncertainty in the measured intensity of each transition is often difficult to estimate. Goldner and Auzel⁶³ take a constant fraction of the experimental Oscillator Strength for the uncertainty. The RMS of this method is independent of the number or magnitude of the included transition. The Chi-square method is analogous to the matrix calculation presented for the standard least square method except that the design matrix X is now given as:

$$X = \begin{bmatrix} \frac{X_{11}}{\sigma_1} & \frac{X_{12}}{\sigma_1} & \dots & \frac{X_{1k}}{\sigma_1} \\ \frac{X_{21}}{\sigma_2} & \frac{X_{22}}{\sigma_2} & \dots & \frac{X_{2k}}{\sigma_2} \\ \dots & \dots & \dots & \dots \\ \frac{X_{n1}}{\sigma_n} & \frac{X_{n2}}{\sigma_n} & \dots & \frac{X_{nk}}{\sigma_n} \end{bmatrix} \quad (24)$$

And the vector Y with the observation is now given by:

$$Y = \begin{bmatrix} \frac{y_1}{\sigma_1} \\ \frac{y_2}{\sigma_2} \\ \cdot \\ \cdot \\ \frac{y_n}{\sigma_n} \end{bmatrix} \quad (25)$$

The fit is applied to the quantities P/σ_i where σ is the uncertainty in the experimental Oscillator Strength P_{exp} . The error of a parameter is given by square root of the respective diagonal matrix elements of the matrix $(X^T X)^{-1}$.

Judd-Ofelt theory though is quite commanding yet for Pr^{3+} , this theory does not seem work well.⁶³ Difficulties are experienced if one tries to fit both the ${}^3\text{H}_4 \rightarrow {}^3\text{F}_3, {}^3\text{F}_4$ and ${}^3\text{H}_4 \rightarrow {}^3\text{P}_{2,1,0}$ transition groups with the same set of T_λ intensity parameter.⁶⁴ Instead of determining parameter set with the inclusion of all the transitions the ${}^3\text{H}_4 \rightarrow {}^3\text{F}_3, {}^3\text{F}_4$ transitions can be excluded. A number of authors preferred to exclude ${}^3\text{H}_4 \rightarrow {}^3\text{P}_2$ transition.^{62,65-67} Eyal et al have included Ω_3 and Ω_5 parameters in the intensities of 4f - 4f transitions of Pr^{3+} White Flore et al⁶⁸ also included odd intensity parameters and also include ${}^3\text{H}_4 \rightarrow {}^1\text{I}_6$ transition in the fitting procedure.

It should be mentioned that the hypersensitive transition for Pr^{3+} , ${}^3\text{H}_4 \rightarrow {}^3\text{F}_2$ has to be included in the fit of Pr^{3+} , because otherwise a negative value of T_2 will be found which has no relevance. Extraction of reliable Ω_2 parameter is often a problem for Pr^{3+} , because ${}^3\text{H}_4 \rightarrow {}^3\text{F}_2$ transition is situated in infrared spectral region and thus cannot be observed in aqueous and in aquated organic solvent in absorption spectrum in UV-Visible region. In order to obtain more reliable intensity parameters Quimby

and Miniscalco⁶⁹ introduced a modified Judd-Ofelt theory in which luminescence branching ratios are included in the fit. We have found that by including T_5 and T_3 parameters and by including ${}^3H_4 \rightarrow {}^1I_6$ transition. Oscillator Strengths for computing purposes improves the closeness between the observed and calculated Oscillator Strength of $4f - 4f$ transition.

1.3.7 :Hypersensitivity

The environment does not affect the intensities of the induced dipole transitions in lanthanides significantly. The dipole strength of particular transition of the lanthanide(III) ion in different matrices does not vary more than a factor two or three. However, a few transitions are very sensitive to the environment and these are much more intense in lanthanides complex, than that for lanthanide (III) aquo ion complex.⁷⁰⁻⁷²

The high sensitivity of spectral intensities for ligand environment as a general phenomenon was first noticed by Moeller et al⁷³⁻⁷⁵ for β -diketonate and EDTA complexes of Nd^{3+} , Ho^{3+} and Er^{3+} much before the advent of Judd-Ofelt Theory. Jorgensen and Judd have called such transitions HYPERSENSITIVE and these transitions obeyed selection rules $|\Delta S|=0$; $|\Delta L|\leq 2$; $|\Delta J|\leq 2$ and these rules are the same as the selection rules for pure quadrupole transitions. But calculations have revealed that the intensities to have a quadrupole character, therefore, hypersensitive transitions have been called pseudoquadrupole in character.⁷⁶⁻⁷⁷

Karraker⁷⁸ has investigated the hypersensitive transitions of Nd^{3+} , Ho^{3+} and Er^{3+} and considered the absorption spectra of six, seven and eight coordinated β -diketonates in nonaqueous media to determine effect of coordination number on the intensity and

fine structure of the spectra. The β -diketonate ligands were chosen because all of them bind to lanthanides (III) in bidentate manner involving two oxygen donor atoms yielding six membered chelate ring. Thus the two main variables were coordination number and geometry of the bonded ligands. Solvents chosen were with low polarity to reduced the solvent effect to the crystal field splitting of the lanthanide ion. His excellent study showed that the hypersensitive transitions showed differences that were characteristic, for the coordination and symmetry of the lanthanide ion. The conclusion was based on following findings:

- i) There is a difference between the appearance of the absorption bands for hypersensitive transitions between six, seven and eight coordinated lanthanide ion;
- ii) Addition of unidentate ligand to solution of six or seven coordinated complexes results in changing the spectra to spectra resembling those of seven or eight coordinated complexes.
- iii) The removal of water from the solution of hydrated complexes results in changing the spectra to spectra resembling the spectra of lower coordination lanthanide;
- iv) There is a correlation between the intensities of hypersensitive transition and coordination number of lanthanide.

In his latter paper Karraker⁷⁹ investigated the effect of strong aqueous chloride on perchlorate solution on hypersensitive transitions. The change in the shape of the band was considered diagnostic marker for the change in the coordination number of lanthanides.

Chopin et al⁸⁰ have made excellent contribution into the absorption spectral intensities of lanthanide complexes in solutions. While systematically analyzing Ln(III) complexes with Poly (amino carboxylic) acids they have suggested different sequence for oscillator strength of hypersensitive transitions for Nd³⁺ and Ho³⁺. The chelates order of oscillator strength was

EDTA>HEDTA>DTPA>DCTA>NTA..... for Nd(III)

HEDTA>DTPA>NTA>EDTA>DCTA.....for Ho(III)

However these workers could not give any explanation for different behaviour of Nd³⁺ and Ho³⁺. Fellow and Choppin⁸⁰ and Choppin⁸¹, however found a good correlation between the oscillator strength and sum of the ligand pK_a for dibasic acid. These workers made three generalizations concerning intensity of hypersensitive transitions :

- i) An increasing basic character of coordination ligand results in increasing ligand absorption intensity;
- ii) Decreasing metal ligand bond distance results in intensity enhancement; and
- iii) The greater is the number of more basic ligand greater is the degree of enhanced intensity.

During our solution spectral studies on Pr(III), Nd(III) and Er(III) complexes with variety of ligands we also have made a number of generalizations. The alkoxides and bimetallic alkoxides of lanthanides in nonpolar solvents like benzene gave quite intense 4f-4f bands and the intensities of both hypersensitive as well as some of the non-hypersensitive (not obeying $|\Delta J|$ selection rules) transitions are affected very significantly by the bulkiness of the alkoxy ligands.

The primary < secondary < tertiary alkoxides group, which has been conserved through n-butanol < isobutanol < secondary butanol < tertiary butanol, Glutathione is synthetic n-pentanol < secondary pentanol < tertiary pentanol < neo pentanol Transport

The branched alky group also were responsible for the lowering of the molecular complexity of metal alkoxides irrespective of lanthanide (III) ion. The solvent effect of these alkoxides was also quite prominent. The polar solvents like DMF, DMSO enhanced the intensities of the both hypersensitive and pseudohypersensitive transitions again irrespective of the nature of metal. Detailed account of hypersensitivity and our new observation on Ligand Mediated Pseudohypersensitivity will be discussed in details in Chapter IV.

1.4 : Glutathione

1.4.1 :Function of Glutathione

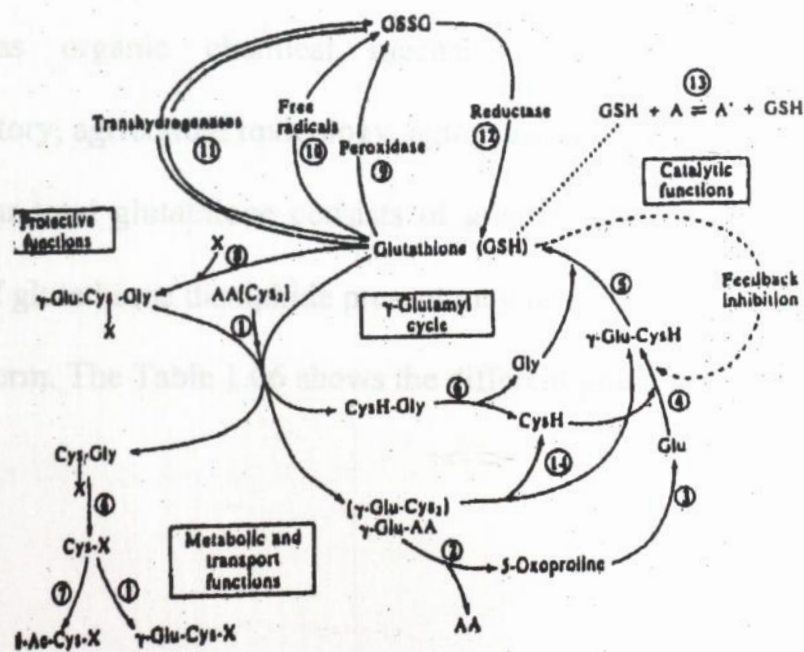


Figure 1.05 : Overview of the metabolism and function of glutathione

Most, but not all, cells contain glutathione. This molecule, which has been conserved through evolution, is adopted to perform many diverse functions. Glutathione is synthesised within the cells and exerts many of its functions intracellularly. Transport of glutathione out of the cell seems to be associated with cell membrane functions such as transport and protection. In higher animals and human, cellular transport of glutathione is related to the transport of amino acid sulphur to other cell : Figure 1.05 summarise information available about the metabolism of glutathione and indicates the biochemical path ways that seems to be connected with the several functions of glutathione. These include cellular protection (against reactive organic oxygen compounds, other toxic compounds of exogenous and endogenous origin. Free radicals) catalysis, metabolism and transport.

The multifunctional properties of glutathione are perhaps most dramatically reflected by continually increasing interest in this molecule by investigation of such divers subjects as organic chemical mechanism enzymology, molecular biology, intermediary, agriculture toxicology, aging and still many other fields.

Intracellular total glutathione consists of greater than 99.5% glutathione, the small amounts of glutathione disulphide present may be an artefact. Glutathione is the major transport form. The Table 1.06 shows the different glutathione levels in different body fluids.

- (i) Depletion of glutathione via intracellular synthesis
- (ii) Depletion of glutathione by the use of the amino acid
- (iii) Depletion of glutathione by the use of the amino acid

Table 1.07 : Glutathione Levels in different Body Fluids :

Body Organ	Total	% Glutathione
Rat :		
Hepatic vein plasma	26.0±4.2 μ M	~80
Aortic plasma	14.5±2.7 μ M	~80
Renal vein plasma	2.6±0.6 μ M	~80
Inferior vena cava plasma	8.1±2.0 μ M	~70
Arterial plasma (no anaesthesia)	25-35 μ M	~85
Bile	2.4 mM	~80-90
Pancreatic juice	0	-
Mouse :		
Arterial blood plasma	25-35 μ M	~85
Urine (after AT-125)	25-30 mM	30-70
Human lymphoid cells	0.12-3.4 nM	> 90

The cellular export of glutathione serves to protect cell membranes against oxidative and other types of damage by maintaining essential thiol groups or other components of the membrane. Export of glutathione also provides a mechanism for reducing compounds in the immediate environment of the cell membrane. Such export facilitates the transport of certain compounds especially disulphides.

Depletion of cellular glutathione has been of great importance as an experimental tool in investigations on mechanism and functions of tripeptide.

- (i) Depletion of glutathione via inhibition of γ -glutamylcysteine synthetase.
- (ii) Depletion of glutathione by the use of oxidising agent.
- (iii) depletion of glutathione by the use of the compounds such as diamide.

- (iv) Depletion of glutathione by the use of compounds that react with glutathione (diethyl maleate, 1-chloro-2,4-dinitrobenzene).
- (v) The decreasing cellular level of glutathione by inhibiting glutathione synthetase level.
- (vi) Depletion of glutathione by administration of buthionine sulphoximine has considerable member of effect on metabolic activity.

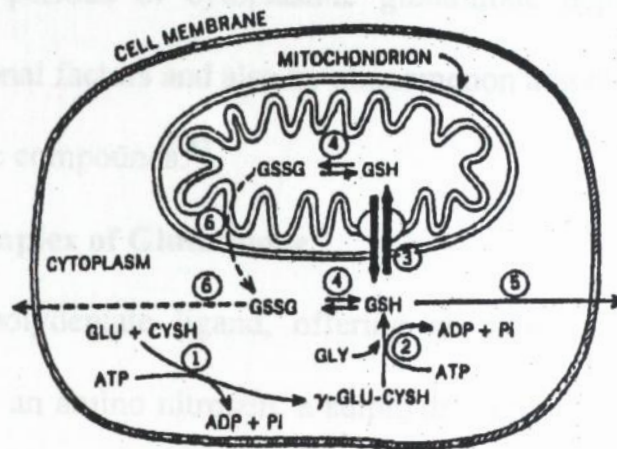


Figure 1.06 : Scheme for synthesis and transport of glutathione in mitochondria and cytoplasm

After administration of buthionine sulphoximine, the level of glutathione in liver and kidney is significantly affected. Figure 1.06 clearly demonstrates the synthesis of glutathione and its transport in mitochondria and cytoplasm. Reversible conversion of glutathione disulphide occurs in both mitochondria and cytoplasm, but the synthesis of glutathione occurs only in cytoplasm. Glutathione, rather the glutathione disulphide, is probably the major transport form, since glutathione is the predominant intra-cellular form. Transport of glutathione-disulphide, which may be formed in mitochondria that are under severe oxidative stress, serves as a mechanism for

protection. The observed rapid labelling of mitochondrial glutathione after administration of isotopically labelled cysteine is in the accord with the view that there is an exchange carrier in the mitochondrial membrane, that is, accessible to both mitochondrial and cytoplasmic glutathione. Glutathione is essential for mitochondrial function. The net efflux of glutathione from mitochondria is very slow. This suggest that, this transport mechanism functions in a manner that conserves mitochondrial glutathione during periods of cytoplasmic glutathione depletion, which may be produced by nutritional factors and also by phenomenon associated with oxidation and the presence of toxic compounds.⁸²

1.4.2 : Metal Complex of Glutathione

Glutathione is a polydentate ligand, offering as potential binding sites of two carboxylate oxygen, an amino nitrogen, a sulphhydryl group and two amide groups.⁸³ The structure of glutathione is such that al its potential binding sites cannot be simultaneously coordinated to the same metal ion, and therefore the coordination chemistry of glutathione is characterized by the formation of protonated and polynuclear complexes. The coordination chemistry of glutathione is very important and is of great interest as a model system. For the binding of metal ion by larger peptides and proteins and because metal-glutathione complexes are involved in the toxicology of several metals. Glutathione present in the cellular system at a relatively high concentration and generally it is the most abundant nonprotein thiol. Because of high affinity of a sulphur for many heavy metals glutathione is involved in their uptake and excretion.^{84,85} And naturally their complexation can explain very well their inter-cellular competition.

The complex of several heavy metals by glutathione in intact erythrocytes has been detected directly and noninvasively by ^1H NMR spectroscopy.⁸⁶⁻⁸⁷

1.4.3 : Acid-Base Chemistry of Glutathione

The acid-base chemistry of glutathione at the molecular level is described by eight microscopic constant as shown in the scheme (Figure 1.07)

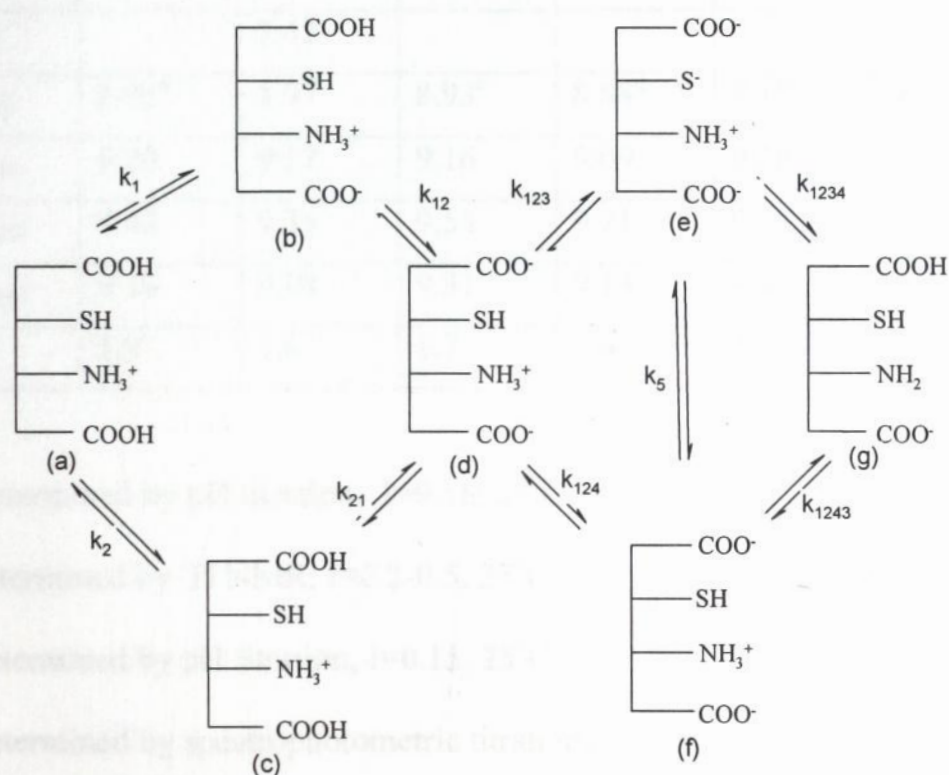


Figure 1.07 : Macroscopic acid dissociation scheme for glutathione

$$K_i = \frac{[\text{H}^+] \times [\text{H}_{4-i}\text{L}]}{[\text{H}_{5-i}\text{L}]}$$

Proton NMR data indicate that two carboxylic acid groups ionize simultaneously over the pH 0.5-6.0 while sulphhydryl and ammonium groups ionize simultaneously over the pH range 7-12.⁸⁸ The value of microscopic constants for sulphhydryl ammonium

group is highly affected by the nature of solvent. Increase in the acetonitrile content in the aquated organic solvent dielectric constant decreases, this has dramatic effect on the on the relative activity of sulphydryl and ammonium group (decrease in the K_a value from 1.6 to 0.4)⁸⁹.

Table 1.08 : Microscopic Acid Dissociation Constant of GSH

pK ₁		2.19 ^b					
pK ₂		3.22					
pK ₁₂		3.45					
pK ₂₁		2.42					
pK ₁₂₃	8.92 ^a	8.97	8.93 ^c	8.88 ^d	9.15 ^d	9.47 ^d	9.64 ^d
pK ₁₂₄	9.20	9.17	9.16	9.09	9.26	9.20	9.28
pK ₁₂₃₄	9.44	9.35	9.53	9.21	9.53	9.56	9.71
pK ₁₂₄₃	9.16	9.08	9.31	9.13	9.46	9.82	10.07
K ₅	1.9	1.6	1.7	1.6	1.3	0.5	0.4

^a Determined by pH titration; I=0.16, 25^oC

^b Determined by ¹H NMR; I=0.2-0.5, 25^oC

^c Determined by pH titration; I=0.15, 25^oC

^d Determined by spectrophotometric titration; I=0.10, 25^oC

The K₁₂₄, K₁₂₃₄ pathways, which involves the more highly charged zwitter-ionic intermediate as acetonitrile content increases. This change in the acid base chemistry with decreasing dielectric constant is of great interest in view of the hydrophobic regions of low dielectric constant in protein. Therefore our study of complexation of glutathione with one, two or three different metal ion simultaneously investigated in different mixed solvents (DMF-H₂O, Dioxane-H₂O and Acetonitrile-H₂O) of different

stoichiometry, will be important and relevant in understanding hetero metal complexation of large proteins involving endogenous metal ions.

The thesis presents the quantitative absorption spectral intensity data analysis with absorption difference, comparative absorption spectroscopy involving 4f-4f transition as PROBE in understanding the coordination and binding characteristics of Glutathione reduced (GSH) and Glutathione oxidise (GSSG) in presence of hard metal ions Pr(III) and Nd(III) and a soft metal ion Zn(II) in process of simultaneous coordination. Since such hetero-bimetallic complexation of GSH/GSSG involving Pr(III)/Nd(III)/Er(III) and Ca(II)/Zn(II) MIMICS the *in vitro* hetero bimetallic simultaneous complexation of these sulphur containing peptides with Ca(II) and Zn(II) occurring both intra and extra cellularly. The effectivity of such effort made in present thesis opens up new vistas of structure and spectra correlation which pave way to make 4f-4f transition spectroscopy on very effective tool in following the progress of several biochemical reaction involving most essential metal ions like Ca^{2+} and Zn^{2+} ions.

The thesis has been divided into following chapters:

- (1) Introduction
- (2) Review
- (2) Experimental
- (3) Tables and Figures
- (4) Results and Discussion
- (5) Summary and Conclusion

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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 3P_0 , 3P_1 , 3P_2 and 1D_2 and they had termed the unique sensitivity

CHAPTER NO. II

REVIEW ON LANTHANIDES : BIOLOGICAL ACTIVITY AND COORDINATION PHENOMENA

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.²⁻⁴ The scope of this review is to survey the biological activity and co-ordination phenomena of lanthanides.

Misra et al⁵ 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. Somerer⁶ had studied the ligand mediated pseudohypersensitivity of the $^3H_4 \rightarrow ^3P_2$, $^3H_4 \rightarrow ^3P_1$, $^3H_4 \rightarrow ^3P_0$ and $^3H_4 \rightarrow ^1D_2$ 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

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:- $^3H_4 \rightarrow ^3P_2$, 3P_1 , 3P_0 and 1D_2 and they had termed the unique sensitivity of such transitions as 'Ligand Mediated Pseudohypersensitivity'. K. Binnemans⁷ discussed the reliability and sensitivity of Judd-Ofelt intensity parameter T_λ ($\lambda=2,4,6$) by comparing experimental absorption spectra with simulated spectra. S.N. Misra et al⁸ 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 al⁹ had studied the behaviour of the phenomenological 4f-4f intensity parameters in compounds of the Nd^{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 upto approximately 5.4 value. For pH values above 5.5, the Nd^{3+} ion hydrolyses. Among the T_λ 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 $\langle P^k \rangle = (P^k_1 + P^k_2)/2$, since at $P^H \sim 5$ both carboxylic groups are expected to be equally deprotonated. In this case, T_2 has increased with $\langle P^k \rangle$, but not linearly.

Tater et al¹⁰ had studied electronic spectral studies on Nd^{3+} doped sulphanilide system. It also provides useful information regarding metal-ligand interaction and change in symmetry around lanthanide ion. S.N. Misra et al¹¹ 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 (β), bonding (b) and covalency (δ) parameters derived from coulombic and spin-orbit interaction parameters.

J.L. Ryan and C.K. Jorgensen¹² 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.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 ξ_{4f} 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^- 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.

Misra¹⁴ had done studies on Pr (III) and fluorouracil, fluorocytosine, fluoroadinine, fluorothymine, fluorouridine, fluorocytidine, fluoroadenosine and fluorothymidine 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-workers¹⁵ 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 (H₂O) (where nucleotide = AMP, ADP & ATP) indicate that the binding of the nucleotide is through phosphoric oxygen. Henrie and co-workers¹⁶ had shown that the low magnitudes of oscillator strengths indicate outer sphere complexation while high values indicate inner sphere complexation. For the present complexes T₂, T₄ and T₆ parameters have low values, indicating thereby the predominance of outer sphere complexation.

Misra et al¹⁷ 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_λ) 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_λ) 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_λ) parameters. Indira¹⁸ 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+CH₃N, DMF+CH₃OH, DMF+dioxane, CH₃OH+CH₃CN and CH₃CN+dioxane. The involvement of π -electron density of diols in complexation with Nd (III) are revealed from the correlations made from the plot of Oscillator strength (Pobs) against T_λ 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 Buddhudu¹⁹ had calculated the values of the Slater-Condon (F_2, F_4, F_6), Racah (E^1, E^2, E^3) and Lande (ξ_{4f}) coefficients, the nephelauxetic ratio (β), the bonding parameter (β) and the Judd-Ofelt Intesity (T_λ) parameters from the reported absorption spectra of Pr³⁺, Nd³⁺ and Er³⁺ ions in an aprotic solvent SeOCl₂ acidified with antimony pentachloride. They had suggested that the nature of bonding is covalent in the laser liquid (for Pr³⁺, Nd³⁺ and Er³⁺ ions). Peacock²⁰ 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_2 with each hypersensitive transition. Hussain et al²¹ 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 δ 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 Iftikhar²² had studied the interaction of trivalent lanthanide thiocyanates and 2, 2'-bipyridyl in ethanol and this results in the formation of the complexes viz; $[Ln(bpy)_n(SCN)_3(H_2O)]_y$ 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 triocyanates 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 al²³ 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. Indira²⁴ 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 Rajnak²⁵ 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 ≈ 6000 - $50,000 \text{ cm}^{-1}$. They had also discovered the variation of the intensity parameters.

Gunnlaugsson et al²⁶ had reported about the synthesis, structural and biological evaluation of Gly, Ala based lanthanide macrocyclic conjugates as supramolecular ribonuclease mimics. Zhang et al²⁷ 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), $[\text{Nd}_2 (\text{glu})_3 (\text{phen})\text{Cl}]_n$ 1, $[\text{Tb} (\text{glu}) (\text{phen})\text{Cl}]_n$ 2 and $[\text{Ho} (\text{glu}) (\text{phen})\text{Cl}]_n$ 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 π - π 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 π - π 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 al²⁸ 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 al²⁹ had studied the complexation of trivalent lanthanides with aromatic (mellitic, pyromellitic, hemimellitic, trimellitic, trimesic, phthalic, isophthalic, 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 unidentate while isophthalate and trimesate replace approximately 1.5 H₂O 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 Xie³⁰ had reported about synthesis and crystal structure of a novel praseodymium complex with β -alanine: $\{[\text{Pr}_2(\text{alanine})_6 (\text{H}_2\text{O})_4] [(\text{ClO}_4)_6 \text{H}_2\text{O}]\}_n$. 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 β -alanine-praseodymium complex exhibits significant differences in both composition and structure than α -alanine lanthanide complex, usually with the core formula $[\text{Ln}(\alpha\text{-alanine})_4(\text{H}_2\text{O})_8]^{6+}$. Since the β -alanine ligand is more slender than α -alanine, it is expected that β -alanine forms more compact structural complexes than α -alanine.

Misra³¹ 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, $\text{Nd}(\text{diket})_3(\text{N})_2$ (where diket is 1-phenyl-1,3-butanedione benzoylacetone, bzac), 1,3-diphenyl-1,3-propanedione (dibenzoylmethane, dbm) and 4,4,4-trifluoro-L-(2-thienyl)-1,3-butanedione (theonyltrifluoroacetone, tffa) 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_λ). Zhao et al³² had reported the synthesis of lanthanide complexes with L-isoleucine : X-ray crystal structure of $[\text{Nd}_2(\text{I-leu})_4(\text{H}_2\text{O})_8][\text{ClO}_4]_6$. They had synthesized two lanthanide complexes, $\text{Ln}_2(\text{I-leu})_4(\text{ClO}_4) \cdot 8\text{H}_2\text{O}$ in aqueous solution (where Ln = Nd or Er, I-leu = L-isoleucine). They had determined the crystal structure of the Nd – complex by X-ray diffraction. The complex is a ring like hexanuclear $[\text{Ln}_2(\text{H}_2\text{O})_8(\text{ClO}_4)_6]^{2+}$ cation.

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 al³³ 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 : $[M(\text{bheg})_2]\text{Cl}\cdot 3\text{H}_2\text{O}$ 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 $[\text{La}(\text{bheg})_2]\text{Cl}\cdot 3\text{H}_2\text{O}$ 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 al³⁴ had studied the synthesis and structure of carboxylate-bridged polynuclear Copper (II):Lanthanum(III) ring : $[\text{La}(\text{H}_2\text{O})_5(\text{CuL})_2][\text{CuL}]\cdot 8\text{H}_2\text{O}$. They had prepared the complex, $[\text{La}(\text{H}_2\text{O})_5(\text{CuL})_2][\text{CuL}]\cdot 8\text{H}_2\text{O}$ by the reaction of the $\text{Na}[\text{CuL}]$ (where L = Schiff base derived from 5-bromosalicylaldehyde and glycyglycine) with $\text{LaCl}_3\cdot n\text{H}_2\text{O}$. 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-workers³⁵ had reported new binuclear model compounds for the study of the 4f-4f exchange interaction. Zhang and Wang³⁶ had studied and investigated and measured the absorption spectrum of Neodymium (III) (Nd^{3+}) doped in poly(methylmethacrylate). They had found that the nephelauxetic effect in the spectrum had been compared to other spectra of Nd^{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 $4f^n$ configuration is a function of F_2 , F_4 , F_6 and ξ_{4f} , they had calculated the Slater- Condon parameters (F_2 , F_4 , F_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 β 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, Lebrun³⁷ 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_4O_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 Choppin³⁸ had investigated the environmental effects of nitrate, sulfate and α -picolinate anions on f-f transitions of lanthanide ions in aqueous solution.

Milchev³² had also investigated about the coordination of lanthanide ions.

Zinner and Brito³⁹ had reported about the synthesis and properties of complexes between lanthanide trifluoroacetates and 2-picoline-N-oxide (2-PicNO)*. They had described the complexes of lanthanide trifluoroacetates with 2-pioline-N-oxide (2-PicNO) with composition $\text{Ln}(\text{CF}_3\text{COO})_3 \cdot 2(2\text{-Pic-NO})$. 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_3CN . 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 al⁴⁰ had reported about the coordination chemistry of lanthanides with Cryptands: An x-ray and spectroscopic study of the complex, $\text{Nd}_2(\text{NO}_3)_6[\text{C}_{18}\text{H}_{36}\text{O}_6\text{N}_2] \cdot \text{H}_2\text{O}$. They had synthesized the complex $\text{Nd}_2(\text{NO}_3)_6[\text{C}_{18}\text{H}_{36}\text{O}_6\text{N}_2] \cdot \text{H}_2\text{O}$ 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 $[\text{Nd}<222>(\text{NO}_3)]^{2+}$ and the anions $[\text{Nd}(\text{NO}_3)_5 \cdot \text{H}_2\text{O}]^{2-}$ and is isostructural with the samarium analogue.

Bukietynska and Mondry⁴¹ had investigated the spectral properties of Nd^{3+} - EDTA solutions at different Nd^{3+} EDTA concentrations within a broad pH region. In order to investigate the formation and the type of bonding in the Nd^{3+} - EDTA species, the analysis of the oscillator strength values of the 'hypersensitive' ${}^4\text{G}_{7/2}$, ${}^4\text{G}_{5/2} \leftarrow {}^4\text{I}_{9/2}$ transition and of the Judd-Ofelt intensity parameters. They had suggested a relatively complete model of the Nd^{3+} - EDTA coordination by the correlation of these results with NMR and kinetic data. Kamenskaya and Mikheev⁴² had also investigated about the coordination compounds of divalent lanthanides

with crown ethers. Santos et al⁴³ had reported about the crystal structures of Neodymium and Holmium Trifluoromethane sulfonate Enneahydrated. Fox et al⁴⁴ had studied about praseodymium nitrate and neodymium nitrate complexation with organophosphorus reagents in supercritical carbon-dioxide solvent. Mehta et al⁴⁵ 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_{λ}) 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 al⁴⁶ 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, ¹NMR and thermal analysis. The results indicate the formation of 1 : 2 (M : L) complexes with the general formula (ML₂.H₂O.X)2H₂O where M = trivalent Y, La, Ce, Pr, Nd, Sm, Gd, Dy, Ho, Er and Yb; HL (or H₂L) = thioschiff base and X = ClO₄⁻ or Cl⁻ ion. They had proposed C.N's 6 and 8 for the lanthanides in these complexes. Takahashi and Ishiguro⁴⁷ 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 Spedding⁴⁸ had studied about the coordination (hydration) of rare earth ions in aqueous chloride solutions from X-ray diffraction in SmCl₃, EuCl₃ 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 La³⁺ through Nd³⁺ are nine coordinated, those between Nd³⁺ and Tb³⁺ are transitional between nine and eight, and those from Tb³⁺ to Lu³⁺ are eight coordinated.

Kumar and Rao⁴⁹ 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) glycol hydrazone, H₃dhbbgh. They had also synthesized rare earth metal complexes of the empirical formulae, [Ln (H₃dhbbgh)₂ Cl₂]Cl.nH₂O and [Ln (dhbbgh) (H₂O)₂], where Ln = 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 (β , $b^{1/2}$, $\delta\%$ and η) 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 ($T_\lambda = 2, 4, 6$) 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 al⁵⁰ 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.

Wong⁵¹ had reported about the configuration interaction of the Pr^{3+} ion. Misra et al⁵² had studied about the neodymium (III)-substituted bismuth titanate thin film generation using metal alkoxo, acyloxo and β -diketonato precursors employing a sol-gel route and using 4f-4f transition spectra as probes to explore kinetic performance. Le Bret et al⁵³ had reported about single crystal and for IR analysis of some lanthanide thiophosphates. Binnemans et al⁵⁴ had investigated about the reliability of Judd-Ofelt Intensity parameters by graphical simulation of the absorption spectrum. Malta et al⁵⁵ had studied the intensity parameters of 4f-4f transitions in the $\text{Eu}(\text{dipivaloylmethanate})_3 \cdot 1, 10\text{-phenanthroline}$ complex. Chen and his co-workers⁵⁶ had investigated about the spectroscopic properties of Nd^{3+} ions in $\text{La}_2(\text{WO}_4)_3$ crystal. Devlin et al⁵⁷ 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_λ ($\lambda = 2, 4, 6$) intensity parameters.

Verma et al⁵⁸ had studied and calculated electronic spectral parameters, viz, Judd-Ofelt (T_λ), Racah (E_k), Slater Condon (F_k), Lande (ξ_{4f}) and bonding parameters (β , $b^{1/2}$, δ and η) 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 al⁵⁹ had reported the lanthanide coordination with α -Amino Acids under near physiological pH conditions: Polymetallic complexes containing the cube-like $[Ln_4(\mu_3-OH)_4]^{8+}$ cluster core. Wang et al⁶⁰ had reported about spectroscopic study of lanthanide (III) complexes with aliphatic dicarboxylic acids. Tang et al⁶¹ 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 al⁶² had studied zinc complexation of glutathione and glutathione-derived peptides. Khan, Saxena and Iftikhar⁶³ had reported mixed ligand lanthanide complexes. Interaction of trivalent lanthanides with 1,10-phenanthroline and thiocyanate in alcohol. Khan and Iftikhar⁶⁴ 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.

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CHAPTER NO. III

EXPERIMENTAL AND METHODS

3.1 Materials and Methods :

The main works in this thesis includes work on complexation of Glutathione reduced (GSH) with hard metal ions Pr(III) or Nd(III) in presence and absence of Ca(II)/Zn(II) in different aquated organic solvents like methanol, acetonitrile, DMF and Dioxane) at pH – 4 at 25⁰C. Pr(NO₃)₃.7H₂O and Nd(NO₃)₃.6H₂O of 99.9% purity was purchased from CDH Analytical Reagents and Glutathione reduced (GSH) of 99.9% purity was purchased from M/s. SRL Pvt. Ltd., Mumbai. It is kept in deep freezer at 0⁰C. Solvents like DMF, dioxane, acetonitrile and methanol were of spectroscopic grade from MERCK. Other chemicals like hydrochloric acid , acetic acid, sodium acetate etc. were from MERCK.

This research work is mainly based on the study of the simultaneous complexation behaviour of Pr(III)/Nd(III) with GSH in presence and absence of Zn(II)/Ca(II) in different aquated organic solvents. To form a complex Ln(III)_GSH the Ln(III):ligand ratio was kept 1:1 and in complexation like Ln(III)-GSH-Ca(II)/Zn(II) the ratio was also kept 1:1:1.

All the complexation were carried out at pH-4 and all the absorption spectra were recorded on Perkin Elmer Lamda-35 UV-visible spectrophotometer upgraded with computer attached, high resolution and expansion of scale in the region 350nm – 1000nm. The temperature of all the observation are maintained at 25⁰C by using water circulating thermostat model- DS-G HAAKE. Most of the bands were expanded to the optimum limits to get maximum resolution.

3.1.1 : Preparation of the Sample Solutions and Reference Solutions

In general procedure, for preparation of the sample solution, Ln(III)nitrate solution was taken first to which the ligand solution was added very slowly. After thorough mixing the buffer solution was added whenever it was needed. Finally to make up the total volume, the pure solvent or aquated solvents or water was added and the mixture was thoroughly mixed. The solutions were scanned for the absorption spectra for the spectral region 350 nm – 1000 nm. For the preparation of reference solution, the above procedure was repeated in which instead of Ln(III) solution the same volume of pure solvent (or water) or solvent mixture were used.

3.1.2 : Preparation of Ln(III) : GSH Complex :

To 1.0ml standard solution of Ln(III) (0.01M), 1 ml solution of ligand of the same concentration was added and it was thoroughly mixed. Finally to make upto 10.0 ml total volume either proper buffer solution or proper solvent was added.

3.1.3 : Preparation of Ln(III) : GSH : Zn(II) Complex

In a similar manner to 1.0 ml standard solution of Ln(III), 1.0 ml of the solution of GSH of equal concentration was added. 1.0 ml of the equivalent standard Zn(II)/Ca(II) solution was added, finally 10.0 ml total volume was made by addition of proper buffer, solvent needed for the spectral analysis as well as for the synthesis of the complex.

3.1.4 : Spectral Analysis of Complexes

The complexes in the solution was scanned in the spectral region 350 nm – 1000 nm. Ln(III) : GSH, Ln(III) : GSH : Ca(II) and Ln(III) : GSH : Zn(II) [Ln(III) : Pr(III)/Nd(III)] were also scanned for elemental analysis, ^1H NMR and IR spectra in order to explore their structural features.

3.2 : Evaluation of Parameters

The presence of quite detailed internal f-electron transition spectra is easily accessible spectral region of most of the lanthanides and the sensitivity of their spectra to the coordination environment and geometry of the complex species makes absorption spectrophotometry an extremely useful tool for studying lanthanide chemistry particularly in solutions both in aqueous and non-aqueous media^{1,2}. The weak narrow line-like bands, in the UV-visible and near infrared region of the spectrum, arise due to Laporte forbidden internal transition within the 4f levels. The crystal fields splitting for the trivalent lanthanides are so small that the spectra of the compounds closely resemble with those of the free ion.

The energy of 4f-4f transitions is composed of two main components, viz. the electrostatic and spin orbit interaction between 4f electrons.

$$E = \sum_k F_k + A_{so} \xi_{4f} \quad (1)$$

where F_k and A_{so} are the angular part of electrostatics and spin orbit interaction respectively. Their value can be calculated applying tensor operator technique, F_k and ξ_{4f} are radial integrals. Thus to define energy level scheme of $4f^n$ configuration it is necessary to have four radial integrals F_2 , F_4 , F_6 and ξ_{4f} which are evaluated by Hartree Fock Method^{3,4}

Using Taylor series expansion the energy level structure of lanthanides can be expressed in the factor order approximation. Then, the energy E_j of the j^{th} energy level is given by

$$E_j(F_k, \xi_{4f}) = E_{oj}(F_k^0, \xi_{4f}^0) + \sum_{k=2,4,6} \frac{\delta E_j}{\delta F_k} \Delta F_k + \frac{\delta E_j}{\delta \xi_{4f}} \Delta \xi_{4f} \quad (2)$$

Where E_{oj} is the zero order energy of the j^{th} level.

$$F_k = F_k^o + \Delta F_k \quad (3)$$

$$\xi_{4f} = \xi_{4f}^o + \Delta \xi_{4f} \quad (4)$$

The difference between the observed E_j and the zero order value, E_j^o can be express as :

$$E_j = \sum_{k=2,4,6} \frac{\delta E_j}{\delta F_k} \Delta F_k + \frac{\delta E_j}{\delta \xi_{4f}} \Delta \xi_{4f} \quad (5)$$

The result of complexation on the spectra is the red shift of all the electronic transitions, the red shift is due to the expansion of the metal orbital radius resulting in the decrease of the inter-electronic repulsion parameters (Slater-Condon, F_k 's or Racah, E_k). This phenomenon is known as nephelauxetic effect, which measures the change in F_k with respect to free ion and expressed by a nephelauxetic ratio ' β ', which is defined as:

$$\beta_1 = \frac{F_k^o}{F_k^f}; \beta_2 = \frac{\xi_{4f}^o}{\xi_{4f}^f}$$

$$\text{and } \beta = \left[\frac{\beta_1 + \beta_2}{2} \right] \quad (6)$$

Where F_k^o and F_k^f refers to parameters in complex and free ion respectively. There is ample evidence to the fact that 4f-orbitals do participate in chemical bonding. The amount of mixing of 4f-orbitals does participate in chemical bonding. The amount of mixing of 4f-orbital and ligand orbital can be given by another bonding parameter ' $b^{1/2}$ ', which is related to nephelauxetic effect and is defined as :

$$b^{1/2} = \left[\frac{1 - \beta}{2} \right]^{1/2} \quad (7)$$

Sinha⁵ introduced another parameter known as the percentage covalency parameter, which is defined as:

$$\delta\% = \left[\frac{1-\beta}{\beta} \right] \times 100 \quad (8)$$

The intensity of the absorption band is measured by the oscillator strength (p), which is directly proportional to the area under the absorption curve. It can be expressed in terms of molar extinction (ϵ_m), energy of the transition in wave number ($\bar{\nu}$) and the refractive index (η) of the medium by the relationship

$$P = 4.31 \times 10^{-9} \left[\frac{9\eta}{(\eta^2 + 1)^2} \right] \int \epsilon_{\max}(\bar{\nu}) d\bar{\nu} \quad (9)$$

where ϵ_{\max} = molar extinction coefficient

$\bar{\nu}$ = energy of the transition in wave number

η = the refractive index of the medium

The experimental values of oscillator strength (P_{exp}) of the absorption bands were calculated by performing Gaussian curve analysis of the curves.

Now oscillator strength (P_{exp}) can be found out from the equation,

$$P = 4.60 \times 10^{-9} \times \epsilon_m \times \Delta\nu_{1/2} \quad (10)$$

where the molar extinction co-efficient ϵ_m is given by the equation

$$\epsilon_m = \frac{\text{Absorbance}}{\text{Concentration} \times l}$$

where l = path length of the cell in cm = 1 cm

The electronic transition of trivalent lanthanides can be electric dipole, magnetic dipole electric quadrupole character. Some transitions have appreciable contributions from more than one mode of electric dipole transition, which in pure f^n configurations are

strictly parity forbidden. However, a weak induced electric dipole transition can occur as a result of interaction of central metal ion with the surrounding ligand field.

Judd⁴ observed that the oscillator strength of an induced electric dipole transition was related to the energy of transition ($\bar{\nu}$), square of the matrix element of unit tensor operator, $U^{(\lambda)}$ connection initial $\langle f^n \psi J |$ and $| f^n \psi' J' \rangle$ through three phenomenological parameters T_λ ($\lambda=2,4,6$). These parameters are related to the radial wave function of the state, refractive index of the media and the ligand field parameters that characterize the environmental field.

$$P = \sum T_\lambda \bar{\nu} \langle f^n \psi J | U^{(\lambda)} | f^n \psi' J' \rangle \quad (11)$$

These three parameters T_2 , T_4 and T_6 are related to the radial wave function of the perturbing configuration and after including weighing factor $(2J + 1)^{-1}$ the equation can be written as :

$$P = \sum T_\lambda \langle f^n \psi J | U^{(\lambda)} | f^n \psi' J' \rangle^2 (2J + 1)^{-1} \quad (12)$$

For calculating matrix element $U^{(\lambda)}$ the eigen vectors were of the form,

$$f^n \psi J = \sum_{\alpha SL} \epsilon^{\alpha SL} | f^n \alpha SL J \rangle \quad (13)$$

and can be calculated by diagonalizing the complete energy matrices. Details of the computation involved have been dealt with separately for praseodymium and neodymium systems.

In order to define the energy parameters we have to calculate four terms i.e. F_2 , F_4 , F_6 and ξ_{4f} . Since there are only five observable spectral bands (${}^4G_{7/2}$, ${}^4G_{5/2}$, ${}^4F_{7/2}$, ${}^4F_{5/2}$, and ${}^4F_{3/7}$) for neodymium, these four terms can be solved using the following equation,

$$E_{\text{obs}} = \sum_{k=2,4,6} \frac{\delta E_j}{\delta F_k} \Delta F_k + \frac{\delta E_j}{\delta \xi_{4f}} \Delta \xi_{4f} \quad (14)$$

By considering F_k 's and ξ_{4f} as empirical derived from least-square fit of the experimental energy level of the Ln(III) ion, which is either free or complexes. Solution of the equation taking into account of the difference in energy and calculating the energy terms using Wong's values and practical differential coefficients for F_2^0 , F_4^0 , F_6^0 and ξ_{4f}^0 for neodymium gave parameters of Slater Condon integrals, in some cases higher than those observed for the aqueous ion. In our complexes, we expect the metal ion to expand so that the bonding parameters become positive and subsequently the Slater-Condon integrals should be lower than that for the aqueous ion. Thus the values, which yield from the above method, are not realistic.

Because of the above shortcomings, a pure solution of the four equations with four unknown is ruled out. Another method known as the partial and multiple regression method⁶⁻¹³ yield the values of only two parameters F_2 and ξ_{4f} .

Equation (14) can now be written as,

$$E_{\text{obs}} = E_{\text{oj}} + \frac{\delta E_j}{\delta F_2} \Delta F_2 + \frac{\delta E_j}{\delta \xi_{4f}} \Delta \xi_{4f} \quad (15)$$

and it can be again express as,

$$\frac{E_{\text{obs}} - E_{\text{oj}}}{\delta E_j / \delta \xi_{4f}} = \Delta \xi_{4f} + \frac{\delta E_j / \delta F_k}{\delta E_j / \delta \xi_{4f}} \Delta F_2 \quad (16)$$

The reported values for the zero order energies and partial derivatives with respect to F_k and ξ_{4f} parameters for Nd(III) ion are given in Table 2.02 on making the following substitutions in equation (3)

$$Y = \frac{E_{\text{obs}} - E_{\text{oj}}}{\delta E_j / \delta \xi_{4f}}, \quad a = \Delta \xi_{4f}$$

$$X = \frac{\delta E_j / \delta F_k}{\delta E_j / \delta \xi_{4f}}, \quad b = \Delta F_2$$

Then the equation(16) can be written in the form,

$$Y = a + Xb$$

Considering the five bands, the above equation becomes the set of equation which can be represented as :

$$Y_1 = a + X_1b$$

$$Y_2 = a + X_2b$$

$$Y_3 = a + X_3b$$

$$Y_4 = a + X_4b$$

$$Y_5 = a + X_5b \quad (17)$$

Where each equation corresponds to an observed band in Neodymium. On solving the above equation by statistical method, we get:

$$b = \frac{\sum XY}{\sum X^2} \quad \text{and} \quad a = \bar{Y} - b\bar{X} \quad (18)$$

$$\text{where, } \sum XY = \sum XY - \frac{\sum X \sum Y}{5}$$

$$\sum X^2 = \sum X^2 - \frac{(\sum X)^2}{5}$$

$$\bar{Y} = \frac{\sum Y}{5} \quad \text{and} \quad \bar{X} = \frac{\sum X}{5}$$

The values thus obtained yield approximate solutions for F_2 and ξ_{4f} . Approximate values for F_4 and F_6 are then got from the following relation :

$$\frac{F_4}{F_2} = 0.13805 \quad \text{and} \quad \frac{F_6}{F_2} = 0.0151$$

In order to get more accurate values of F_k 's and ξ_{4f} their values are lightly perturbed so that the root mean square deviation demoted by

$$\sigma = \left[\frac{\sum (E_{\text{cal}} - E_{\text{obs}})^2}{5} \right]^{1/2}$$

is reduced, care is being taken that the values of F_k 's and ξ_{4f} do not exceed those reported for the aqueous Nd(III) system. Their derivation of these values and their refinement were carried out using a program written in FORTRAN-77 language for the PENTIUM-IV Computer system.

In Neodymium complexes, one generally observes ten bands in the electronic spectrum. Since the number of the bands exceeds the number of parameters, exact solution is not possible and statistical methods have to be employed to get the solutions. Mathematically correct solutions is the one which makes the weighted difference the squares of observed and calculated values (i.e. r.m.s. minimum)

$$\sigma = \left[\frac{\sum (E_{\text{cal}} - E_{\text{obs}})^2}{N} \right]^{1/2}$$

is the minimum number, where N is the number of observations,

We can write equation (14) as :

$$E_{\text{obs}} = E_{\text{oj}} + \frac{\delta E_j}{\delta F_2} \Delta F_2 + \frac{\delta E_j}{\delta F_4} \Delta F_4 + \frac{\delta E_j}{\delta F_6} \Delta F_6 + \frac{\delta E_j}{\delta \xi_{4f}} \Delta \xi_{4f} \quad (19)$$

Dividing equation (19) by $\delta E_j / \delta F_2$ we get,

$$\frac{E_{\text{obs}} - E_{\text{oj}}}{\delta E_j / \delta F_2} = \Delta F_2 + \frac{\delta E_j / \delta F_4}{\delta E_j / \delta F_2} \Delta F_4 + \frac{\delta E_j / \delta F_6}{\delta E_j / \delta F_2} \Delta F_6 + \frac{\delta E_j / \delta \xi_{4f}}{\delta E_j / \delta F_2} \Delta \xi_{4f} \quad (20)$$

Let us make the following substitutions in equation(20)

$$Y = \frac{E_{\text{obs}} - E_{\text{oj}}}{\delta E_j / \delta F_2}; P = \frac{\delta E_j / \delta F_4}{\delta E_j / \delta F_2}; Q = \frac{\delta E_j / \delta F_6}{\delta E_j / \delta F_2}; R = \frac{\delta E_j / \delta \xi_{4f}}{\delta E_j / \delta F_2}$$

$$a = \Delta F_2 \quad b_1 = \Delta F_4 \quad b_2 = \Delta F_6 \quad b_3 = \Delta \xi_{4f}$$

The reported values for zero order energies and partial derivatives are given in Table 2.02.

The above equations can be utilized in equation(19) in the following form for calculation of a , b_1 , b_2 and b_3 .

$$Y_1 = a + b_1 P_1 + b_2 Q_1 + b_3 R_1$$

$$Y_2 = a + b_1 P_2 + b_2 Q_2 + b_3 R_2$$

$$Y_3 = a + b_1 P_3 + b_2 Q_3 + b_3 R_3$$

$$Y_4 = a + b_1 P_4 + b_2 Q_4 + b_3 R_4$$

$$Y_5 = a + b_1 P_5 + b_2 Q_5 + b_3 R_5$$

$$Y_6 = a + b_1 P_6 + b_2 Q_6 + b_3 R_6$$

$$Y_7 = a + b_1 P_7 + b_2 Q_7 + b_3 R_7$$

$$Y_8 = a + b_1 P_8 + b_2 Q_8 + b_3 R_8$$

$$Y_9 = a + b_1 P_9 + b_2 Q_9 + b_3 R_9$$

$$Y_{10} = a + b_1 P_{10} + b_2 Q_{10} + b_3 R_{10}$$

These equations can be solved by the partial regression method and give solution as below

$$a = Y - b_1 p_1 - b_2 q_1 - b_3 r_1$$

$$b_1 = c_{11} \sum p_1 Y + c_{12} \sum q_1 Y + c_{13} \sum r_1 Y$$

$$b_2 = c_{21} \sum p_1 Y + c_{22} \sum q_1 Y + c_{23} \sum r_1 Y$$

$$b_3 = c_{31} \sum p_1 Y + c_{32} \sum q_1 Y + c_{33} \sum r_1 Y$$

(22)

Where, $Y = \frac{\sum Y}{10}$, $p_1 = \frac{\sum P_1}{10}$, $q_1 = \frac{\sum Q_1}{10}$, $r_1 = \frac{\sum R_1}{10}$

$$\sum p_1 Y = \sum P_1 Y - \frac{\sum P_1 \sum Y}{10}$$

$$\sum q_1 Y = \sum Q_1 Y - \frac{\sum Q_1 \sum Y}{10}$$

and $\sum r_1 Y = \sum R_1 Y - \frac{\sum R_1 \sum Y}{10}$

For neodymium system, the value of C_{11} , C_{12} , C_{13} , C_{22} , C_{23} and C_{33} are approximately :

$$\begin{aligned} C_{11} &= 4268.95 \times 10^{-4} & C_{22} &= 29.95 \times 10^{-4} \\ C_{12} &= 183.40 \times 10^{-4} = C_{21} & C_{23} &= 1565.31 \times 10^{-4} = C_{32} \\ C_{13} &= -50413.00 \times 10^{-4} = C_{31} & C_{33} &= 834696.70 \times 10^{-4} \end{aligned}$$

The values of F_k obtained using these constants and equations are found to be higher than the aquo system in some cases. Since the metal ion expands on complexation such a situation is usually not realistic.

Though the RMS values for the ten bands obtained for neodymium can be reduced by small perturbations of the value, by imposing the boundary condition same as in the case of praseodymium. It is important that there is sufficient measure of agreement between individual values, especially for the strong intensities. The strong intensities should match as perfectly as possible for the model to be corrected.

An inspection of the spectrum of neodymium shows that five of the ten bands are quite intense and we feel that it would be more realistic to attempt a fit for these bands, instead of considering all the bands. To obtain approximate values of F_k 's and ξ_{4f} we have used the coefficients C_{11} and C_{33} , which are mentioned earlier. The approximate values, thus acquired were checked to see that they do not exceed the values quoted for the neodymium aquo system. The parameters P, Q, R and A were then perturbed to get the best fit as was done for the praseodymium system.

The observed oscillator strength (P_{obs}) of the transition energies were expressed in terms of parameters defined by Judd and Ofelt known as the T_2 , T_4 and T_6 parameters which are given by the following equation,

$$\frac{P_{obs}}{Y} = [(U^2)]^2 T_2 + [(U^4)]^2 T_4 + [(U^6)]^2 T_6 \quad (23)$$

These values are procured using Carnall's co-efficients for aquo system. Four

neodymium complexes, five equations exist for the observed values of the five bands. Since $[U^{(2)}]^2$ has zero value for the ${}^4F_{3/2}$ transition level, finally they turn into ordinary simultaneous equations which give the values of T_2 , T_4 and T_6 by simple calculations. Matrix elements for Nd(III) are given in table 2.03. However, an inspection of the results showed that because of the scarcity of the number of observed bands, the values obtained for T_2 are meaningless and T_4 and T_6 values are very crude approximations. This may also be due to the fact that we have used quoted for the aquo system.

This does not introduce much error in T_6 , though one would expect that this T_6 value is not exactly correct. The calculation of T_2 involves T_4 and T_6 and suffer from the disadvantage that its value is affected by inaccuracies incurred in both T_4 and T_6 . In some cases, it turns out a negative value, a physically unacceptable solution. However, we believe that our conclusions about structure derived from T_4 and T_6 do have some meaning.

For Pr(III) ${}^3H_4 \rightarrow {}^3F_3$ transition occurring around 5200cm^{-1} shows hypersensitivity (Table 2.01), however, the ${}^3H_4 \rightarrow {}^3P_2$, ${}^3H_4 \rightarrow {}^3P_1$, ${}^3H_4 \rightarrow {}^3P_0$ and ${}^3H_4 \rightarrow {}^1D_2$ transitions also have been found minor changes in the immediate coordination environment around Pr(III)^{14,15}, though these transitions cannot be regarded as hypersensitive as these do not obey selection rules.

In case of neodymium complexes some additional pseudohypersensitive bands were discerned. Peacock observed hypersensitivity with ${}^4I_{9/2} \rightarrow {}^4G_{5/2}$, while Choppin observed hypersensitivity with ${}^4G_{7/2} \rightarrow {}^4K_{13/2}$, transition in addition to ${}^4G_{5/2}$. Two more transitions ${}^4I_{9/2} \rightarrow {}^4F_{7/2}$ and ${}^4I_{9/2} \rightarrow {}^4F_{5/2}$ further discovered to deviate from usual trend and display unusual high intensification and wide variation of oscillator strength in our studies of Nd(III) complexes with ligands having widely differing binding characteristics¹⁶⁻¹⁸.

We have coined the term LIGAND MEDIATED PSEUDOHYPERSENSITIVE for such observation and considered these transitions as pseudohypersensitive¹⁶⁻¹⁸. Approximate values of T_2 , T_4 and T_6 can be obtained by statistical methods by using the co-efficients C_{11} to C_{33} , which are known values. These co-efficients are modified as

$$\begin{aligned} C_{11} &= 3.896 & C_{12} &= -6.56 & C_{13} &= 1.55 \\ C_{22} &= 18.21 & C_{23} &= -2.44 & C_{33} &= 5.30 \end{aligned}$$

Using the values of C_{11} to C_{33} etc. the values of T_2 , T_4 and T_6 in the form of b_1 , b_2 and b_3 have been computed using equation (22). The method has yielded the usual r.m.s. deviation, when oscillator strength of all bands computed from T_λ parameters by using the Judd-Ofelt relation (equation 22) were compared with the observed ones. The matrix elements for Nd(III) are shown in Table 2.03.

Table 2.01 Hypersensitive transitions for Pr(III) and Nd(III) ion :

Lanthanide	Transitions	Approximate wave number $\times 10^3 \text{ cm}^{-1}$
Pr(III)	$^3H_4 \rightarrow ^3F_2$	23.10
Nd(III)	$^4I_{9/2} \rightarrow ^4G_{5/2}$	17.10

Table 2.01 The zero order energies and partial derivatives with respect to F_4 and ξ_{4f} parameters for Nd(III) :

Energy Level	$E_{0j}^{(a)}$	$\delta E_j / \delta F_2$	$\delta E_j / \delta F_4$	$\delta E_j / \delta F_6$	$\delta E_j / \delta \xi_{4f}$
$^4F_{3/2}$	11523.34	35.27	39.50	-588.9	1.02
$^4F_{5/2}$	12606.77	34.93	39.36	-631.4	2.58
$^4F_{7/2}$	13453.73	35.02	41.04	-602.5	3.24
$^4G_{5/2}$	17357.56	54.98	63.01	-991.2	1.29
$^4G_{7/2}$	19288.93	41.95	101.66	-620.8	4.13
(a)	$F_2^0 = 331.567 \text{ cm}^{-1}$		$F_4^0 = 49.057 \text{ cm}^{-1}$		
	$F_6^0 = 5.170 \text{ cm}^{-1}$		$\xi_{4f}^0 = 906.00 \text{ cm}^{-1}$		

Table 2.03 Matrix elements for Nd(III) :

Energy Level	$[U^{(2)}]^2$	$[U^{(4)}]^2$	$[U^{(6)}]^2$
${}^4F_{3/2}$	0	0.2299	0.0547
${}^4F_{5/2}$	0.0009	0.2361	0.3973
${}^4H_{9/2}$	0.0092	0.0076	0.1196
${}^4F_{7/2}$	0.0010	0.0420	0.4249
${}^4S_{3/2}$	0	0.027	0.2354
${}^4G_{5/2}$	0.8968	0.4091	0.0355
${}^2G_{7/2}$	0.0755	0.1848	0.0316
${}^4G_{7/2}$	0.0551	0.1569	0.0547
${}^4G_{9/2}$	0.0046	0.0611	0.0407
${}^4K_{13/2}$	0.0068	0.0002	0.0313

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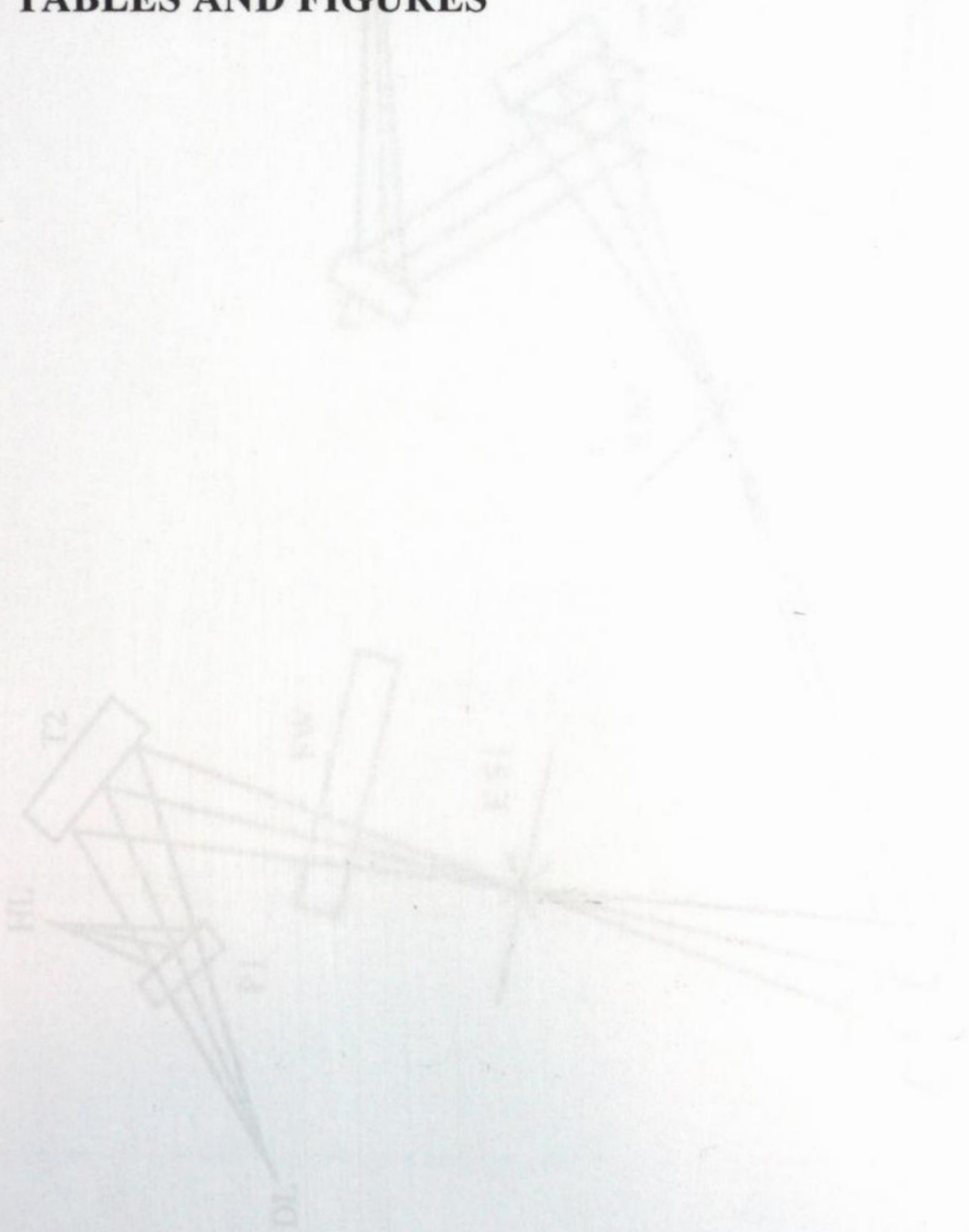
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CHAPTER NO. IV

TABLES AND FIGURES

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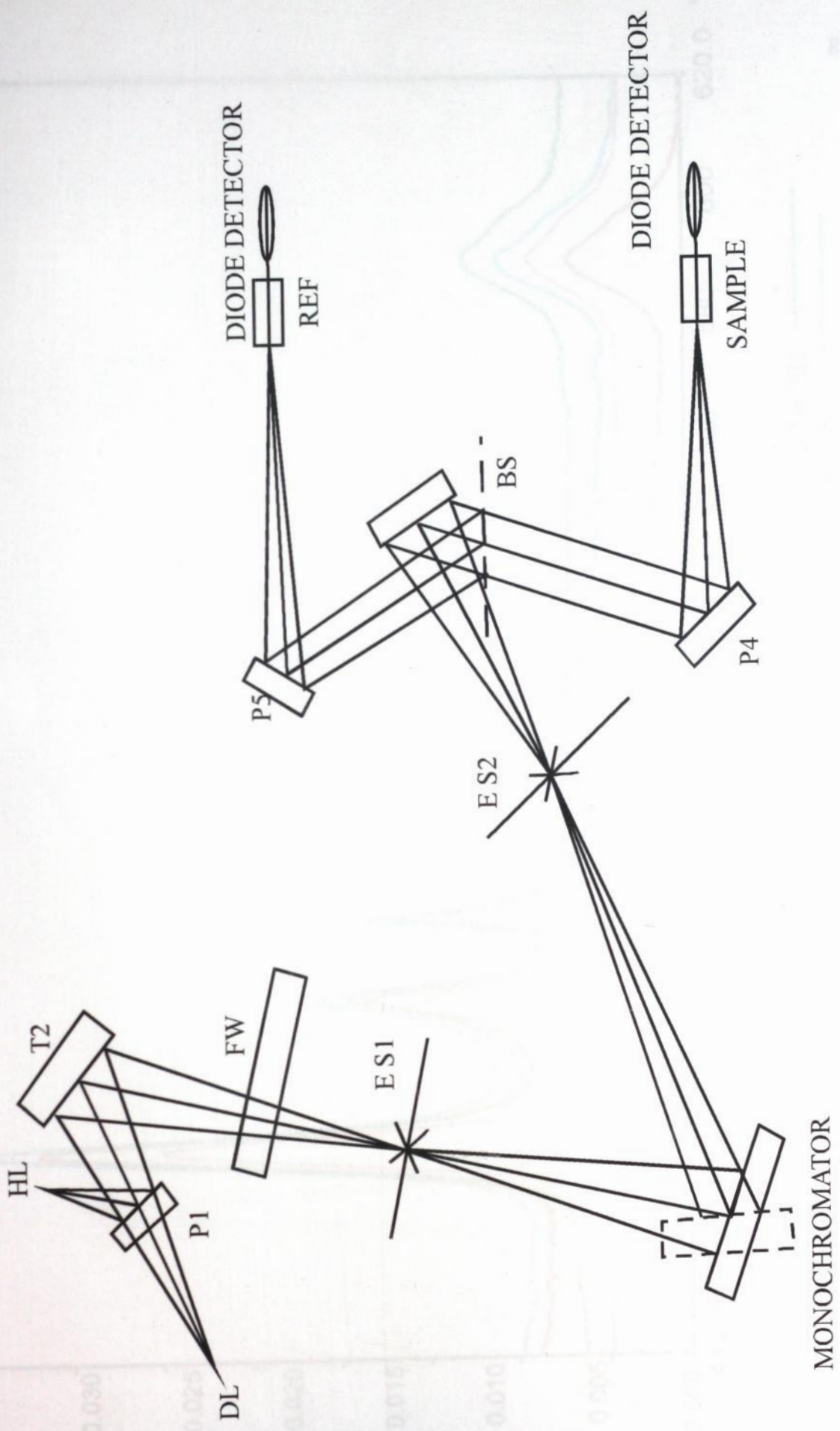


Figure : Double Beam Spectrophotometer

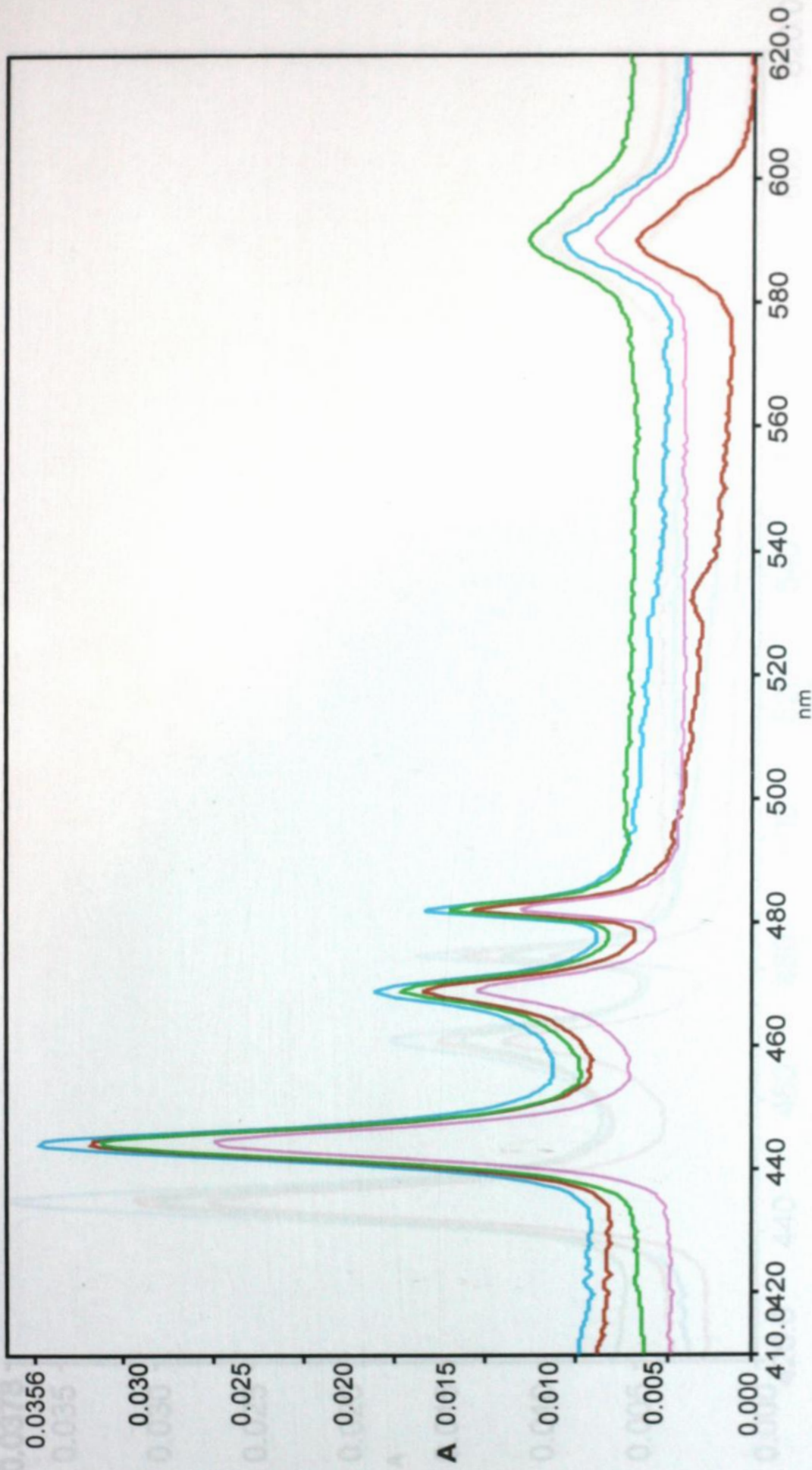


Figure 4.01

Comparative absorption spectra of Pr(III) Pr(III):GSH $\text{Pr(III):GSH:Ca(II)}$ $\text{Pr(III):GSH:Zn(II)}$ and $\text{Pr(III):GSH:Zn(II)}$ in acetonitrile (CH_3CN)

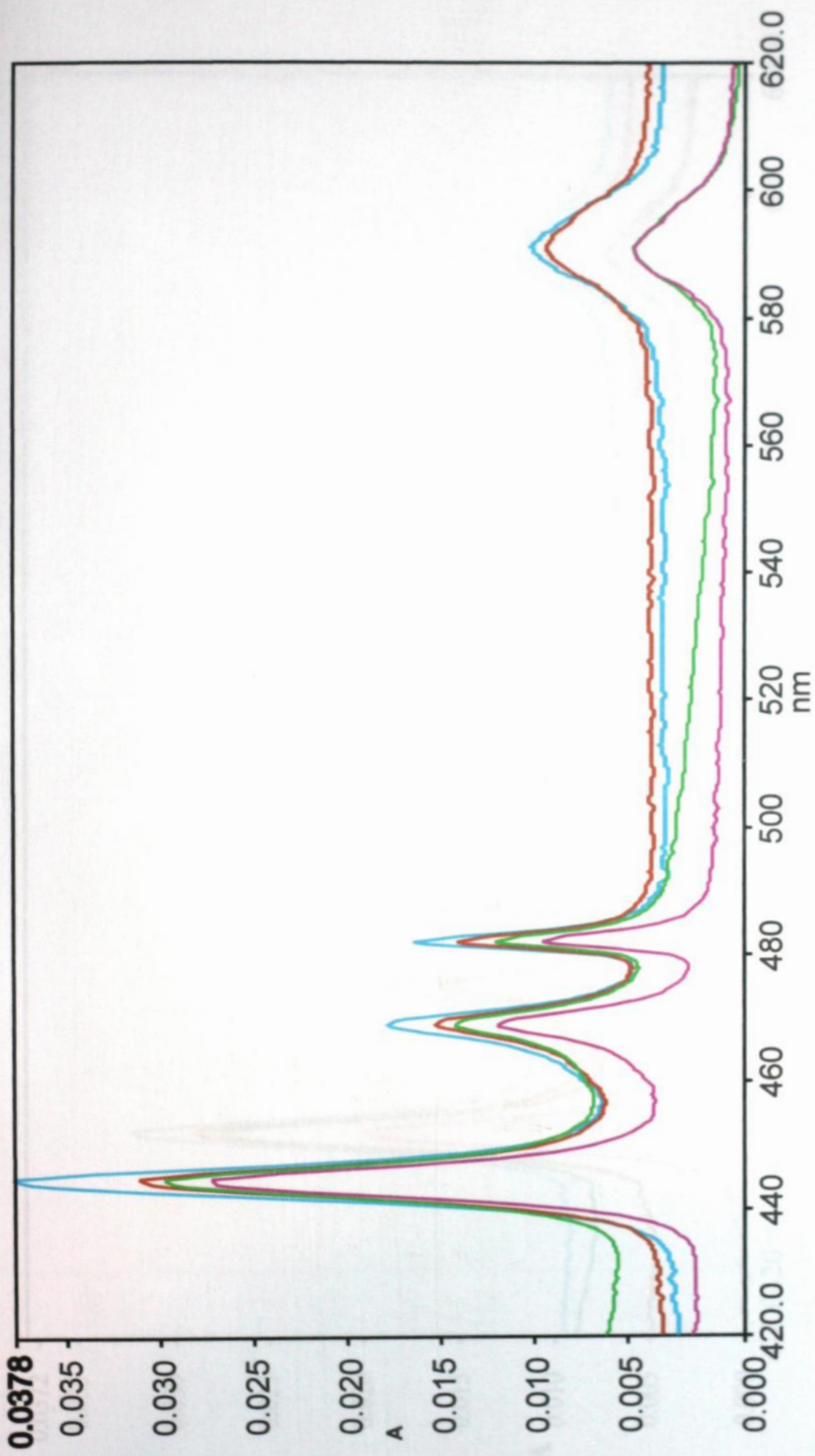


Figure 4.02

Comparative absorption spectra of Pr(III)
 Pr(III):GSH:Ca(II) — Pr(III):GSH:Zn(II) and Pr(III):GSH
 in DMF

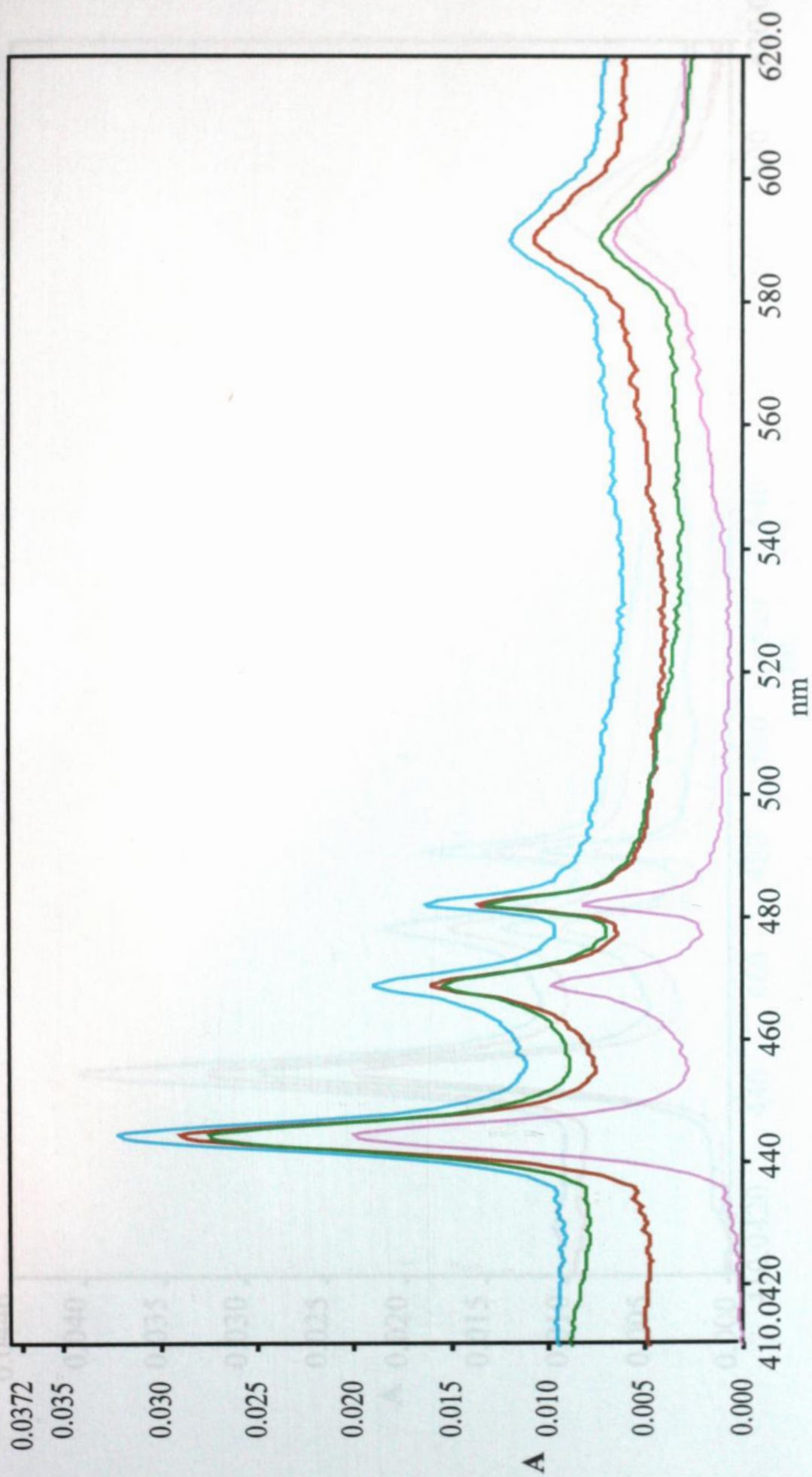


Figure 4.03

Comparative absorption spectra of Pr(III) — Pr(III):GSH —
 Pr(III):GSH:Ca(II) — and Pr(III):GSH:Zn(II) —
 in dioxane

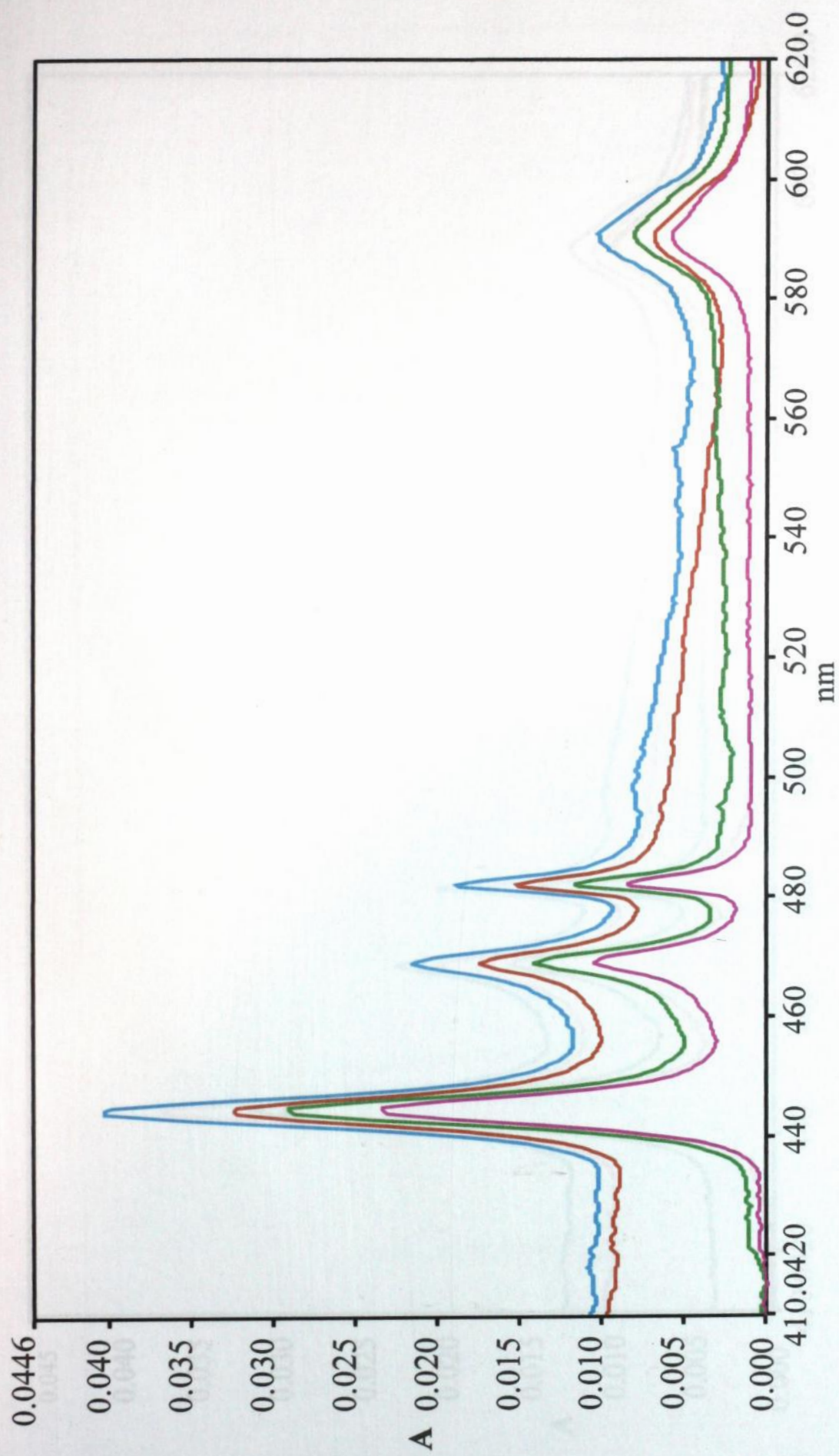


Figure 4.04
 Comparative absorption spectra of Pr(III)
 Pr(III):GSH:Ca(II) — Pr(III):GSH:Zn(II) —
 and Pr(III):GSH — —
 in methanol (CH₃OH)

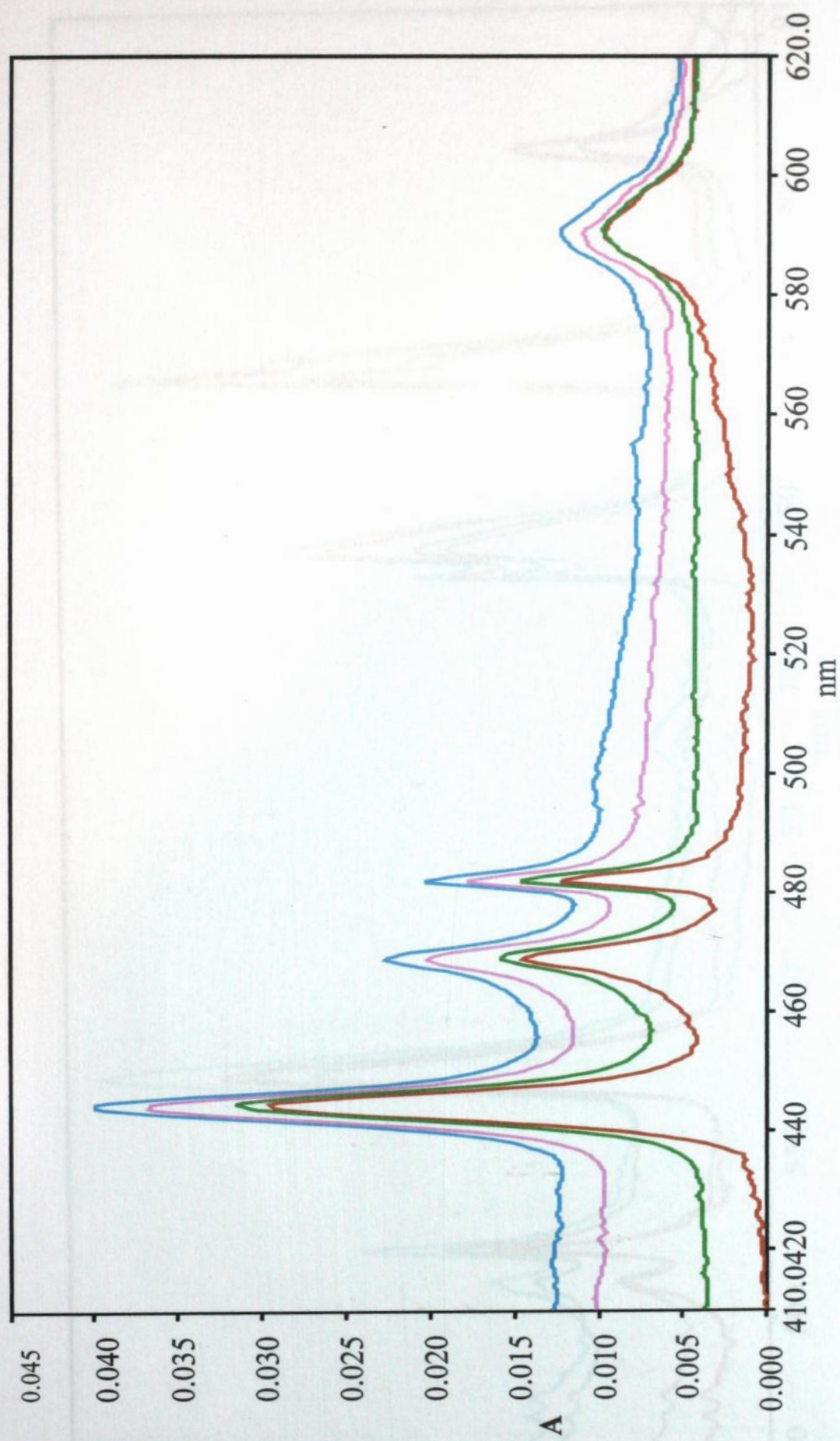


Figure 4.05
 Comparative absorption spectra of Pr(III):GSH:Zn(II) in different solvents-
 DMF —, acetonitrile —, dioxane —, and methanol —

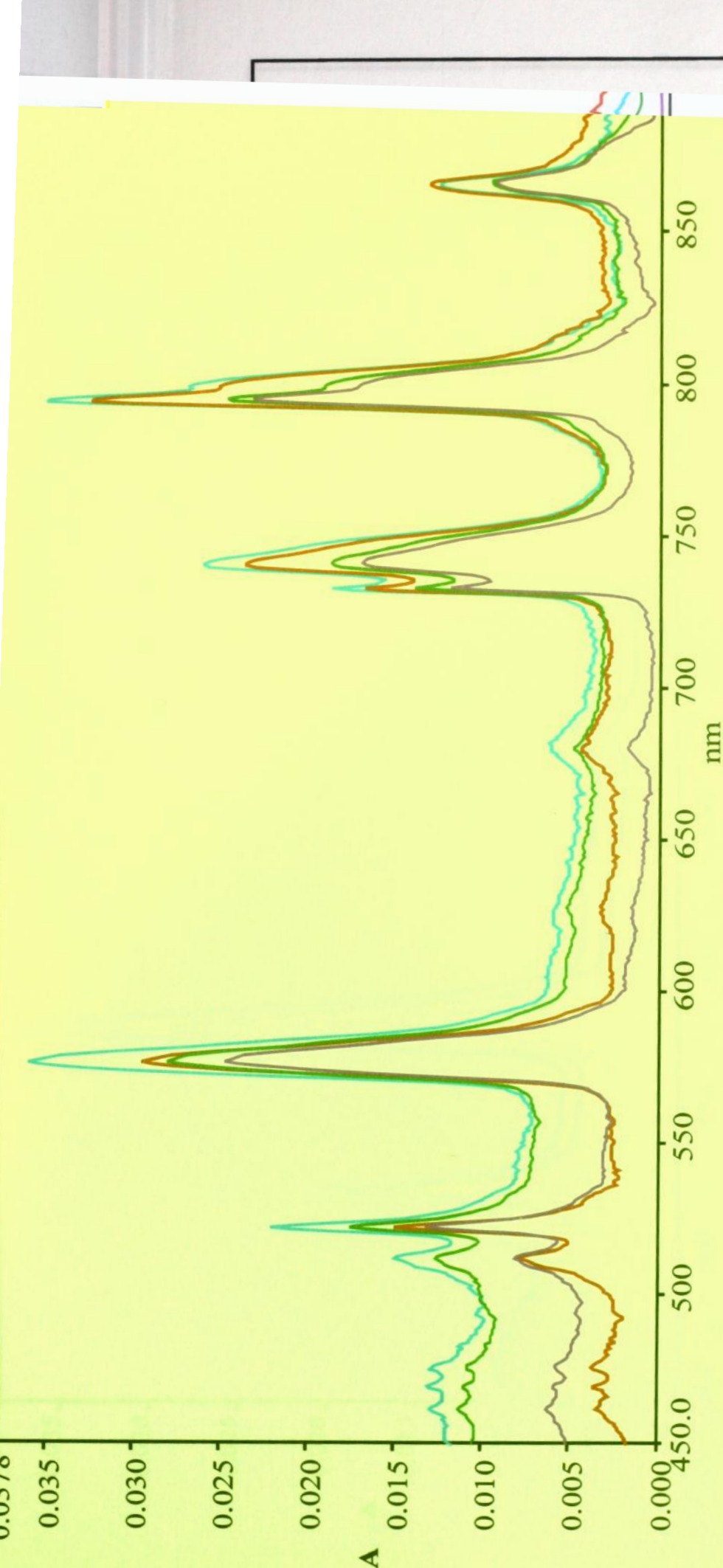


Figure 4.06

Comparative absorption spectra of Nd(III) ———, Nd(III):GSH ———
 Nd(III):GSH:Ca(II) ——— and Nd(III):GSH:Zn(II) ———
 in acetonitrile (CH₃CN)

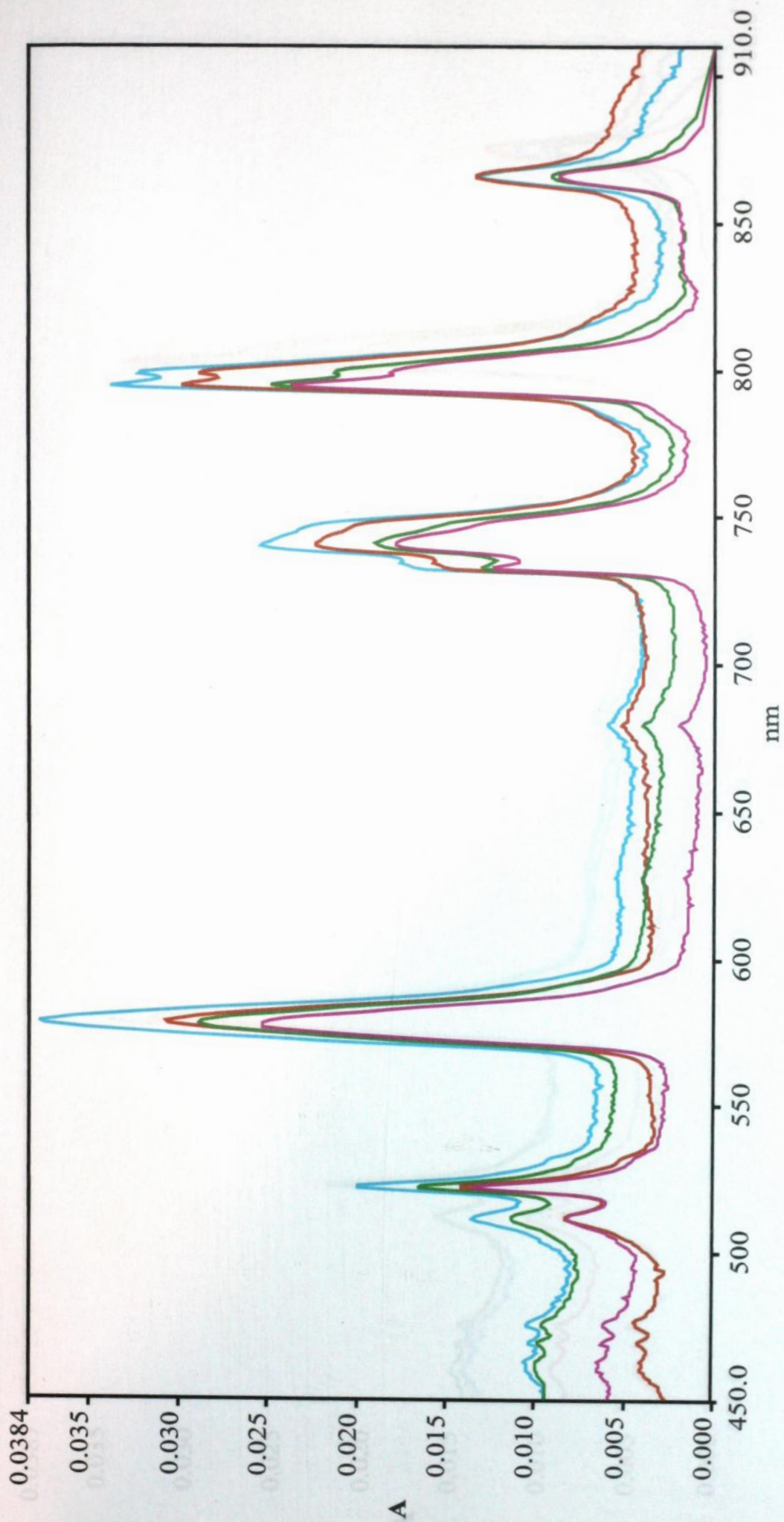


Figure 4.07

Comparative absorption spectra of Nd(III) —, Nd(III):GSH —
 and Nd(III):GSH:Ca(II) — and Nd(III):GSH:Zn(II) —
 in DMF

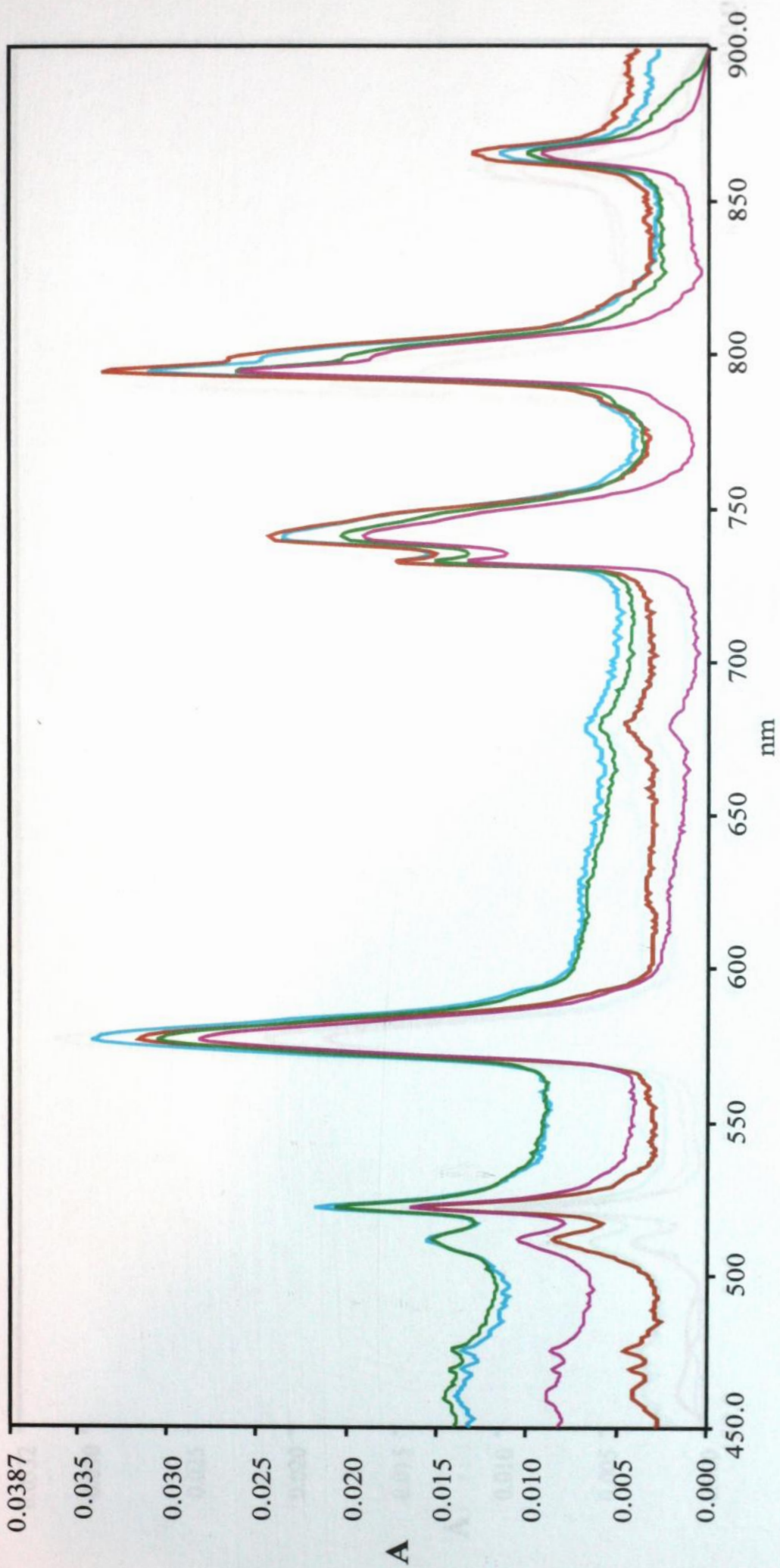


Figure 4.08

Comparative absorption spectra of Nd(III) —, Nd(III):GSH —
 Nd(III):GSH:Ca(II) — and Nd(III):GSH:Zn(II) —
 in dioxane

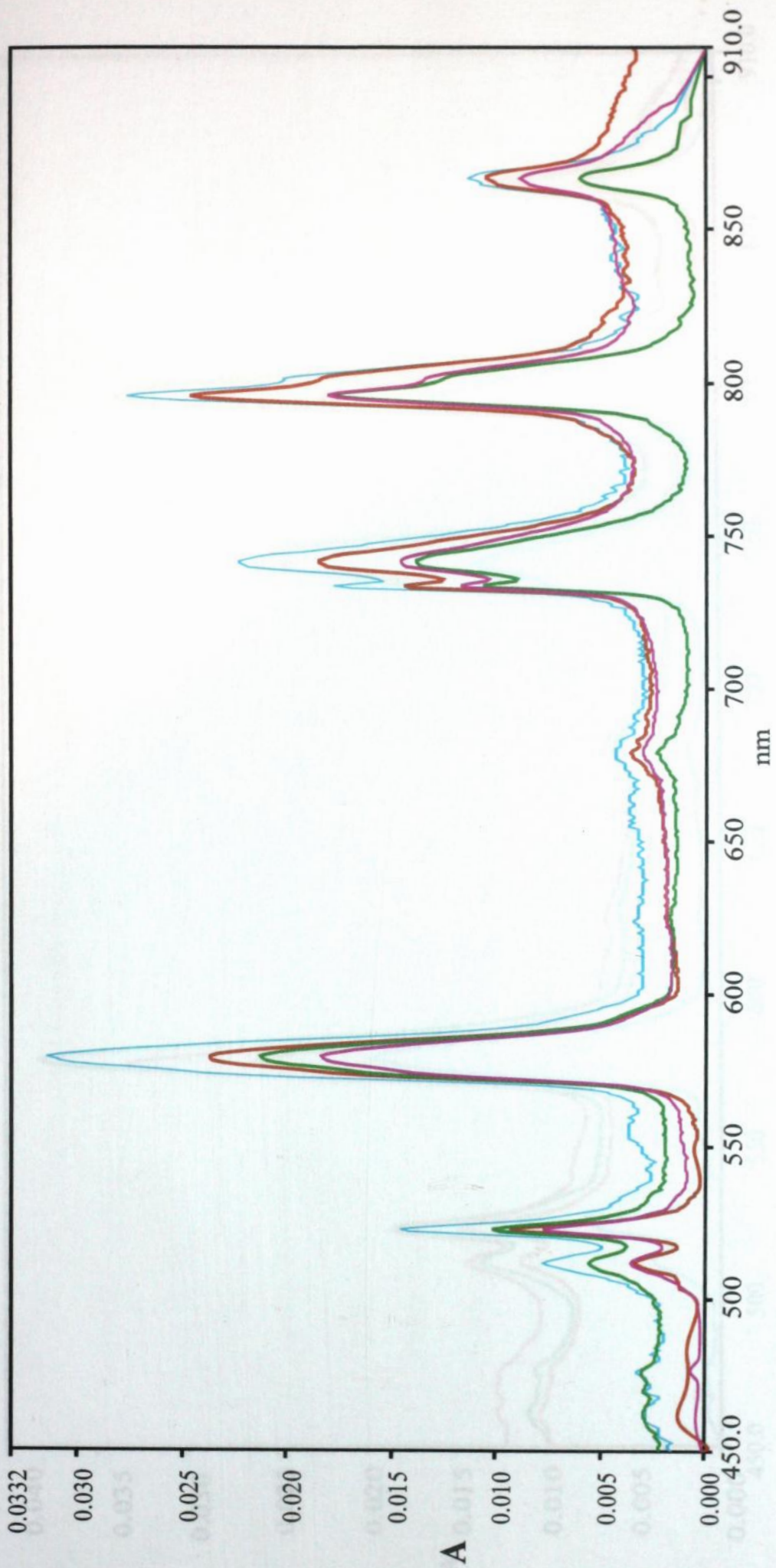


Figure 4.09
 Comparative absorption spectra of Nd(III) —, Nd(III):GSH —, Nd(III):GSH:Ca(II) — and Nd(III):GSH:Zn(II) — in methanol (CH₃OH)

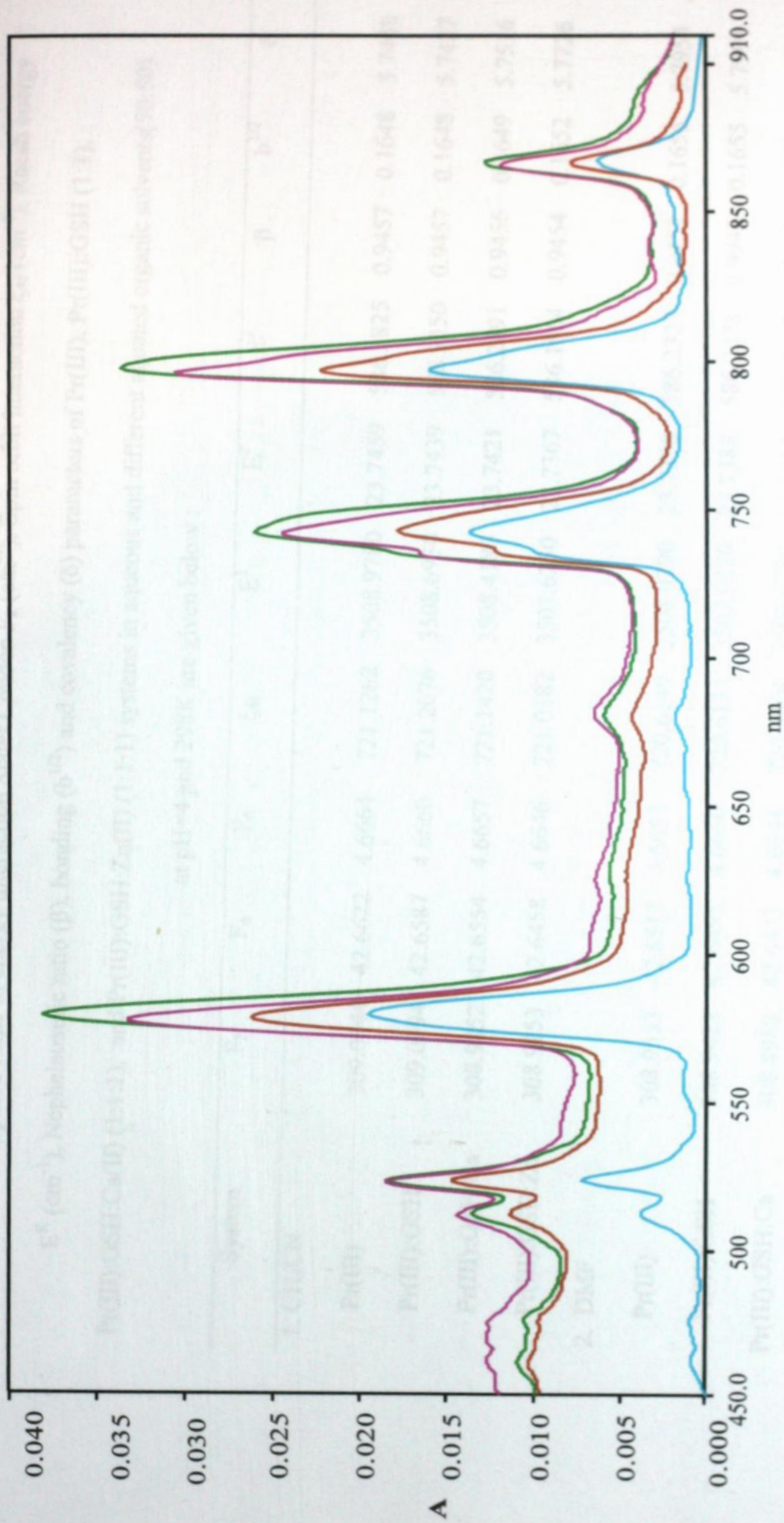


Figure 4.10
Comparative absorption spectra of Pr(III):GSH:Zn(II) in different solvents
DMF —, acetone —, dioxane —, methanol —

Table 4.01 : Computed value of energy interaction Slater Condon F_k (cm^{-1}), Spin orbit interaction ξ_{4f} (cm^{-1}), Racah energy

E^k (cm^{-1}), Nephelauxetic ratio (β), bonding ($b^{1/2}$) and covalency (δ) parameters of Pr(III), Pr(III):GSH (1:1),

Pr(III):GSH:Ca(II) (1:1:1), and Pr(III):GSH:Zn(II) (1:1:1) systems in aqueous and different aqated organic solvents(50:50)

at pH=4 and 298K are given below :

System	F_2	F_4	F_6	ξ_{4f}	E^1	E^2	E^3	β	$b^{1/2}$	δ
1. CH_3CN										
Pr(III)	308.9789	42.6543	4.6664	721.1262	3508.9780	23.7459	586.3825	0.9457	0.1648	5.7448
Pr(III):GSH	309.0094	42.6587	4.6660	721.2076	3508.6930	23.7439	586.3350	0.9457	0.1648	5.7427
Pr(III):GSH:Ca	308.9852	42.6554	4.6657	721.1420	3508.4180	23.7421	586.2891	0.9456	0.1649	5.7516
Pr(III):GSH:Zn	308.9153	42.6458	4.6646	721.0182	3507.6250	23.7367	586.1564	0.9454	0.1652	5.7726
2. DMF										
Pr(III)	308.9553	42.6513	4.6652	720.6349	3508.0790	23.7398	586.2323	0.9452	0.1655	5.7954
Pr(III):GSH	308.9423	42.6495	4.6650	720.6133	3507.9320	23.7388	586.2078	0.9945	0.1655	5.7991
Pr(III):GSH:Ca	308.8988	42.6435	4.6644	720.3864	3507.4380	23.7354	586.1252	0.9450	0.1659	5.8237

System(Contd.)	F ₂	F ₄	F ₆	ξ _{4f}	E ¹	E ²	E ³	β	b ^{1/2}	δ
Pr(III):GSH:Zn	308.8655	42.6389	4.6639	720.3102	3507.0600	23.7329	586.0620	0.9449	0.1660	5.8350
3. Dioxane										
Pr(III)	308.9964	42.6570	4.6658	721.3854	3508.5460	23.7429	586.3104	0.9458	0.1646	5.7312
Pr(III):GSH	308.9883	42.6558	4.6657	721.3931	3508.4550	23.7423	586.2951	0.9458	0.1646	5.7319
Pr(III):GSH:Ca	308.9789	42.6545	4.6656	721.4216	3508.3470	23.7416	586.2771	0.9458	0.1646	5.7313
Pr(III):GSH:Zn	309.0288	42.6614	4.6663	722.4818	3508.9140	23.7454	586.3719	0.9466	0.1634	5.6421
4. Methanol										
Pr(III)	308.9919	42.6563	4.6658	720.7278	3508.4940	23.7426	586.3018	0.9453	0.1653	5.7823
Pr(III):GSH	308.9919	42.6563	4.6658	720.7278	3508.4940	23.7416	586.2761	0.9452	0.1655	5.7924
Pr(III):GSH:Ca	308.9617	42.6522	4.6653	720.5670	3508.1520	23.7403	586.2444	0.9452	0.1656	5.7995
Pr(III):GSH:Zn	308.9087	42.6448	4.6645	720.6706	3507.5500	23.7362	586.1439	0.9452	0.1656	5.8003
5. MeCN + DMF										
Pr(III)	308.7965	42.6294	4.6628	722.4115	3506.2760	23.7276	585.9311	0.9462	0.1640	5.6854

System(Contd.)	F ₂	F ₄	F ₆	ξ _{4f}	E ¹	E ²	E ³	β	b ^{1/2}	δ
Pr(III):GSH	308.7397	42.6215	4.6620	722.3372	3505.6310	23.7232	585.8232	0.9461	0.1642	5.7004
Pr(III):GSH:Ca	308.7004	42.6161	4.6614	722.1996	3505.1850	23.7202	585.7487	0.9459	0.1644	5.7173
Pr(III):GSH:Zn	308.6782	42.6130	4.6610	722.0649	3504.9330	23.7185	585.7067	0.9458	0.1646	5.7312
6. CH ₃ CN:Dioxane	309.0903	42.6575	4.6659	721.5108	3508.3905	23.7412	586.3177	0.9468	0.1647	5.7349
Pr(III)	309.0568	42.6653	4.6668	721.8173	3509.2310	23.7476	586.4249	0.9462	0.1640	5.6883
Pr(III):GSH	309.0262	42.6611	4.6663	721.5729	3508.8840	23.7452	586.3669	0.9460	0.1644	5.7120
Pr(III):GSH:Ca	309.0068	42.6584	4.6660	721.5538	3508.6640	23.7437	586.3301	0.9459	0.1644	5.7166
Pr(III):GSH:Zn	308.9525	42.6509	4.6652	721.4927	3508.0470	23.7396	586.2271	0.9460	0.1643	5.7075
7. DMF : Dioxane	309.0004	42.6587	4.6660	721.5184	3508.9940	23.7479	586.3550	0.9457	0.1648	5.7418
Pr(III)	309.0103	42.6589	4.6661	721.1907	3508.7030	23.7440	586.3367	0.9457	0.1648	5.7438
Pr(III):GSH	308.9918	42.6563	4.6658	721.1761	3508.4930	23.7426	586.3016	0.9456	0.1649	5.7480
Pr(III):GSH:Ca	308.9762	42.6542	4.6655	721.1297	3508.3160	23.7414	586.2720	0.9456	0.1649	5.7541
Pr(III):GSH:Zn	308.9238	42.6469	4.6648	721.0628	3507.7220	23.7374	586.1727	0.9455	0.1651	5.7677

System(Contd.)	F ₂	F ₄	F ₆	ξ _{4f}	E ¹	E ²	E ³	β	b ^{1/2}	δ
8. CH ₃ OH:Dioxane										
Pr(III)	309.0438	42.6635	4.6666	721.4194	3509.0840	23.7466	586.4003	0.9459	0.1645	5.7208
Pr(III):GSH	309.0268	42.6612	4.6663	721.3656	3508.8920	23.7453	586.3681	0.9458	0.1646	5.7277
Pr(III):GSH:Ca	309.0003	42.6575	4.6659	721.3368	3508.5900	23.7432	586.3177	0.9458	0.1647	5.7343
Pr(III):GSH:Zn	308.9850	42.6554	4.6657	721.6026	3508.4160	23.7421	586.2886	0.9459	0.1644	5.7164
9. Methanol:DMF										
Pr(III)	309.0511	42.6645	4.6667	721.2996	3509.1670	23.7471	586.4142	0.9458	0.1646	5.7288
Pr(III):GSH	309.0380	42.6627	4.6665	721.2788	3509.0180	23.7461	586.3893	0.9458	0.1646	5.7325
Pr(III):GSH:Ca	309.0094	42.6587	4.6660	721.2184	3508.6940	23.7439	586.3350	0.9457	0.1648	5.7418
Pr(III):GSH:Zn	308.9849	42.6554	4.6657	721.1275	3508.4160	23.7421	586.2886	0.9456	0.1649	5.7528
10. Methanol:CH ₃ CN										
Pr(III)	309.10	42.6721	4.6667	721.6064	3509.7930	23.7514	586.5188	0.9461	0.1642	5.6963
Pr(III):GSH	309.0883	42.6696	4.6672	721.6066	3509.5890	23.7500	586.4847	0.9461	0.1642	5.6992

Table 4.02 : Computed and Observed values of Energies(cm^{-1}) and R.M.S. values for

Pr(III):GSH (1:1), Pr(III):GSH:Ca(II) (1:1:1) and Pr(III):GSH:Zn(II) (1:1:1) in aqueous and different

aquated organic solvents(50:50) at pH = 4 and 298K are given below :

System	$^3\text{H}_4 \rightarrow ^3\text{P}_2$	$^3\text{H}_4 \rightarrow ^3\text{P}_1$	$^3\text{H}_4 \rightarrow ^3\text{P}_0$	$^3\text{H}_4 \rightarrow ^1\text{D}_2$	R.M.S.				
	Eobs	Ecal	Eobs	Eobs	Ecal				
1. CH_3CN									
Pr(III)	22492.13	22445.42	21316.51	21235.44	20742.58	20677.24	16944.27	17130.22	109.09
Pr(III):GSH	22491.62	21234.01	21315.14	21234.01	20740.43	20675.64	16943.70	17129.31	108.96
Pr(III):GSH:Ca	22489.60	22442.18	21311.51	21232.05	20739.14	20673.81	16942.84	17128.00	108.53
Pr(III):GSH:Zn	22485.05	224636.83	21307.88	21226.66	20734.84	20668.67	16936.23	17124.43	110.36
2. DMF									
Pr(III)	22491.12	22437.61	21316.51	21227.94	20739.57	20670.75	16924.48	17125.16	118.02
Pr(III):GSH	22486.56	22436.62	21313.33	21226.95	20738.71	20669.80	16927.35	17124.50	115.73

System	$^3H_4 \rightarrow ^3P_2$		$^3H_4 \rightarrow ^3P_1$		$^3H_4 \rightarrow ^3P_0$		$^3H_4 \rightarrow ^1D_2$		R.M.S.
	Eobs	Ecal	Eobs	Ecal	Eobs	Ecal	Eobs	Ecal	
Pr(III):GSH:Ca	22484.54	22432.54	21307.88	21223.00	20736.99	20666.31	16921.90	17121.84	117.13
Pr(III):GSH:Zn	22483.53	22429.91	21301.52	21220.36	20735.27	20663.83	16920.76	17120.08	116.51
3. DXN									
Pr(III)	22487.68	22444.16	21319.42	21233.81	20738.24	20675.06	16945.10	17129.23	108.53
Pr(III):GSH	22487.47	22443.65	21319.10	21233.27	20737.64	20674.51	16944.50	17128.88	108.71
Pr(III):GSH:Ca	22487.32	22443.16	21319.01	21232.72	20736.82	20673.90	16943.93	17128.53	108.89
Pr(III):GSH:Zn	22487.17	22451.86	21318.69	21240.44	20734.76	20679.43	16971.88	17133.90	95.77
4. CH ₃ OH									
Pr(III)	22491.12	22440.54	21314.69	21230.87	20741.72	20673.49	16932.51	17127.11	114.14
Pr(III):GSH	22489.60	22439.11	21313.78	21229.52	20741.29	20672.35	16930.21	17126.19	114.90
Pr(III):GSH:Ca	22487.58	22437.70	21311.51	21228.12	20740.43	20671.07	16929.64	17125.25	114.58
Pr(III):GSH:Zn	22484.54	22434.64	21309.24	21224.82	20736.13	20667.55	16927.92	17123.12	114.48

System	$^3H_4 \rightarrow$	3P_2	$^3H_4 \rightarrow$	3P_1	$^3H_4 \rightarrow$	3P_0	$^3H_4 \rightarrow$	1D_2	R.M.S.
	Eobs	Ecal	Eobs	Ecal	Eobs	Ecal	Eobs	Ecal	
5. CH ₃ CN:DMF									
Pr(III)	22486.56	22435.81	21304.70	21223.88	20719.38	20662.99	16948.58	17123.02	103.34
Pr(III):GSH	22482.52	22431.60	21296.53	21219.60	20715.94	20658.86	16947.43	17120.19	102.00
Pr(III):GSH:Ca	22478.98	22428.26	21295.63	21216.30	20713.80	20655.85	16942.26	17117.99	103.81
Pr(III):GSH:Zn	22476.96	22426.08	21293.81	21214.21	20712.94	20654.03	16939.11	17116.58	104.75
6. CH ₃ CN:DXN									
Pr(III)	22491.12	22450.41	21317.42	21239.75	20740.43	20680.12	16960.94	17133.26	101.27
Pr(III):GSH	22490.61	22447.12	21216.96	21236.64	20739.57	20677.51	16952.60	17131.14	104.97
Pr(III):GSH:Ca	22489.09	22445.71	21316.05	21235.20	20738.28	20676.11	16951.16	17130.19	105.28
Pr(III):GSH:Zn	22484.54	22441.73	21310.15	21231.15	20734.84	20672.19	16949.44	17127.52	104.54
7. DMF : Dioxane									
Pr(III)	22488.59	22444.12	21315.60	21234.00	20740.43	20675.66	16945.13	17129.30	108.11

System	$^3H_4 \rightarrow ^3P_2$		$^3H_4 \rightarrow ^3P_1$		$^3H_4 \rightarrow ^3P_0$		$^3H_4 \rightarrow ^1D_2$		R.M.S.
	Eobs	Ecal	Eobs	Ecal	Eobs	Ecal	Eobs	Ecal	
Pr(III):GSH	22486.06	22442.79	21314.69	21232.65	20739.14	20674.34	16944.56	17128.41	107.94
Pr(III):GSH:Ca	22484.54	22441.51	21313.33	21231.37	20738.28	20673.16	16943.41	17127.55	108.07
Pr(III):GSH:Zn	22479.99	22437.63	21311.51	21227.44	20734.84	20669.36	16939.11	17124.96	109.19
8. CH ₃ OH : CH ₃ CN									
Pr(III)	22491.62	22452.69	21324.69	21242.38	20744.74	20683.19	16958.35	17134.92	103.99
Pr(III):GSH	22490.10	22451.48	21323.78	21241.12	20743.45	20681.93	16957.49	17134.09	104.04
Pr(III):GSH:Ca	22488.08	22450.19	21322.87	21239.85	20742.58	20680.76	16956.34	17133.25	104.22
Pr(III):GSH:Zn	22486.56	22448.28	21321.05	21237.95	20741.29	20678.99	16954.04	17131.97	104.78
9. CH ₃ OH : DMF									
Pr(III)	22491.62	22452.69	21324.69	21242.38	20744.74	20683.19	16958.35	17134.92	103.99
Pr(III):GSH	22490.10	22451.48	21323.78	21241.12	20743.45	20681.93	16957.49	17134.09	104.04
Pr(III):GSH:Ca	22488.08	22450.19	21322.87	21239.85	20740.00	20675.66	16945.99	17129.34	107.81

System	$^3\text{H}_4 \rightarrow ^3\text{P}_2$	$^3\text{H}_4 \rightarrow ^3\text{P}_1$	$^3\text{H}_4 \rightarrow ^3\text{P}_0$	$^3\text{H}_4 \rightarrow ^1\text{D}_2$	R.M.S.
	Eobs Ecal	Eobs Ecal	Eobs Ecal	Eobs Ecal	
Pr(III):GSH:Zn	22483.03 22442.09	21316.51 21231.98	20738.71 20673.77	16943.41 17127.95	108.51
10. CH ₃ OH : Dioxane					
Pr(III)	22496.18 22447.54	21320.14 21237.26	20741.72 20678.46	16946.28 17131.51	109.02
Pr(III):GSH	22494.66 22446.12	21317.42 21235.86	20740.86 20677.16	16945.71 17130.57	108.67
Pr(III):GSH:Ca	22493.14 22444.18	21316.05 21233.88	20739.14 20675.24	16943.41 17129.26	109.29
Pr(III):GSH:Zn	22506.30 22444.48	21311.51 21233.87	20737.42 20674.67	16941.11 17129.33	110.92

Table 4.03 : Observed and Computed Values of Oscillator Strengths ($P \times 10^6$) and Judd-Ofelt ($T_\lambda \times 10^{10}$) parameters Pr(III), Pr(III):GSH, Pr(III) : GSH : Ca(II) and Pr(III) : GSH : Zn(II) for pH=4

System	$^3H_4 \rightarrow ^1D_2$		$^3H_4 \rightarrow ^3P_0$		$^3H_4 \rightarrow ^3P_1$		$^3H_4 \rightarrow ^3P_2$		T_2	T_4	T_6
	Pobs	Pcal	Pobs	Pcal	Pobs	Pcal	Pobs	Pcal			
1. DMF											
Pr(III)	0.6968	0.6968	0.2778	0.3898	0.5093	0.3957	2.2675	2.2675	8.09	1.09	7.15
Pr(III) : GSH	1.0130	1.0130	0.3881	0.6226	0.8700	0.6320	2.7043	2.7043	50.60	1.74	8.42
Pr(III) : GSH:Ca	0.5622	0.5622	0.4095	0.5520	0.7044	0.5599	2.7662	2.7662	-55.71	1.54	8.67
Pr(III) : GSH : Zn	0.7372	0.7372	0.3893	0.5701	0.7620	0.5785	2.8002	2.8002	-18.13	1.59	8.77
2. Dioxane											
Pr(III)	0.6003	0.6003	0.3514	0.5151	0.6893	0.5231	2.5495	2.5495	-32.78	1.44	7.99
Pr(III) : GSH	0.6264	0.6264	0.3533	0.5099	0.6768	0.5178	2.6502	2.6500	-33.53	1.42	8.32
Pr(III) : GSH:Ca	0.4186	0.4186	0.3290	0.4699	0.6200	0.4770	1.9885	1.9885	-37.07	1.31	6.18
Pr(III) : GSH : Zn	0.6318	0.6318	0.3465	0.5249	0.7140	0.5329	2.4215	2.4215	-17.20	1.47	7.56
3. CH ₃ CN											
Pr(III)	0.5118	0.5118	0.3501	0.4840	0.6274	0.4915	2.7629	2.7629	-66.88	1.35	8.71

System (Contd.)	$^3\text{H}_4 \rightarrow ^1\text{D}_2$		$^3\text{H}_4 \rightarrow ^3\text{P}_0$		$^3\text{H}_4 \rightarrow ^3\text{P}_1$		$^3\text{H}_4 \rightarrow ^3\text{P}_2$		T_2	T_4	T_6
	Pobs	Pcal	Pobs	Pcal	Pobs	Pcal	Pobs	Pcal	Pobs	Pobs	Pcal
Pr(III) : GSH:Ca	0.5341	0.5341	0.4493	0.5041	0.5674	0.5118	2.0788	2.0788	-16.79	1.41	6.45
Pr(III) : GSH : Zn	0.3078	0.3078	0.3098	0.4553	0.6099	0.4622	2.8709	2.8709	-120.1	1.27	9.08
4. CH_3OH											
Pr(III)	0.9217	0.9217	0.3673	0.5251	0.6935	0.5332	2.5603	2.5603	39.61	1.47	8.01
Pr(III) : GSH	0.9052	0.9052	0.2988	0.5519	0.8169	0.5601	2.7518	2.7518	23.15	1.54	8.61
Pr(III) : GSH: Ca	0.5997	0.5997	0.3038	0.4431	0.5912	0.4498	2.3122	2.3122	-17.14	1.24	7.26
Pr(III) : GSH : Zn	0.4935	0.4935	0.6959	0.5048	0.3185	0.5125	2.0166	2.0166	-21.87	1.41	6.24
5. Dioxane: CH_3CN											
Pr(III)	0.6980	0.6980	0.3583	0.5167	0.6853	0.5245	2.7571	2.7571	-166.83	1.44	8.66
Pr(III) : GSH	0.7796	0.7796	0.4195	0.5771	0.7457	0.5858	2.7585	2.7585	-5.64	1.61	8.62
Pr(III) : GSH: Ca	0.9507	0.9507	0.5343	0.7195	0.9183	0.7303	3.5719	3.5719	-20.82	2.01	11.19
Pr(III) : GSH : Zn	0.9609	0.9609	0.5296	0.7036	0.8908	0.7142	3.6624	3.6624	-24.59	1.96	11.49
6. DMF:Dioxane											
Pr(III)	0.7243	0.7243	0.3684	0.5300	0.7022	0.5381	2.6496	2.6496	-11.21	1.48	8.30

System (Contd.)	$^3\text{H}_4 \rightarrow ^1\text{D}_2$		$^3\text{H}_4 \rightarrow ^3\text{P}_0$		$^3\text{H}_4 \rightarrow ^3\text{P}_1$		$^3\text{H}_4 \rightarrow ^3\text{P}_2$		T_2	T_4	T_6
	Pobs	Pcal	Pobs	Pcal	Pobs	Pcal	Pobs	Pcal			
Pr(III) : GSH:Ca	0.5075	0.5075	0.3487	0.4225	0.5037	0.4288	2.6126	2.6126	-57.64	1.18	8.26
Pr(III) : GSH : Zn	0.8208	0.8208	0.4503	0.6197	0.8007	0.6288	2.5204	2.5204	19.08	1.73	7.81
7. CH ₃ OH:DMF	0.4500	0.4500	0.3111	0.3716	0.4500	0.3716	2.6126	2.6126	-57.64	1.18	8.26
Pr(III) : GSH:Ca	0.7997	0.7997	0.3765	0.5809	0.7973	0.5898	2.6198	2.6198	7.79	1.62	8.17
Pr(III) : GSH	0.7505	0.7505	0.3800	0.5649	0.7611	0.5734	2.6082	2.6082	-2.61	1.58	8.14
Pr(III) : GSH:Ca	0.5188	0.5188	0.3470	0.5251	0.7136	0.5329	2.5985	2.5985	-54.48	1.47	8.14
Pr(III) : GSH : Zn	0.7488	0.7488	0.4191	0.6270	0.8470	0.6361	0.8182	0.8182	114.44	1.75	2.22
8.DMF:CH ₃ CN	0.5841	0.5841	0.3765	0.5809	0.7973	0.5898	2.6198	2.6198	7.79	1.62	8.17
Pr(III)	0.6569	0.6569	0.3755	0.5091	0.6524	0.5168	2.7227	2.7227	-31.26	1.42	8.56
Pr(III) : GSH	0.7097	0.7097	0.3742	0.4864	0.6076	0.4937	2.7459	2.7459	-20.63	1.36	8.65
Pr(III) : GSH:Ca	0.7845	0.7845	0.4175	0.5766	0.7466	0.5851	2.6845	2.6845	0.16	1.61	8.38
Pr(III) : GSH : Zn	0.7172	0.7172	0.4071	0.5682	0.6794	0.5463	2.7884	2.7884	-21.74	1.50	8.75
9.CH ₃ OH:Dioxane											

Table 4.04 : Computed values of energy interaction Slater Condon $F_k(\text{cm}^{-1})$, spin orbit interaction $\xi_{4f}(\text{cm}^{-1})$.Nephelauxetic ration (β), bonding ($b^{1/2}$), covalency (δ) parameters for Nd(III), Nd(III):GSH,

Nd(III):GSH:Ca(II) and Nd(III):GSH:Zn(II) system in different aquated organic solvents at pH = 4 at 25°C :

System	F_2	F_4	F_6	ξ_{4f}	β	$b^{1/2}$	δ
1. Solvent-CH₃OH							
Nd(III)	329.9268	48.1191	5.1316	630.3109	0.9988	0.0247	0.1217
Nd(III):GSH	329.9122	48.1233	5.1313	930.4989	0.9989	0.0236	0.1117
Nd(III):GSH:Ca	329.8999	48.1224	5.1311	930.7920	0.9989	0.029	0.1101
Nd(III):GSH:Zn	329.8822	48.1217	5.1310	930.8920	0.9990	0.0225	0.1009
2. Solvent-DMF							
Nd(III)	329.7506	48.0432	5.1632	936.9598	1.0121	0.0779	1.1977
Nd(III):GSH	329.6665	48.0692	5.1631	939.3620	1.0139	0.0833	1.3689
Nd(III):GSH:Ca	329.6312	48.0691	5.1630	939.3412	1.0140	0.0842	1.3927
Nd(III):GSH:Zn	329.6118	48.0690	5.1629	940.3386	1.0145	0.0851	1.4274
3. Solvent-Dioxane							
Nd(III)	330.0494	48.1105	5.1288	929.1102	1.0074	0.0610	0.7391
Nd(III):GSH	329.9625	48.1026	5.1220	929.1096	1.0082	0.0601	0.8147
Nd(III):GSH:Ca	329.4131	48.100	5.1215	929.1010	1.0083	0.0603	0.7315

System(Contd.)	F ₂	F ₄	F ₆	ξ _{4f}	β	b ^{1/2}	δ
Nd(III):GSH:Zn	329.0654	48.0939	5.1208	929.0977	1.0084	0.0607	0.7305
4. Solvent-CH ₃ CN							
Nd(III)	329.9409	48.1148	5.1349	931.0499	1.0087	0.0659	0.8600
Nd(III):GSH	329.9155	48.1052	5.1306	929.8215	1.0089	0.0627	0.7872
Nd(III):GSH:Ca	329.3205	48.1047	5.1279	929.8320	1.0090	0.0591	0.6723
Nd(III):GSH:Zn	329.1208	48.1046	5.1213	926.8599	1.0091	0.0550	0.6018
5. Solvent-CH ₃ CN:Dioxane							
Nd(III)	329.9739	48.1417	5.1329	929.9167	1.0081	0.0636	0.8027
Nd(III):GSH	329.9562	48.1376	5.1308	929.4261	1.0088	0.0623	0.7692
Nd(III):GSH:Ca	329.3205	48.1014	5.1123	928.5201	1.0089	0.0601	0.6932
Nd(III):GSH:Zn	329.1288	48.0941	5.1249	928.0430	1.0091	0.0580	0.6672
6. Solvent- CH ₃ CN : CH ₃ OH							
Nd(III)	329.9846	48.0825	5.1305	930.4892	1.0081	0.0638	0.8070
Nd(III):GSH	329.9819	48.0752	5.1304	930.6191	1.0082	0.0639	0.8112
Nd(III):GSH:Ca	329.4321	48.0712	5.1291	928.5231	1.0084	0.0602	0.7031
Nd(III):GSH:Zn	329.1447	48.0696	5.1227	927.7653	1.0085	0.0568	0.6409
7. Solvent- CH ₃ CN : DMF							
Nd(III)	329.9221	48.1222	5.1359	931.2720	1.0088	0.0665	0.8772

System (Contd.)	F ₂	F ₄	F ₆	ξ _{4f}	β	b ^{1/2}	δ
Nd(III):GSH	329.8899	48.1075	5.1324	935.5252	1.0118	0.0768	1.1619
Nd(III):GSH:Ca	329.8721	48.1012	5.1432	936.2310	1.0119	0.0771	1.1920
Nd(III):GSH:Zn	329.8611	48.0820	5.1581	936.5738	1.0123	0.0785	1.2170
8. Solvent- CH ₃ OH : DMF							
Nd(III)	329.7210	48.1231	5.1259	931.2327	1.0120	0.0649	0.8716
Nd(III):GSH	329.5923	48.1121	5.1201	929.3124	1.0121	0.0712	1.1531
Nd(III):GSH:Ca	329.3745	48.0971	5.1321	929.4272	1.0131	0.0751	1.1724
Nd(III):GSH:Zn	329.2456	48.0012	5.1521	928.0123	1.0145	0.0781	1.2030
9. Solvent- Dioxane : DMF							
Nd(III)	329.7530	48.0532	5.1631	935.4562	1.0097	0.0732	1.1766
Nd(III):GSH	329.6712	48.0320	5.1621	936.1012	1.0121	0.0797	1.2710
Nd(III):GSH:Ca	329.6432	48.0199	5.1619	936.4513	1.0122	0.0812	1.3029
Nd(III):GSH:Zn	329.4320	48.0190	5.1617	936.6712	1.0124	0.0856	1.3171
10. Solvent- CH ₃ CN : DMF							
Nd(III)	329.9458	48.1360	5.1521	934.5612	1.0001	0.0632	1.0279
Nd(III):GSH	329.7912	48.1345	5.1517	935.1213	1.0123	0.0712	1.1324
Nd(III):GSH:Ca	329.5732	48.1340	5.1514	935.1021	1.0732	0.0732	1.1737
Nd(III):GSH:Zn	329.0123	48.1330	5.1512	935.0971	1.0130	0.0737	1.1949

Table 4.05. Computed and Observed values of Energies(cm^{-1}) and R.M.S. values for Nd(III), Nd(III):GSH (1:1), Nd(III):GSH:Ca(II) (1:1:1) Nd(III):GSH:Zn(II) (1:1:1) in aqueous and different aquated organic solvents(50:50) at pH-4 are given below :

System	$^4I_{9/2} \rightarrow ^4F_{3/2}$		$^4I_{9/2} \rightarrow ^4F_{5/2}$		$^4I_{9/2} \rightarrow ^4F_{7/2}$		$^4I_{9/2} \rightarrow ^4G_{5/2}$		$^4I_{9/2} \rightarrow ^4G_{7/2}$		RMS	
	E_{obs}	E_{cal}	E_{obs}	E_{cal}	E_{obs}	E_{cal}	E_{obs}	E_{cal}	E_{obs}	E_{cal}		
1. Solvent- CH_3OH												
Nd(III)	11542.68	11476.47	12569.60	12600.19	13484.18	13460.33	17324.42	17278.75	19144.25	19249.67	100.9700	
Nd(III):GSH	11542.41	11475.86	12568.97	12599.84	13483.81	13460.13	17324.12	17277.68	19143.89	19249.78	101.6940	
Nd(III):GSH:Ca(II)	11542.31	11475.43	42568.69	12599.56	13483.42	13460.02	17324.32	17176.68	19143.99	19249.70	102.7321	
Nd(III):GSH:Zn(II)	11542.15	11474.78	12568.34	12599.36	13483.27	13459.93	17323.52	17275.84	19142.42	19249.61	103.0389	
2. Solvent-DMF												
Nd(III)	11538.95	11461.89	12559.66	12595.18	13490.54	13460.17	17290.57	17252.41	19134.73	19249.22	110.4541	
Nd(III):GSH	11538.28	11455.36	12559.34	12591.91	13485.63	13458.86	17273.25	17240.66	19134.36	19250.82	111.6868	
Nd(III):GSH:Ca(II)	11538.20	11453.45	12558.97	12591.02	13484.37	13458.57	17273.64	17239.23	19133.03	19250.82	112.7324	
Nd(III):GSH:Zn(II)	11538.15	11452.77	12558.71	12590.74	13483.99	13458.41	17268.77	17236.13	19132.17	19250.81	113.3604	

System (Contd.)	${}^4I_{9/2} \rightarrow {}^4F_{3/2}$		${}^4I_{9/2} \rightarrow {}^4F_{5/2}$		${}^4I_{9/2} \rightarrow {}^4F_{7/2}$		${}^4I_{9/2} \rightarrow {}^4G_{5/2}$		${}^4I_{9/2} \rightarrow {}^4G_{7/2}$		RMS
	E_{obs}	E_{cal}	E_{obs}	E_{cal}	E_{obs}	E_{cal}	E_{obs}	E_{cal}	E_{obs}	E_{cal}	
3. Solvent - Dioxane											
Nd(III)	11544.81	11480.28	12570.71	12602.16	13488.54	13461.46	17323.52	17285.16	19149.38	19250.08	96.8813
Nd(III):GSH	11541.08	11476.70	12570.71	12600.46	13485.27	13460.68	17322.98	17278.97	19146.09	19249.91	98.5990
Nd(III):GSH:Ca(II)	11545.02	11478.36	12570.79	12602.50	13489.32	13461.20	17322.95	17282.02	19148.23	19249.75	97.6723
Nd(III):GSH:Zn(II)	11545.34	1148078	12570.87	12602.68	13490.18	13461.91	17322.92	17285.99	19149.02	19249.65	96.7888
4. Solvent-CH ₃ CN											
Nd(III)	11539.75	11474.99	12569.76	12599.67	13485.09	13460.42	17320.22	17275.89	19145.72	19250.18	99.2197
Nd(III):GSH	11541.88	11478.52	12570.24	12601.44	13488.18	13461.25	17323.82	17282.06	19147.92	19249.92	97.6620
Nd(III):GSH:Ca(II)	11547.32	11482.01	12573.10	12602.13	13487.24	13461.68	17287.07	17287.67	19149.32	19249.99	95.7562
Nd(III):GSH:Zn(II)	11550.68	11485.54	12574.66	12604.21	13486.72	13461.83	17328.62	17294.61	19152.32	19250.07	93.8272
5. CH ₃ CN:Dioxane											
Nd(III)	11542.28	11477.24	12569.45	12600.22	13484.54	13460.22	17323.22	17325.32	19148.29	19148.65	75.9795
Nd(III):GSH	11543.35	11478.60	1256897	12600.90	13485.99	13460.50	17325.32	17282.33	19148.65	19250.65	98.9487
Nd(III):GSH:Ca(II)	11545.31	11480.32	12570.32	12602.10	13488.02	13461.36	17324.97	17287.01	19149.31	19250.12	96.3217

System	$^4I_{9/2} \rightarrow ^4F_{3/2}$		$^4I_{9/2} \rightarrow ^4F_{5/2}$		$^4I_{9/2} \rightarrow ^4F_{7/2}$		$^4I_{9/2} \rightarrow ^4G_{5/2}$		$^4I_{9/2} \rightarrow ^4G_{7/2}$		RMS
	E_{obs}	E_{cal}	E_{obs}	E_{cal}	E_{obs}	E_{cal}	E_{obs}	E_{cal}	E_{obs}	E_{cal}	
Nd(III):GSH:Zn(II)	11547.48	11483.62	12572.45	12603.98	13491.27	13462.44	17324.42	17290.95	19151.58	19249.74	94.6086
6. $\text{CH}_3\text{CN} : \text{CH}_3\text{OH}$											
Nd(III)	11541.08	11477.27	12568.02	12601.25	13490.36	13461.45	17323.82	17279.88	19144.98	19249.13	100.5584
Nd(III):GSH	11539.88	11477.09	12569.60	12601.28	13489.63	13461.55	17324.12	17279.56	19144.62	19248.89	99.4722
Nd(III):GSH:Ca(II)	11541.08	11480.37	12571.23	12602.79	13491.21	13461.31	17325.32	17285.46	19149.74	19248.93	95.3276
Nd(III):GSH:Zn(II)	11546.11	11484.65	12573.24	12604.67	13492.36	13462.85	17327.42	17292.78	19151.22	19249.19	94.0320
7. $\text{CH}_3\text{CN} : \text{DMF}$											
Nd(III)	11544.94	11474.25	12568.34	12599.25	13484.54	13460.19	17313.02	17274.60	19144.98	19250.44	101.2220
Nd(III):GSH	11542.55	11464.78	12566.44	12595.64	13485.81	13459.91	17280.11	17257.13	19146.45	19252.45	101.6806
Nd(III):GSH:Ca(II)	11544.63	11464.32	12563.54	12595.76	13485.79	13459.13	17255.23	19144.32	19252.01	105.7902	98.6237
Nd(III):GSH:Zn(II)	11544.68	11462.84	12562.66	12595.18	13489.27	13460.19	17273.54	17253.54	19143.52	19251.89	106.5208
8. $\text{CH}_3\text{CN} : \text{CH}_3\text{OH}$											
Nd(III)	11543.08	11477.47	12569.99	12610.79	13485.18	13461.33	17325.42	17179.75	19145.25	19250.67	101.9700
Nd(III):GSH	11543.41	11476.86	2569.60	12610.39	13484.81	13461.13	17325.12	17178.86	19144.89	19250.78	102.9630
Nd(III):GSH:Ca(II)	11543.32	11476.43	12569.69	12599.56	13484.42	1361.02	17325.32	17277.68	19144.99	19250.70	103.3723

System	${}^4I_{9/2} \rightarrow {}^4F_{3/2}$		${}^4I_{9/2} \rightarrow {}^4F_{5/2}$		${}^4I_{9/2} \rightarrow {}^4F_{7/2}$		${}^4I_{9/2} \rightarrow {}^4G_{5/2}$		${}^4I_{9/2} \rightarrow {}^4G_{7/2}$		RMS
	E_{obs}	E_{cal}	E_{obs}	E_{cal}	E_{obs}	E_{cal}	E_{obs}	E_{cal}	E_{obs}	E_{cal}	
9. Dioxane : DMF											
Nd(III):GSH:Zn(II)	11543.15	11476.78	12569.34	12599.36	13484.27	13460.93	17324.52	17276.48	19143.42	19250.61	104.9803
Nd(III)	11539.95	11462.98	12560.66	12560.81	13491.45	13461.71	17291.75	17253.14	19135.37	19250.22	111.4545
Nd(III):GSH	11539.28	11456.63	12560.43	12592.19	13486.36	13459.68	17174.52	17241.66	19135.63	19251.28	112.6878
Nd(III):GSH:Ca(II)	11539.02	11454.54	12559.79	12592.20	13485.73	13459.75	17274.46	17240.32	19134.30	19251.28	113.3245
Nd(III):GSH:Zn(II)	11539.51	11453.77	12559.71	12591.74	13484.99	13459.14	17269.77	17237.31	19133.71	19251.18	113.1104
10. CH ₃ CN : DMF											
Nd(III)	11545.81	11481.28	12571.71	12603.61	13489.45	13462.64	17324.52	17286.6	19150.38	19251.08	97.8312
Nd(III):GSH	11542.08	11477.70	12571.71	12601.64	13486.72	13461.89	17323.89	17279.79	19147.09	19250.92	97.5909
Nd(III):GSH:Ca(II)	11546.02	11479.63	12571.79	12603.05	13490.23	13461.20	17323.85	17283.02	19149.23	19250.75	98.6237
Nd(III):GSH:Zn(II)	11546.34	11480.87	12571.87	12603.68	13491.81	13461.91	17323.80	17286.99	19150.02	19250.65	97.8878

Table 4.06 : Observed and computed values of oscillator strengths ($P \times 10^6$) and Judd-Ofelt parameters for Nd(III) : GSH in different aquated organic solvents in pH = 4 at 25°C (Ground State of Nd(III) : $^4I_{9/2}$)

System	$^4G_{7/2}$ Pobs (Pcal)	$^4G_{5/2}$ Pobs (Pcal)	$^4F_{7/2}$ Pobs (Pcal)	$^4F_{5/2}$ Pobs (Pcal)	$^4F_{3/2}$ Pobs (Pcal)	T ₂	T ₄	T ₆
1. Nd(III) : GSH in DMF	8.744 (3.313)	11.495 (12.151)	11.880 (15.304)	10.578 (17.450)	1.660 (0.7499)	5.61	19.01	41.97
2. Nd(III) : GSH in CH ₃ OH	7.675 (5.901)	16.250 (16.988)	11.797 (15.566)	9.319 (18.793)	2.155 (2.074)	9.08	24.45	48.37
3. Nd(III) : GSH in Dioxane	17.008 (15.485)	19.547 (20.877)	13.790 (20.006)	11.330 (25.706)	2.736 (1.315)	9.04	38.04	63.73
4. Nd(III) : GSH in CH ₃ CN	7.260 (4.873)	14.951 (15.612)	12.952 (16.563)	10.735 (19.218)	2.432 (1.569)	8.11	22.32	48.09
5. Nd(III) : GSH in DMF + CH ₃ CN	11.653 (8.016)	20.817 (21.885)	13.574 (18.783)	10.708 (23.500)	2.310 (2.756)	11.43	33.27	60.89
6. Nd(III) : GSH in DMF + CH ₃ OH	9.190 (7.571)	19.670 (20.577)	12.691 (17.128)	9.633 (21.250)	2.200 (2.774)	11.21	29.69	55.81
7. Nd(III) : GSH in CH ₃ OH + CH ₃ CN	7.771 (5.301)	14.922 (15.636)	10.965 (14.962)	9.563 (17.939)	1.929 (1.786)	8.19	22.88	45.69
8. Nd(III) : GSH in	9.420	15.499	11.040	8.920	2.010	8.19	25.54	47.46

CH ₃ OH + Dioxane	(5.754)	(16.284)	(15.114)	(18.670)	(1.836)			
System (Contd.)	⁴ G _{7/2} Pobs (Pcal)	⁴ G _{5/2} Pobs (Pcal)	⁴ F _{7/2} Pobs (Pcal)	⁴ F _{5/2} Pobs (Pcal)	⁴ F _{3/2} Pobs (Pcal)	T ₂	T ₄	T ₆
9. Nd(III) : GSH in CH ₃ CN + Dioxane	11.323 (7.458)	20.023 (21.043)	14.541 (19.212)	10.786 (23.742)	2.818 (2.429)	10.68	32.56	60.61
10. Nd(III) : GSH in DMF + Dioxane	7.860 (8.313)	21.810 (22.685)	13.705 (18.591)	10.930 (22.760)	2.662 (3.223)	12.86	30.93	60.42

Table 4.07 : Observed and computed values of oscillator strengths ($P \times 10^6$) and Judd-Ofelt parameters for Nd(III) : GSH : Ca(II) in different aquated organic solvents in pH = 4 at 25°C (Ground State of Nd(III) : $^4I_{9/2}$)

System	$^4G_{7/2}$ Pobs (Pcal)	$^4G_{5/2}$ Pobs (Pcal)	$^4F_{7/2}$ Pobs (Pcal)	$^4F_{5/2}$ Pobs (Pcal)	$^4F_{3/2}$ Pobs (Pcal)	T ₂	T ₄	T ₆
1. Nd(III) : GSH: Ca in DMF	6.759 (4.527)	18.924 (19.528)	21.725 (27.722)	20.822 (30.390)	6.555 (0.9008)	9.27	28.67	72.10
2. Nd(III) : GSH: Ca in Dioxane	5.531 (1.528)	10.505 (10.884)	15.241 (20.158)	16.598 (21.563)	5.138 (0.3673)	4.01	18.28	48.71
3. Nd(III) : GSH: Ca in CH ₃ OH	9.214 (1.400)	11.484 (12.057)	18.434 (24.522)	19.753 (26.701)	6.572 (0.9881)	3.22	24.12	48.95
4. Nd(III) : GSH: Ca in dioxane	12.421 (2.736)	12.093 (12.920)	16.957 (20.875)	13.959 (23.763)	3.992 (0.2236)	4.16	25.32	54.04
5. Nd(III) : GSH: Ca in CH ₃ CN	9.820 (4.289)	17.905 (18.662)	21.069 (27.535)	20.409 (30.752)	6.589 (0.4556)	7.78	31.10	71.91
6. Nd(III) : GSH: Ca in CH ₃ OH + DMF	9.460 (4.447)	15.792 (16.544)	15.661 (21.595)	15.891 (24.750)	4.507 (0.8346)	7.26	27.34	58.99
7. Nd(III) : GSH: Ca in CH ₃ OH + CH ₃ CN	6.481 (1.103)	9.744 (10.159)	17.490 (19.799)	14.040 (20.993)	4.500 (0.4906)	3.63	17.10	47.09
8. Nd(III) : GSH: Ca in DMF + Dioxane	6.851	16.149	21.400	22.267	8.100	6.46	28.27	70.38

System (Contd.)	⁴ G _{7/2} Pobs (Pcal)	⁴ G _{5/2} Pobs (Pcal)	⁴ F _{7/2} Pobs (Pcal)	⁴ F _{5/2} Pobs (Pcal)	⁴ F _{3/2} Pobs (Pcal)	T ₂	T ₄	T ₆
9. Nd(III) : GSH: Ca in CH ₃ CN + Dioxane	(3.021) 4.428	(16.688) 10.495	(28.199) 17.561	(30.741) 13.645	(0.1521) 4.512	4.64	15.86	46.58
10. Nd(III) : GSH: Ca in CH ₃ OH + Dioxane	(1.528) 7.699	(10.815) 12.663	(919.424) 17.730	(20.359) 19.276	(0.1221) 6.142	4.61	23.42	58.43
	(2.072)	(13.189)	(23.796)	(25.870)	(0.4338)			

Table 4.08 : Observed and computed values of oscillator strengths ($P \times 10^6$) and Judd-Ofelt parameters for Nd(III) : GSH : Ca(II) in different aquated organic solvents in pH = 4 at 25°C (Ground State of Nd(III) : ${}^4I_{9/2}$)

System	${}^4G_{7/2}$ Pobs (Pcal)	${}^4G_{5/2}$ Pobs (Pcal)	${}^4F_{7/2}$ Pobs (Pcal)	${}^4F_{5/2}$ Pobs (Pcal)	${}^4F_{3/2}$ Pobs (Pcal)	T ₂	T ₄	T ₆
1. Nd(III) : GSH: Ca in DMF	7.520 (7.795)	19.350 (20.132)	13.025 (17.195)	10.100 (20.840)	2.340 (2.747)	11.29	27.57	54.79
2. Nd(III) : GSH: Ca in Dioxane	20.330 (8.662)	22.650 (24.230)	17.590 (23.250)	11.690 (29.840)	2.910 (2.178)	10.45	43.93	73.85
3. Nd(III) : GSH: Ca in CH ₃ OH	10.050 (4.621)	13.780 (14.580)	12.730 (16.043)	9.360 (19.273)	2.480 (1.145)	6.59	24.41	47.12
4. Nd(III) : GSH: Ca in dioxane	5.750 (4.199)	13.340 (13.880)	12.078 (15.132)	9.940 (17.300)	2.370 (1.371)	7.31	19.25	43.20
5. Nd(III) : GSH: Ca in CH ₃ CN	26.530 (11.257)	27.030 (29.080)	17.950 (25.220)	11.150 (17.550)	3.160 (2.833)	12.11	55.98	85.46
6. Nd(III) : GSH: Ca in CH ₃ OH + DMF	11.970 (5.060)	14.510 (15.434)	13.110 (16.640)	9.250 (20.370)	2.395 (1.197)	6.75	27.06	49.79
7. Nd(III) : GSH: Ca in CH ₃ OH + CH ₃ CN	16.970 (6.758)	17.990 (19.280)	14.150 (19.408)	10.430 (24.840)	2.790 (1.509)	7.87	36.31	60.74

8. Nd(III) : GSH: Ca in DMF + Dioxane	13.210 (9.067)	22.860 (24.069)	14.280 (19.840)	10.550 (25.388)	2.690 (3.074)	12.36	37.68	65.96
System (Contd.)	$^4G_{7/2}$ Pobs (Pcal)	$^4G_{5/2}$ Pobs (Pcal)	$^4F_{7/2}$ Pobs (Pcal)	$^4F_{5/2}$ Pobs (Pcal)	$^4F_{3/2}$ Pobs (Pcal)	T ₂	T ₄	T ₆
9. Nd(III) : GSH: Ca in CH ₃ CN + Dioxane	15.870 (7.504)	19.490 (20.768)	14.290 (19.530)	10.150 (25.150)	3.080 (1.946)	9.08	37.37	62.54
10. Nd(III) : GSH: Ca in CH ₃ OH + Dioxane	12.570 (5.484)	15.610 (16.593)	12.710 (17.467)	10.740 (21.404)	2.260 (1.375)	7.42	28.47	52.57

Pr^{3+} spectral intensity calculation.^{5,6} First of all, it has been assumed that the configurations, which are mixed into the $4f^n$ configurations are degenerate. Only the barycentres of those

CHAPTER NO. V

RESULTS AND DISCUSSION

5.1 : Hypersensitivity and Intensity Analysis

5.1.1 : Success and Failure of Judd-Ofelt Theory

Over the years Judd-Ofelt theory has been proved to be quite successful for the intensity analysis of trivalent lanthanide ions. The intensity of f-f transitions between J multiplets in the spectrum can be rationalized by only three phenomenological parameters T_λ , Ω_λ and Ξ_λ . One can even make predictions about the intensity parameters, which cannot be observed experimentally (e.g. infrared 4f-4f transitions in aqueous solution). These parameters sets are useful tool to derived the relationship between spectral parameters and structural properties of different classes of Ln (III) complexes.

For Pr^{3+} , the Judd-Ofelt theory does not seem to work well.¹⁻⁴ Difficulties are experienced if one tries to fit both ${}^3H_4 \rightarrow {}^3F_3, {}^3F_4$ and the ${}^3H_4 \rightarrow {}^3P_{2,1,0}, {}^1I_6$ transitions with the same set of Ω_λ parameters³ instead of determining a parameter set with inclusion of all the transitions, the ${}^3H_4 \rightarrow {}^3F_3, {}^3F_4$ transition can be excluded. Of course the agreement will then be worse between the experimental and calculated oscillator strength for the latter transitions. Other authors preferred to exclude ${}^3H_4 \rightarrow {}^3P_2$ transition.⁵⁻⁷ It is also found that T_6 parametric values are appreciably higher than the values extrapolated from other lanthanide ions in the same matrix.² There are several reasons for the weak applicability of Judd - Ofelt theory for

Pr^{3+} spectral intensity calculation.^{2,3} First of all, it has been assumed that the configurations, which are mixed into the $4f^n$ configurations are degenerate. Only the barycentres of these excited configurations are considered. The $4f^1 5d^1$ & configuration of Pr^{3+} starts at about $45,000 \text{ cm}^{-1}$ above the ground state, while those of other lanthanides (except Tb^{3+}) starts above $60,000 \text{ cm}^{-1}$. It has been argued that the low energetic position of the disturbing excited configuration is the main reason for the anomalous behavior of Pr^{3+} . A second assumption is that the energy difference between the ground J' level of $4f^n$ configuration and the barycentre of the excited disturbing configuration, can be considered to be equal to the energy difference between the excited J' level of $4f^n$ configuration and the barycentre of the same excited disturbing configuration. This approximation is good only if the barycentre is situated at a very high energy. Once again this is not the case for Pr^{3+} . Since this approximation enables to cancel out part of intensity from the terms with odd λ value, we can expect parameters with odd λ values to give non-negligible contributions to the intensity of 4f-4f transitions of Pr^{3+} .

$$P_{ED} = \sum_{\lambda} \Omega_{\lambda} \langle f^N [SL] J \| U^{(\lambda)} \| f^N [S'L'] J' \rangle^2 \quad (1)$$

Eyal et al⁵ have concluded that Ω_3 and Ω_5 parameters in the intensity fitting of Pr in ZBLA glass, Florez et al⁸ also fitted the intensities of 4f-4f transitions of Pr^{3+} doped fluorindate glasses in terms of odd intensity parameters and found that it was necessary for a good fit to incorporate $^3\text{H}_4 \rightarrow ^1\text{I}_6$ transitions in fitting procedure.

Levey⁹ assumed that $4f^1 5d^1$ configuration dominates as the perturbing configuration in the induced electric dipole transition and calculated energy denominators explicitly. Three additional odd Ω_λ parameters have been considered in their scheme.

It should be mentioned also that the hypersensitive transition ${}^3F_2 \rightarrow {}^3H_4$ has to be included in a fit of Pr^{3+} system, because otherwise a negative value for $\Omega_2(T_2)$ parameter is found (just as found sometimes by inclusion of ${}^3H_4 \rightarrow {}^3P_2$ transition in the fitting procedure). As the parameters with negative value has no physical relevance extraction of a reliable $\Omega_2(T_2)$ parameter is often a problem for Pr^{3+} since the ${}^3H_4 \rightarrow {}^3F_2$ transition is situated in infrared spectral region ($\sim 5500 \text{ cm}^{-1}$) and thus cannot be observed in an aqueous solution of the Pr^{3+} complexes (it is masked by vibrational transitions). In order to find more reliable intensity parameters for Pr^{3+} , Quimby and Minniscalco introduced a modified Judd - Ofelt theory in which, luminescence branching ratios are included in the fit. Kornienko et al¹⁰ have tried to take into account the influence of excited state of Pr^{3+} on the dipole strength.

$$D = e^2 \sum_{\lambda=2,4,6} \Omega_\lambda [1 + 2\alpha(E_j + E_j' - 2E_f^0)] |\langle f^N \Psi' J' \| U^{(\lambda)} \| f^N \Psi J \rangle|^2 \quad (2)$$

With E_j the energy of ground state ${}^{2S+1}L_j$, E_j' is the energy of excited state ${}^{2S+1}L_j'$, E_f^0 the energy of the center of gravity of the $4f^2$ configuration ($\sim 10000 \text{ cm}^{-1}$) and $\alpha = 1/2 [E(4f5d) - E(4f)]$. The Kornienko Parameter α , has a value of $\sim 10^{-5} \text{ cm}$, but in practice it is treated as an additional fitting parameter. The method of Kornienko has effectively been applied to Pr^{3+} doped glasses by Bunnell et al¹¹, Alcalá and Cases¹² and Medeiro Neto et al¹³. Goldner and Auzel⁴ pointed out the fact that α parameter has to be set to a value which is inconsistent with experiment.

We have also been actively involved in intensity data analysis of Pr^{3+} complexes derived from wide range of coordinating ligands. We have noted that the difference between the observed oscillator strengths and calculated oscillator strengths of Pr^{3+} , 4f-4f transitions was much higher than that observed for the Nd^{3+} , Dy^{3+} and Er^{3+} complexes. The oscillator strengths of $4f^n - 4f^n$ intra configurational transitions was expressed through Judd-Ofelt (T_λ) parameters employing the matrix elements of unit tensor operator of rank λ i.e. $[U^{(2)}]^2$, $[U^{(4)}]^2$ and $[U^{(6)}]^2$. We have experienced lot of problems while analyzing Pr^{3+} , solution spectral intensity data. One generally uses Carnalls' Coefficients for aquo system to get these values. In case of Pr^{3+} $[U^{(2)}]^2$ and $[U^{(6)}]^2$ have zero values for the levels 3P_1 and 3P_0 , the ordinary simultaneous equations yielded the values of T_2, T_4 and T_6 by simple calculations. An inspection of the results showed that because of the scarcity of the member of the observed bands, the values obtained for T_2 are meaningless, because these have negative value. T_4 and T_6 values are somewhat reasonable and we have used the values from Carnall et al paper quoted for Pr^{3+} aquo ions. An examination of Carnall's Coefficient for T_4 shows that, they are very nearly equal in case of 3P_1 and 3P_0 bands. Hence these bands should have the same intensity. This is usually not so, and so often found that the intensity of 3P_1 band is always greater than 3P_0 band. We have then adopted to eliminate the above discrepancy. One way of making the oscillator strength 3P_0 and 3P_1 same as to assume that difference in the intensity of 3P_1 from that of 3P_0 arises from an additional contribution i.e. intensity difference is in positive side and attribute this difference to a correction factor T_7 . On the other hand, one can assume that the original intensity as that of 3P_1 and attribute this to the difference to a negative correction factor T_8 . It is too early to say which of these approaches is the correct

one. However, as expected the introduction of correction factor T_c (T_7 or T_8) eliminates this discrepancy significantly, in case of most of the Pr^{3+} complexes. This though serves as mainly a fudge factor, may have some implications. We are not in position now to theoretically evaluate the significance of either T_7 or T_8 and what it means in quantum mechanical terms. But we believe that such a kind of correction is helpful though its effect is not known properly. Our final idea is to use various weighting factors to make T_2 positive but we do not want to carry out such work until the nature of T_7 or T_8 is known with certainty.¹⁴⁻¹⁶

5.1.2 Selection Rules for Hypersensitivity:

In the free ion approximation the states of $4f^n$ configurations are taken as linear combination of Russell-Saunders coupled states $|f^N \alpha SLJ \rangle$:

$$|f^N \alpha [SL]J \rangle = \sum_{S,L} A(S,L) |f^N \alpha SLJ \rangle \quad (3)$$

In these intermediate coupled states, the quantum numbers S & L , although convenient for purposes of labeling are not good and are enclosed in square bracket. To save the space, the wave function defined in equation (3) will frequently be written as $|f^N \Psi J \rangle$.

Considering the crystal field as a first order perturbation and mixing in states of higher energy opposite parity configuration $|n \alpha'' [S''L''] J'' M'' \rangle$ (which will be written $|\Psi'' \rangle$) We may write $|A \rangle$ and $|B \rangle$ as follows:

$$|A\rangle = |f^N \Psi J M\rangle + \sum_k \frac{\langle \Psi'' | f^N \Psi J M | V^{CF} | \Psi'' \rangle}{E(4f^N J) - E(\Psi'')} \quad (4a)$$

$$|B\rangle = |f^N \Psi' J' M'\rangle + \sum_k \frac{\langle \Psi'' | f^N \Psi' J' M' | V^{CF} | \Psi'' \rangle}{E(4f^N J') - E(\Psi'')} \quad (4b)$$

Where k stands for all the quantum number of excited configuration. The dipole strength

$D = e^2 \langle A | D_q^{(1)} | B \rangle^2$ of a transition from $fA |A\rangle$ to $|B\rangle$ is then,

$$D = \left[e \sum_{k,t,o} A_{t,p} \left\{ \frac{\langle f^N \Psi J M | D_q^{(1)} | \Psi'' \rangle \langle \Psi'' | D_q^{(1)} | f^N \Psi' J' M' \rangle}{E(4f^N J) - E(\Psi'')} + \frac{\langle f^N \Psi J M | D_q^{(1)} | \Psi'' \rangle \langle \Psi'' | D_q^{(1)} | f^N \Psi' J' M' \rangle}{E(4f^N J') - E(\Psi'')} \right\} \right] \quad (5)$$

The procedure named 'closure' given by Groffith¹⁷ in 1960 simplifies above equation (5) by application to both half of the equation (5) and equation $E(4f^N J) - E(\Psi'')$ and $E(4f^N J') - E(\Psi'')$ and replacing them by an average energy denominator $\Delta E(\Psi')$ results in relationship,

$$D = \left[e \sum_{p,t,\text{even}\lambda} (-1)^{p+q} A_{t,p} [\lambda] E_{(t,\lambda)} \begin{pmatrix} 1 & \lambda & t \\ q & -p-q & p \end{pmatrix} (1\lambda\lambda) \langle f^N \Psi J M | U_{-p-q}^{(\lambda)} | f^N \Psi' J' M' \rangle \right] \quad (6)$$

where

$$\Xi_{(t,\lambda)} = 2 \sum (-1)^{f+l} [f][l] \begin{Bmatrix} 1 & \lambda & t \\ f & 1 & f \end{Bmatrix} \langle f \| C^{(1)} \| l \| C^{(1)} \| f \rangle \langle 4f | r | ne \rangle \langle ne | r' | 4f \rangle \Delta E(\Psi^n)^{-1} \quad (7)$$

And there is an implicit summation over n and l of all configurations that it is desired to mix in reducing the matrix elements of equation (6) gives another expression:

$$P_{ED} = \chi \left[\frac{8\pi^2 m c \omega}{h} \sum_{p,e,even} (-1)^{p+q} [\lambda\lambda]_{tp} \begin{pmatrix} 1 & \lambda & t \\ q & -p-q & p \end{pmatrix} \begin{pmatrix} J & \lambda & J' \\ -M & -p-q & M' \end{pmatrix} \right]^2 \Xi_{(tp)} \langle f^N \Psi J \| U^{\lambda\lambda} \| f^N \Psi J' \rangle \quad (8)$$

Equation (8) makes Judd - Ofelt theory effective, in dealing with the transitions between individual stark levels (whose wave functions are in linear combination of $f^N \alpha [SL]JM$ states).

In solution, however such transitions cannot usually be distinguished and it is convenient to sum overall the stark levels of ground state. We can sum over the components of $D_q^{(1)}$ and the components of $D_p^{(0)}$, which is appropriate for isotropic light. The 3-j symbols of equation (8) vanish and are replaced by a factor of $3^{-1} (2J+1)^{-1} (2t+1)^{-1}$ and thus finally

We have,

$$P_{ED} = \sum_{\lambda=2,4,6} \sigma \tau_{\lambda} \langle f^N \alpha [SL]J \| f^N [S'L']J' \rangle^2 (2J+1)^{-1} \quad (9a)$$

$$\mathfrak{S}\lambda = \chi \left[\frac{8\pi^2 m c}{3h} \right] [\lambda] \sum_{p,t} |A_{t,p}|^2 (t,\lambda) (2t+1)^{-1} \quad (9b)$$

Above notations are from Carnall et al¹⁸, for solution studies \mathfrak{T}_λ are slightly different from T_λ , those used by Judd in original paper.

$$T_\lambda = \mathfrak{T}_\lambda (2J+1)^{-1} C^{-1} \quad (10)$$

Many authors use alternative notations Ω_λ for isotropic spectra of ions in crystals. Because refractive index correction χ varies with wavelength and that is not incorporated in Judd-Ofelt parameters.

$$P_{ED} = \chi \left[\frac{8\pi^2 mc}{3h} \right] \sigma \sum_{\lambda=2,4,6} \Omega_\lambda \langle f^N \alpha [SL] J \| U^{(\lambda)} \| f^N [S'L'] J' \rangle^2 (2J+1)^{-1} \quad (11a)$$

$$\Omega_\lambda = [\lambda] \sum_{p,t} |A_{p,t}|^2 \Xi(t, \lambda) (2t+1)^{-1} \quad (11b)$$

Since $T_\lambda, \mathfrak{T}_\lambda$ and Ω_λ parameters are interrelated as shown above, and are empirical in nature and hence it does not make any significant difference, as to which notation should be used, but definitely one type of notation should be used throughout the investigation.

5.1.2.1 Variation of $\mathfrak{T}_\lambda, T_\lambda$ and Ω_λ with Number of Electrons:

Restricting ourselves to an isostructural series of complexes we have removed one variable of equation (11b), the crystal field parameter. The expression for Ω_λ then becomes,

$$\Omega_\lambda = \sum_{p,t} C_{p,t} \sum_t \Xi(t, \lambda) \quad (12)$$

Where $C_{p,t}$ are now a set of constants and are functions of structure of the host. Assuming that the only perturbing configurations are $4f^{n-1} 5d$ and $4f^{n-1} f$, the values of 't' that are nonzero may be obtained by considering the $\langle 1 \| C^{(1)} \| f \rangle$ matrix element of equation (4).

For $4f^t 5d (l=2)$, $t \leq 5$ for $4f^{n-1} ng (l=4)$, $t \leq 7$. The 6-j symbols then give the value of 't' associated with each value of λ . Noting that 't' must be odd, we have finally that the only nonzero $\Xi_{(t,\lambda)}$ are $\Xi_{(12) (3,2) (3,4) (5,4) (5,6)}$ and $(7,6)$. The values of $\Xi_{(t,\lambda)}$ can be calculated via equation (6) from published values of radial integrals and configurational energies. Krupke¹⁹ have listed six $\Xi_{(t,\lambda)}$ parameters for Pr^{3+} , Nd^{3+} , Eu^{3+} , Tb^{3+} , Er^{3+} and Tm^{3+} . In each case the value of $\Xi_{(t,\lambda)}$ decreases monotonically from Pr^{3+} to Tm^{3+} , since sum of a series of monotonic curves. Judd-Ofelt theory predicts that the variation of Ω_λ (T_λ or \mathfrak{F}_λ) parameters across the isostructural series of lanthanide ions should be monotonic.

5.1.3 Definition and Experimental Evidence of Hypersensitivity:

Table 4.01 Hypersensitive transitions for trivalent lanthanide ions :

Ion	Transition	Approximate Wave Number (Cm ⁻¹)	Ion	Transition	Approximate Wave Number (Cm ⁻¹)
Pr^{3+}	$^3\text{H}_4 \rightarrow ^3\text{F}_2$	5200	Dy^{3+}	$^6\text{H}_{15/2} \rightarrow ^6\text{F}_{11/2}$	7700
Nd^{3+}	$^4\text{I}_{9/2} \rightarrow ^5\text{G}_{5/2}$	17300	Ho^{3+}	$^5\text{I}_8 \rightarrow ^5\text{G}_6$	22100
Pm^{3+}	$^5\text{I}_4 \rightarrow ^5\text{G}_2, ^5\text{G}_3$	18000		$^5\text{I}_8 \rightarrow ^3\text{H}_6$	27700
Sm^{3+}	$^6\text{H}_{5/2} \rightarrow ^4\text{F}_{1/2}, ^4\text{F}_{3/2}$	6400	Er^{3+}	$^4\text{I}_{15/2} \rightarrow ^2\text{H}_{11/2}$	19200
Eu^{3+}	$^7\text{F}_1 \rightarrow ^5\text{D}_1$	18700		$^4\text{I}_{15/2} \rightarrow ^4\text{G}_{11/2}$	26400
	$^7\text{F}_0 \rightarrow ^5\text{D}_2$	21500	Tm^{3+}	$^3\text{H}_6 \rightarrow ^3\text{F}_4$	5900
	$^7\text{F}_2 \rightarrow ^5\text{D}_0$	16300		$^3\text{H}_6 \rightarrow ^3\text{H}_4$	12700
Gd^{3+}	$^8\text{S}_{7/2} \rightarrow ^6\text{P}_{5/2}, ^6\text{P}_{7/2}$	3250		$^3\text{H}_6 \rightarrow ^1\text{G}_4$	21300
Tb^{3+}	None reported	----			

Table 5.01 Hypersensitive transitions for trivalent lanthanide ions

Out of the observed 4f - 4f bands, a few transitions are found very sensitive towards environment around Ln(III) ion. Jorgensen and Judd have called such transitions HYPERSENSITIVE transitions and found that all such transitions obeyed selection rules $|\Delta S| = 0$; $|\Delta L| \leq 2$ and $|\Delta J| \leq 2$. These selection rules are same as the selection rules for pure quadrupole transition. The calculations however revealed, that the intensities of hypersensitive transitions are often too large for these transitions to have quadrupole character and thus these transitions have been given name Pseudoquadrupole transition.²⁰⁻²⁵ A list of hypersensitive transition is given in the Table 5.01.

Karraker^{26,27} has studied the hypersensitive transitions of Nd(III), Ho(III) and Er(III) in detail. In his first paper²⁶, he considered the absorption spectra of six, seven and eight coordinated β -diketonates in nonaqueous solution to determine the effects of coordination number on intensity and fine structure of the spectra. The selection of β -diketonates of lanthanide for investigation was made, because all of these ligands coordinated with lanthanide in bidentate manner, through oxygen donor atoms, so that the coordination number and the geometry of the bonding groups were the major experimental variables. The choice for nonaqueous solvent as medium is because these solvents have low polarity to reduce solvent effect to crystal field splitting of lanthanide ions. He concluded that hypersensitive transitions show differences that are characteristic for coordination and symmetry of lanthanide ion. The conclusions are on the following findings:

- i) There is a difference between the appearances of the absorption band for hypersensitive transition for six, seven or eight coordinated lanthanide ion.

- ii) The addition of unidentate ligand hexafluoroacetyl acetone (HFAA) to a solution of six or seven coordinated chelate, results in changing the spectra to spectra resembling those of seven and eight coordinated complexes.
- iii) The removal of water from the solution of hydrated lanthanide β -diketonate complexes results in changing the spectra to spectra of lower coordinated lanthanide β -diketonate complexes.
- iv) There is a correlation between the intensities of hypersensitive transition and coordination number.

Karraker²⁷ in his latter publication investigated the effects of strong aqueous chloride and perchlorate solution on hypersensitive transitions. The change in the band shape was used to recognize hypersensitive and non-hypersensitive transition and changes in coordination. The shape of all Nd(III) absorption bands (both hypersensitive and non-hypersensitive transition) change when electrolyte concentration and temperature changes. The change in the shape of the bands was attributed to the change in the coordination number.

Fellows and Choppin^{22,28} reported excellent findings showing the relationship between the ligand pKa and the oscillator strength of hypersensitive transitions of Nd^{3+} , Ho^{3+} with dibasic and polybasic acids. For aminopolycarboxylate ligands, the order of oscillator strength is EDTA > HEDTA > DTPA > DCTA > NTA in case of Nd^{3+} and HEDTA > DTPA > NTA > EDTA > DCTA for Ho^{3+} . This discrepancy in the order of ligands for Nd^{3+} and Ho^{3+} complexes could not be explained by Fellow and Choppin. The oscillator strengths of the hypersensitive transitions show only moderate variation for different ligands and correlation could be given between oscillator strengths of hypersensitive transitions and pKa of ligands.

But good correlation was shown between hypersensitive transition oscillator strength and sum of ligand pKa (ΣpK) for dibasic ligands.

While working with the complexing behavior of structurally related complexes of lanthanides with wide variation of structural and binding characteristics, we have clearly shown some generalizations.²⁹⁻³¹

- i) The chelated ligands imparted significantly more intensification to 4f - 4f bands than the analogous ligands in mono dentate mode of binding (unidentate acetate, halogen substituted acetates and fluorinated carboxylates and their bidentate/dimeric binding forms).
- ii) The introduction of fluorine in the coordinating ligands enhanced significantly the intensities of 4f - 4f transitions. The intensification of 4f - 4f band and significant increase in the covalent character in the metal-ligand bond are observed in complexes of lanthanides with fluorine containing carboxylic acid (aromatic) β -diketonates^{32,33}, Schiffbase and nucleic base and nucleosides.³⁴⁻³⁵
- iii) The lanthanide alkoxides³⁶ bimetallic heteroleptic and trimetallic heteroleptic alkoxides containing highly branched alcohols, imparted remarkable intensification to the hypersensitive and pseudohypersensitive bands of lanthanides as compared to the analogous compounds with unbranched alcohol.
- iv) We have used quantitative 4f- 4f transition spectral data analysis and the variation of Judd-Ofelt (T_λ) intensity parameters as Monitoring Parameters in following controlled hydrolysis of heterobimetallic and heterotrimetallic alkoxide precursors

(containing one or two lanthanide ions) via Sol-Gel route, for the synthesis of NOVEL Heterometal oxide ceramics of tremendous electronic, optical and mechanical applications.

- v) We have used comparative absorption and absorption difference spectroscopy involving 4f-4f transitions to probe the kinetics of simultaneous complexation of two or three chemically different metal ions to multidonor biomolecules like glutathione oxidized and lysozyme.

5.1.4 : Models for Hypersensitivity

5.1.4.1 : Covalency Model

Hypersensitivity is described by T_2 parameter, if $U^{(4)}$ and $U^{(6)}$ matrix elements for hypersensitive transitions are small. Poluektov³⁷⁻³⁹ proposed a power law between oscillator strength and the matrix element $U^{(2)}$. Henrie and Henrie^{40,41} did not consider the absolute magnitude of T_2 parameter as a measure of hypersensitivity but the relative magnitude of T_2 with respect to T_4 and T_6 .

A covalency model was developed for the origin of hypersensitivity of 4f - 4f transitions. The idea for that model came from the observation of the charge transfer transitions in lanthanide complexes. The energies and intensities of the charge transfer transitions are very sensitive to the type of ligand and to the lanthanide ion. In fact, the energy of metal-ligand charge transition is a function of metal orbital energy, the inter electron repulsion energy and the ligand energy. Henrie et al argued that sensitivity to the ligand environment is intrinsically built into a model for hypersensitivity, if the hypersensitive transitions gain some charge

transfer character. This covalency model describing the mixing of charge transfer states into the f^n configurations, provides a theoretical basis for the correlation of the intensity of hypersensitive transitions with the ligand pKa. The hypersensitive transition of Eu^{3+} , $^3\text{D}_2 \rightarrow ^7\text{F}_0$ is more sensitive to the environment than any other transition of a trivalent lanthanide. This is due to the relatively low energy of hypersensitive transition, (ie intensity is inversely proportional to square of the energy difference between the hypersensitive transition and the charge transfer transition. On the basis of the same arguments, it is possible to explain the greater sensitivity for Ho^{3+} than for $\text{Pr}^{3+}/\text{Nd}^{3+}$. Blasse^{42,43} also found correlation between the intensity of hypersensitive transition $^5\text{D}_2 \rightarrow ^7\text{F}_0$ and charge transfer energy.

5.1.4.2 : Dynamic Coupling Model

Mason et al⁴⁴⁻⁴⁶ have developed a new theoretical model. Dynamic Coupling Model (or ligand polarization model) states that the dipoles are induced by the charge distribution caused by f-f transition. Thus the f-electrons polarize the ligands and the ligand wave functions are polarized by lanthanide ion. The dynamic coupling mechanism gives a contribution to parameter of the expansions of odd part of crystal field potential contains the term A_{3q} . These terms are present if the point group contains no center of symmetry. In this case the induced dipoles can combine into a non-vanishing dipole moment. This dipole moment can interact with the radiation field and the point groups in question are C_s , C_n , C_{nv} , C_{3h} , D_n , D_{3h} , D_{2d} , S_4 , T and T_d . Therefore the model can give good explanation for the observed high intensities of trihalides NdCl_3 , NdI_3 in vapor phase, Kuroda et al^{47,48} demonstrated that the intensity of the hypersensitive $^7\text{F}_0 \rightarrow ^5\text{D}_2$ transition of Eu^{3+} in different systems with D_3 symmetry can be described adequately only if anisotropic ligand namely Dynamic Coupling (DC) and Static Coupling (SC). Both

polarization is considered. These workers ignored J-mixing. The Dynamic Coupling (DC) model predicts the sequence $I^- > Br^- > Cl^- > H_2O > F^-$ for the intensity of hypersensitive transitions.

Kirby and Palmer⁴⁹ investigated the hypersensitive transitions $^4I_{9/2} \rightarrow ^4G_{5/2}, ^2G_{7/2}$ of Nd in Nd (DBM)₃.H₂O and calculated the oscillator strength in terms of dynamic coupling model. The same authors reported⁶⁷ an intensity study of Eu (DBM)₃.H₂O, Ho(DBM)₃.H₂O and Er(DBM)₃.H₂O and found that Ω_2 parameter does not vary in Ln (DBM)₃.H₂O series, as predicted by dynamic coupling model, and also remarked that $^5I_8 \rightarrow ^5G_5$ transitions of Ho³⁺, which is formally not a hypersensitive transition, is unusually intense in Ho(DBM)₃.H₂O.

5.1.4.3 : The Modification of Parameterization Scheme

The parameterization scheme by Judd-Ofelt for J multiplet transition intensities in terms of Ω_λ or T_λ parameters is quite general. It is only limited to the assumption of one electron-one photon interaction. The parameterization scheme is independent of the nature of metal-ligand interaction. The parameterization scheme for intensity given by Axe⁵¹ later modified and this modified version uses in addition to one electron one photon assumption, the supreme position approximation. This means that all metal - ligand pair wise interactions have to be cylindrically symmetric (e.g. have C_∞ local symmetry) and independent.

Reid and Richardson⁵²⁻⁵⁷ developed a most widely accepted parameterization scheme which is essentially identical to the scheme of Newman and Balasubramanian and which thus only requires the one electron one photon approximation. Richardson et al pointed out that the intensity parameters can be interpreted and calculated in terms of two intensity mechanisms, namely Dynamic Coupling (DC) and Static Coupling (SC). Both in the static and in dynamic

coupling models, the interactions are purely electrostatic and thus overlap between the charge distributions of ligand and the central metal ion, is neglected. In SC model, the electronic configuration of lanthanide ion is perturbed by the ligand. The ligands produce a static potential of odd parity around Ln^{3+} ion, so that the 4f state of mixed parity are formed. Transition between these states can be induced directly by the electric dipole component of the incident light. The ligands can be polarized isotropically by the lanthanide ion. Model calculation for intensity parameters have been reported for a series of Nd^{3+} , Ho^{3+} and Er^{3+} complexes, with trigonal symmetry by Richardson et al. The ligands in the complexes are structurally related and were oxydiacetate (ODA), dipicollinate (DPA), iminodiacetate (IDA), methyliminodiacetate (MIDA), chelidonate (CDO) and chelidamate (CDA). The calculations took into account both the static coupling (SC) and dynamic coupling (DC) mechanisms as well as contribution arising from interferences between transition moments by static and dynamic coupling models (SC, DC). The [SC] and [DC] contributions are always positive, whereas the contributions from [SC, DC] may either be positive or negative in signs, depending on the relative phase of SC and DC electric dipole transition moment. The phase relationship depends on the geometrical distribution of ligand charge and polarisability around Ln^{3+} ion. The authors found calculated Ω_2 parameters are dominated by [DC] and [SC, DC] contributions and the calculated Ω_6 parameters are dominated solely by [SC] contribution. The calculated Ω_4 parameters were found to vary from complex to complex and from the radial integrals. No doubt there have substantial discrepancies between the experimental and calculated values of Ω_λ parameters. Gorller Wairand and Binnemans⁵⁸ have attributed this to a number of factors, some of these are:

- i) J-mixing.
- ii) Linear and non linear shielding of electrons from the electrostatic crystalline electric field, resulting from the distortion of the closed 5s and 5p shells outside the 4f shell by lattice charges.
- iii) The relativistic effects, and
- iv) The effects of electron correlation.

While working on solution electronic spectral properties of lanthanide complexes with a large number of coordinating ligands including biomolecular and macrocyclic ligands with wide range of structural and functional characteristics, during two decade we have come to conclusion that the parameters T_4 and T_6 or (Ω_4 and Ω_6) and f are mostly ignored for spectral interpretation, similarly those correlation studies mainly centered around the findings of hypersensitive transitions. The transitions other than hypersensitive transitions were either considered almost insensitive or with negligible sensitivity. No doubt there have been earlier reports on the observed sensitivities of some of the transitions, which do not obey selection rules. Peacock admitted that the transitions $^3H_4 \rightarrow ^3P_2$ and $^3H_4 \rightarrow ^1D_2$ do not obey $|\Delta J|$ selection rules, yet showed remarkable sensitivity towards coordination changes. Devlin et al⁶⁰⁻⁶² also admitted that the sensitivity of hypersensitive transitions was no doubt very high towards even minor changes around lanthanide immediate coordination environment, but a number of transitions, which did not obeyed $|\Delta J|$ selection rules, yet showed substantial sensitivity towards minor coordination changes.

During our studies on around 1500nm spectra of Pr^{3+} and Nd^{3+} complexes, each and hundreds spectra of Ho^{3+} , Er^{3+} and Eu^{3+} recorded in solutions both aqueous and in aquated organic solvents, we have found that a number of transitions of these lanthanide (III) ions which did not obey $|\Delta J|$ selection rules, yet showed significant sensitivity toward even small coordination changes as a result of change in the binding mode of the ligand, hydrogen ion concentration, dielectric constant, basicity of the solvent, denticity and normalized bite of the ligand. The extent of intensification of these 4f - 4f bands (nonhypersensitive transitions) has tempted us to consider these transitions as Pseudohypersensitive Transitions and the observation as Ligand Mediated Pseudohypersensitivity (LMP).⁶³⁻⁶⁷

The idea of LMP was discussed and critically analyzed in very recent monograph of Goriler-Wairand and Binnemans.⁵⁹ No doubt we have no idea about the origin of high sensitivity shown by the transitions which do not obey $|\Delta J|$ selection rules, but we feel strongly that selection rules can be relaxed in solutions and hence some other transition can become somewhat more sensitive.

5.2 : Discussion Of Absorption Spectra - Coordination Aspect

The 4f-4f absorption spectra of lanthanide complexes in solution exhibit absorption bands, which may be assigned to specific ground multiplet to excited multiplet transitions. Each multiplet-to-multiplet transition manifold is generally comprised out a number of unresolved transitions between individual crystal field level of ground state and excited multiplet state, transitions occur via electric dipole mechanism. The total oscillator strength of a multiplet-to-multiplet transition manifold $\Psi J - \Psi' J'$ can be expressed by

$$P = \left(\frac{8\pi^2 mc}{3h} \right) \chi \Psi'J'(2J+1)^{-1} \sum_{\lambda} \Omega_{\lambda} \langle \Psi J \| U^{(\lambda)} \| \Psi'J' \rangle^2 \quad (13)$$

Where $\lambda = 2, 4, 6$ and $\nu\Psi'J'$ is the $\Psi J - \Psi'J'$ transition energy in wave number, χ is Lorentz field correction for the refractive index of sample medium, $U^{(\lambda)}$ is an irreducible unit tensor operator of the rank λ and $\Omega_{\lambda}(T_{\lambda})$ are the quantities for parameters which contain all the details of lanthanide-ligand radiation field interactions, relevant to 4f-4f electric dipole process.

The experimental oscillator strength of a multiplet-to-multiplet transition $\Psi J - \Psi'J'$ can be expressed in simplified way,

$$P = (4.32 \times 10^{-9}) \int \epsilon(\bar{\nu}) d\nu \quad (13)$$

Where ϵ is the molar absorptivity and $\bar{\nu}$ is the energy expressed in cm^{-1} and the integration is over the transition region of interest, combining both equation (13) and (14) we get expression

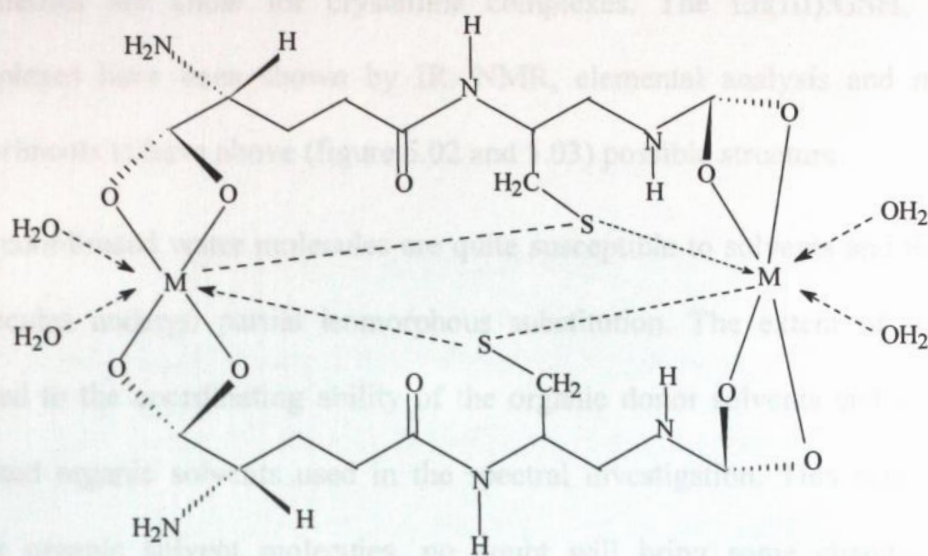
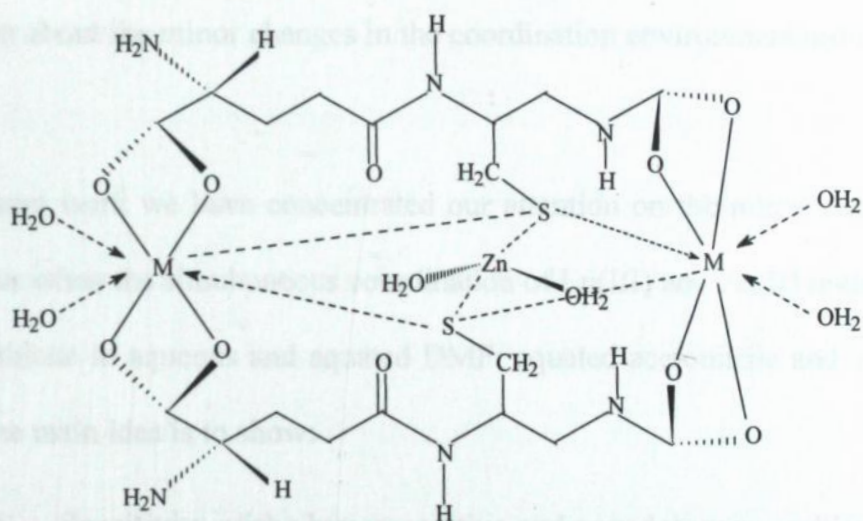
$$I(\Psi'J') = (2.5 \times 10^{19}) \chi \Psi'J'(2J+1)^{-1} \sum_{\lambda} T_{\lambda} \langle \Psi J \| U^{(\lambda)} \| \Psi'J' \rangle^2 \quad (15)$$

$$\text{Where } I(\Psi'J') = \int \epsilon(\bar{\nu}) d\nu \quad (16)$$

In which the integration is over the entire $\Psi J - \Psi'J'$ absorption band and the T_{λ} parameters are expressed in unit of cm^{-2} . Expression (15) provides the basis for analyzing empirical intensity data in terms of T_{λ} parameters. Values of $I(\Psi'J')$ and $\bar{\nu}(\Psi'J')$ are obtained from the absorption measurements and $U^{(\lambda)}$ have been taken for five 4f-4f transition manifold used in

present study from Carnall et al. These T_λ parameters are then adjusted to optimize fits between calculated and experimentally determined values of $I(\Psi'J')$ for all $\Psi J - \Psi'J'$ transitions accessible to measurements in the region of interest.

Devlin et al⁶¹ have quantitatively analyzed the absorption spectral intensity data for multiplet to multiplet transitions of Nd(III), Ho(III) and Er(III) in terms of Judd-Ofelt T_λ intensity parameters for structurally closely related complexes formed by tridentate ligands. The ligands differed only with respect to their central (middle) donor moiety and the geometries of their chelate ring formed on complexation with lanthanide(III) ions. These small chemical and structural differences were shown to produce significant variation in the intensities of certain absorption bands and their relative perturbation differences were readily apparent in T_λ parameters determined for these complexes. Comparison of oscillator strength, experimental and calculated values of T_λ parameters clearly suggest specific correlation between intensities, lanthanide ligand radiation interaction mechanism, ligand structure (geometry, polarizability and charge) and lanthanide ($4f^n$) electronic properties. Since in solution lanthanide complexes involve either octacoordinated or nonacoordinated species. In more common nonacoordinated complex involving e.g. tridentate ligand thus expected to have LnL_6L' coordination polyhedron, in which 'L' donor atoms (six number provided two tridentate or three bidentate ligands) are located at the vertices of a trigonal prism (which may be regular or distorted depending upon the nature, normalized bite of the ligand) and the 'L'' donor atoms occupy capping positions on normal to the rectangular faces of the In octacoordinated lanthanide complex species, the geometries may be cubic square anti prism and dodecahedral.

Figure 5.02 : Proposed Structure of $\text{Ln}_2(\text{GSH})_2(\text{H}_2\text{O})_2$ Figure 5.02 : Proposed Structure of $\text{Ln}_2(\text{GSH})_2\text{Zn}(\text{H}_2\text{O})_6$

The choice of these coordination polyhedra, no doubt depends upon the normalized bite of the chelating ligand and its nature. No doubt there are only little differences in the energies of these species and lanthanide complexes being highly labile, it becomes really extremely difficult to assign any geometry with authenticity in solution. All the structures and

geometries are known for crystalline complexes. The Ln(III):GSH, Ln(III):GSH:Zn(II) complexes have been shown by IR, NMR, elemental analysis and molecular modeling experiments to have above (figure 5.02 and 5.03) possible structure.

The coordinated water molecules are quite susceptible to solvents and therefore these water molecules undergo partial isomorphous substitution. The extent of water substitution is related to the coordinating ability of the organic donor solvents and solvent percentage in aquated organic solvents used in the spectral investigation. This substitution of water by polar organic solvent molecules, no doubt will bring some changes in the immediate coordination environment around lanthanide (III) ion and hence will be reflected by variation of spectral intensity parameters. The variation of spectral parameters thus provides information about the minor changes in the coordination environment around lanthanide (III) ion.

In the present work we have concentrated our attention on the minor coordination changes which occur when the simultaneous coordination of Ln(III) and Zn(II) undergo complexation with glutathione in aqueous and aquated DMF; aquated acetonitrile and aquated dioxane in solvent. The main idea is to show:

- i) Sensitivity of the hypersensitive and pseudohypersensitive 4f-4f transitions to the very minor changes in the immediate coordination environment around lanthanide during heterobimetallic complexation due to the aquated organic solvents of varying degree of aquation.

- ii) The effect of H^+ ion concentration on complexation is reflected via the variation of oscillator strengths of 4f-4f bands and consequently through the variation of Judd-Ofelt (T_λ) parameters.
- iii) To lend support Ligand Mediated Pseudohypersensitivity.
- iv) Compositional dependence of T_λ parameters. There has been significant work carried out in exploring the compositional dependence of Intensity (T_λ) parameters but all these studies were confined to crystalline or solid complexes or salts.

The solvents we used are water as well as aquated organic solvents (DMF, MeCN, dioxane and methanol) with varying degree of aquation. Dimethylformamide(DMF) and methanol are oxygen donor solvents, while acetonitrile does not possess oxygen donor site, which is most favored coordination site for hard metal ion Pr(III)/Nd(III)/Er(III). Hence the presence of acetonitrile in aquated organic solvent do compete with more favored coordinating H_2O ligand for Pr(III)/Nd(III)/Er(III). The difference shown via comparative absorption and absorption difference spectroscopy of Ln(III):GSH and Ln(III):GSH:Zn complex system is being used as Marker also for the relative coordinating ability of different solvents. Since the metal stoichiometry is kept same through out the study during different sets of complexation, hence the quantification of the solvent effect is made easy. In general the increased proportion of the polar organic solvent enhances noticeably the oscillator strengths of different 4f – 4f transitions. Increased oscillator strength of 4f-4f bands is indicator of increased interaction between

metal orbitals and ligand orbitals. Greater intensification of 4f-4f bands, is also an indicator of increase in the degree of inner sphere complexation. Increased oscillator strengths of 4f-4f bands appears to be related to the decrease in the metal ligand distance.^{68,69}

The variation of oscillator strengths of 4f-4f bands both hypersensitive transitions, also leads to significant variation in the magnitudes of Judd-Ofelt intensity parameters. It must always be kept in mind that lanthanide complexes are essentially electrostatic in nature and exhibit very high lability and therefore one is expected to find more than one interconverting species existing at a time. Since the GSH ligand has three types of coordinating sites, hard donor sites like carboxylic groups; basically soft donor sites like sulphhydryl group and borderline donor sites like peptide groups and amino group. The borderline donor sites have equal preference for hard metal ion or soft metal ion and therefore making the complexes highly fluxional in nature. All these things clearly suggest that changes in absorption spectral intensities in different solvents of varying composition will not be very high, but no doubt significant to be easily detectable. We find dimethylformamide (DMF) most effective solvent as it has been found in earlier studies, is also better coordinating ligand very capable in competing with H₂O for lanthanide coordinating sites. Comparative absorption spectra of individual 4f-4f bands of Ln(III):GSH, Ln(III):GSH:Ca and Ln(III):GSH:Zn have been recorded and the oscillator strengths of these transitions are listed in the Tables 4.01 - 4.08. Some typical comparative absorption spectra of Ln(III): GSH and Ln(III):GSH:Zn(II) are given in the

thesis by recording each of the considered five 4f-4f bands. These individual bands have been recorded with much improved resolution and after excluding the effect of free ligand. Thus the oscillator strength values observed are sufficiently accurate, as for obtaining reliable Judd-Ofelt intensity (T_λ) parameters, the oscillator strength accuracy is most relevant.

Judd-Ofelt (T_λ) intensity parameters determined experimentally show substantial sensitivity towards coordination changes caused by the presence of polar organic solvents of varying composition. The magnitude of oscillator strengths (both observed and calculated) varies regularly with the nature and composition of the solvent. Since the 4f-4f transition absorption pattern does not change nor there is any remarkable change in the magnitude of Judd-Ofelt (T_λ) intensity parameters, clearly suggests that basically coordination polyhedra of Ln(III):GSH or Ln(III):GSH:Ca(II) or Ln(III) : GSH : Zn(II) does not change. No doubt minor changes do occur but these do not inflict any remarkable effect on the coordination geometry. The discussion of T_λ parameters and their compositional dependence and sensitivity as a whole will be discussed in later section of this chapter.

The minor changes in the coordination environment due to the variation of solvents and their composition as well as pH variation, bring changes in the energy interaction, nephelauxetic and bonding parameters, along with the variations observed in intensity parameters (oscillator strengths of 4f — 4f bands, and computed values of Judd—Ofelt (T_λ) intensity parameters). The magnitude of changes in the nephelauxetic, bonding,

covalency parameters (all are included in energy interaction parameters) is significant less than that observed in intensity parameters.

5.3 GLUTATHIONE:

5.3.1 Structural Features and Complexation Explored Through Quantitative

4f- 4f Transition Spectral Analysis:

While undergoing reactions with metal ion, glutathione acts like polydentate ligand, offering two carboxylate oxygen, an amino nitrogen, a sulphhydryl group and two amide groups as potential donor sites. No doubt the structure of glutathione is such that all its potential binding sites cannot simultaneously coordinated to the same metal ion, due to spatial orientation of different groups glutathione skeleton. The sulphhydryl group of glutathione (GSH) is extremely sensitive towards oxidation, which is catalyzed by the presence of metal ions, with concomitant reduction of metal ion. Such interaction is responsible for changing the activity of GSH with cellular components.

The coordination chemistry of glutathione is of great interest, because it serves as model stem for understanding the binding of metal ions by larger peptides, proteins and in a number of metalloenzymes.⁷⁰⁻⁷² The complexation of Glutathione with metals is also of great relevance, as it serves as an indicator for the chemistry of thiol-disulphide interchange reactions⁷³⁻⁷⁴. Glutathione is widely present both intra and extra cellularly in relatively high concentration and it is the most abundant non protein thiol in our body. Glutathione metabolism (Figure 1.05) shows clearly the biochemical path ways which are connected mostly directly and sometimes indirectly with several functions of glutathione

like cellular protection (against reactive oxygen compounds, other toxic compounds of endogenous and exogenic origin, free radicals) catalysis, metabolism and transport.

Complexation of several endogenous metal ions by this tripeptide in intact erythrocytes has been detected directly and noninvasively by NMR spectroscopy⁷⁵⁻⁷⁸.

5.3.2 Glutathione Acid-Base Chemistry:

The acid base chemistry of GSH at the molecular level is described by eight microscopic constants shown in Figure 1.07 using the co-ionisation scheme.

The acidities of different functional groups change significantly with the dielectric constants of the solvents. The acidity of the sulphhydryl and ammonic group changes dramatically from 1.6 to 0.4 (k's)

Glutathione is known to involve in a number of cellular functions like maintenance of membrane integrity and cytoskeletal organization, regulation of protein conformation, enzymatic activity and promotion of neurotransmitter release⁷⁴.

A number of biochemical and physiological roles are played in animal metabolism by (GSH) and Glutathione oxidized (GSSG). Depletion of glutathione levels brings;⁷⁹

- a) A decreased level of glutathione in blood plasma tissue and cells in suspension culture.
- b) Increased sensitivity of cells to radiation under hypoxic and aerobic conditions, oxidative damage to certain cells.
- c) Decreased damage to embryonic tissues.

- d) Reversal of drug and radiation rescotance.
- e) Increased damage to embryonic tissues.
- f) Formation of cataract in newborn rats.
- g) Inhibition of development of thermo tolerance, and
- h) Decreased synthesis of leukotriences and prostoglandin.

Orrenius and Bellomo^{79,80} and other coworkers^{81,82} have shown very clearly about the very important role of glutathione in maintenance of intracellular Ca(II) ion homeostasis. This activity is apart from other activities of glutathione, like maintenance of membrane integrity, cytoskeltal organization, regulation of protein conformation, enzymatic activity and promotion of neurotransmitter release. Above findings are based upon studies with both intact cells and subcellular organdies, functions exposed to toxins which caused thiol depletion and subsequent disruption of intracellular Ca(II) ion homeostasis. When intracellular GSH is depleted and protein thiols are affected a combination of Ca(II) ion release from intracellular stores and inhibition of Ca(II) extrusion produces marked increase in cytosolic Ca(II) concentration followed by loss of cell viability. If the toxic challenge is withdrawn before this occurs, if the hepatocytes are treated with thiol reducing agents, the inhibition of Ca(II) transport and increase in cytosolic Ca(II) becomes transient and then recovers from toxic insult. This has been shown to exist clearly that interference with GSH and protein thiol dependent regulation of cellular Ca(II) metabolism is important in the development of oxidative injury to hepatocytes⁸³.

5.3.3 Glutathione and Calcium Metabolism:

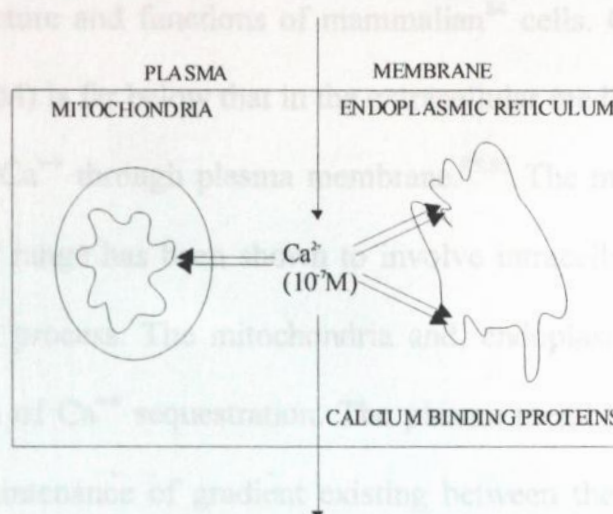


Figure 5.03 Schematic representation of transport and compartmentation processes involved in regulation of intracellular Ca^{2+}

Glutathione has been known to involve in a number of cell functions like maintenance of membrane integrity and cytoskeletal organization, regulation of protein conformation and enzymatic activity and promotion of neurotransmitter release.⁷⁴ There have been several detailed studies which provided strong proof that Glutathione is involved in maintaining intracellular calcium ion homeostasis from the studies with both intact cells, subcellular organdies fractions exposed to toxins which cause thiol depletion and subsequently disrupt intracellular Ca^{++} homeostasis⁷⁹⁻⁸¹ calcium ion functions as an intracellular messenger in mammalian cells. It plays a central role in muscle contraction, secretion of exocrine, endocrine and neurocrine products, control of cell metabolism, regulation of cell growth and differentiation.⁸⁴

A disruption of intracellular calcium ion homeostasis may therefore lead to dramatic changes in both structure and functions of mammalian⁸⁴ cells. Cytosolic ionic calcium concentration ($\sim 10^{-7}$ M) is far below that in the extracellular medium ($\sim 10^{-3}$ M) despite a continuous influx of Ca^{++} through plasma membrane.^{85,86} The maintenance of cytosolic Ca^{++} within a narrow range has been shown to involve intracellular binding, as well as compartmentalization process. The mitochondria and, endoplasmic reticulum represent the predominant sites of Ca^{++} sequestration. The plasma membrane Ca^{++} pump plays a major role in the maintenance of gradient existing between the extra and intracellular environment by actively extruding Ca^{++} from the cell.⁸⁷

Mitochondria have long been known to be able to accumulate and retain Ca^{++} at the expense of energy provided by coupled respirations of ATP hydrolysis. The mechanism involved in enters mitochondria electrophoretically in response to membrane potential, negative developed across the inner membrane during electron transport. Release of Ca^{++} from mitochondria can be induced either by factors that cause collapse of the transmembrane potential or selective inhibitors of uniport carrier. Because of simultaneous operation in both influx and efflux system, a slow continuous cycling of Ca^{++} occurs across inner membrane of mitochondria. Transport and compartmentalization process involved in the regulation of intracellular Ca^{++} homeostasis in hepatocytes is shown in Figure 5.03. Most of extra-mitochondrial Ca^{++} present in cell is sequestered within the recognized to play important role as intracellular store of Ca^{++} mobilized following hormonal stimulation of liver.⁸⁸

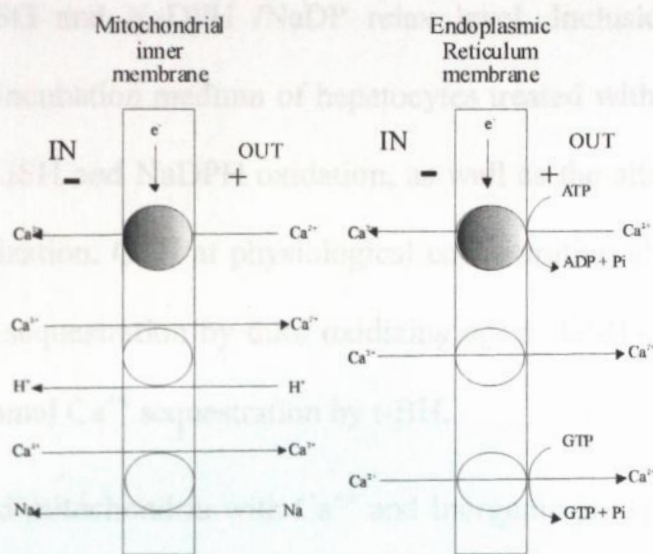


Figure 5.04 Mechanism and routes of Ca^{2+} transport in liver

Famuiski and Carafoli⁸⁹ demonstrated that calmodulin and Ca^{++} stimulated the phosphorylation of 20 KD microsomal protein which in turn can act to accelerate Ca^{++} uptake. Dephosphorylation of this protein, controlled by a Ca^{++} dependent protein phosphate can deactivate the uptake mechanism. Beneditti et al⁹⁰ reported ATP dependent Ca^{++} sequestration by liver microsomes, is significantly stimulated in presence of glucose-6-phosphate. This stimulation of Ca^{++} sequestration by glucose-6-phosphate hydrolysis could not be due to intravesicular formation of phosphate, serving as Ca^{++} entrapping agent. The depletion of glutathione and protein thiols can affect several cell functions, including various enzymes and transport activities like. Ca^{++} translocases, whose modification can result in disruption of intracellular Ca^{++} homeostasis which appears to play very important role in the development of toxic cell injury.^{91,92} Ca^{++} release both from mitochondria and endoplasmic reticular pools and this release is preceded by GSH and Na DPH oxidation and appears to be intimately related to the

decreased GSH/GSSG and NADPH /NaDP relax level. Inclusion of reducing agent dithiothrietol in the incubation medium of hepatocytes treated with t-butylhydroperoxide (t-BH) can prevent GSH and NADPH oxidation, as well as the alteration in intracellular Ca^{++} compartmentalization. GSH at physiological concentration abolished the inhibition of microsomal Ca^{++} sequestration by thiol oxidizing agent. GSH can protect against the inhibition of microsomal Ca^{++} sequestration by t-BH.

Treatment of isolated mitochondria with Ca^{++} and Inorganic phosphates was pursued by Savage et al⁹³ while monitoring the release of mitochondrial Glutathione. The permeability of inner membrane was increased when isolated mitochondria was treated with Ca^{++} in Inorganic phosphates, which was ascribed to mediation through a non-selective Ca^{++} dependent pore. TI permeability of inert membrane change cause towards rapid efflux of glutathione and calcium along with the loss of couple functions with large amplitude swelling. These workers found the release of both glutathione and calcium inhibited by the addition of CYCLOSPORIN-A, a potent inhibitor of permeability transition. All these, as well as so many other findings suggest that liver microsomal Ca^{++} pump activity may be modulated by alteration of the intracellular thiol disulphide balance⁹⁴. Depletion of intracellular GSH seems critical and prerequisite for the alteration in and protein thiols are affected a combination of Ca^{++} extrusion produces a marked increase in cytosolic Ca^{++} concentration followed by loss of cell viability. In our body calcium is one of the most abundant metal ion and plays very important role in several physiological and biochemical processes. Since Ca^{++} is diamagnetic, hence

spectroscopically uninformative ion. Lanthanides on the other hand are paramagnetic (Except La^{3+} and Lu^{3+}), but resemble very closely in ionic sizes and in coordination characteristics with that of Ca^{++} and therefore have successfully been used in isomorphous substitution of Ca^{++} ion from the biomolecules, as well as structural probe in following a number of biochemical reactions involving Ca^{++} .

It is therefore, that we have used the 4f - 4f transition spectra of lanthanide(III) ions as ABSORPTION SPECTRAL PROBE in investigation, the changes in the conformation, binding characteristics of biomolecules and in exploring intricacies of Ln(III) biomolecular^{95,96} interaction. We have taken an important tripeptid (biomolecule) though very important biochemically, yet easily available for our study. The γ -L-glutamyl-L-cysteinyl glycine named as GLUTATHIONE reduced (GSH), has been chosen because it occurs intracellularly and plays several important biochemical activities, interacting strongly with Zn^{2+} on one hand but is equally involved in complexation with Ca^{++} found intra as well as extracellularly. This tripeptide has been shown as mentioned above control Ca^{++} influx and efflux intracellularly as well as participating a number of biochemical reactions involving Zn^{2+} . It is a multidentate ligand possessing eight potential donor sites. Some of which are favoured by hard metal ions like Ca^{++} and therefore also Ln(III) while others opt for some metal ions like Zn^{2+} , Cd^{2+} and Hg^{2+} .

Biological fluids are multimetal multiligand systems, where different metal ions compete for different binding sites of the biomolecular ligands, while different ligating sites experience competition for endogenous metal ions. Thus in such systems, there is a

competition for endogenous metal ions. Thus in such systems, the interactions of combining atoms can be antagonistic (i.e., the two metal ions competing for identical donor sites of the biomolecule) or stimulative when different metal ions go for different coordinating site of the biomolecular ligand. As we have discussed earlier the living cell comprises of both hard metal ion like Na^+ , K^+ , Ca^{2+} and Mg^{2+} at the same time cytoplasm contain soil metal ions like Zn(II) and Cu(II) . Animal cell also contain sulphur proteins in thiolate and disulphide forms and glutathione reduced being the most abundant of the lot. Paramagnetic Pr(III) and Nd(III) are chosen for the present study because all these lanthanides(III) resemble Ca(II) so much, that these have been used as PROBES in structural studies. The Nd(III) ion has extensively been used spectrophotometrically, because their 4f - 4f spectral intensity analysis though is not suitable to that extent, but Pr(III) ion resembles very closely in size to Ca(II) both in octacoordinated and nonacoordinated structures (Table 1.04).

The important event taking place in menadione induced perturbation of intracellular thiol and Ca^{2+} homeostasis and development of cytotoxicity in hepatocytes as shown in Figure 5.05.

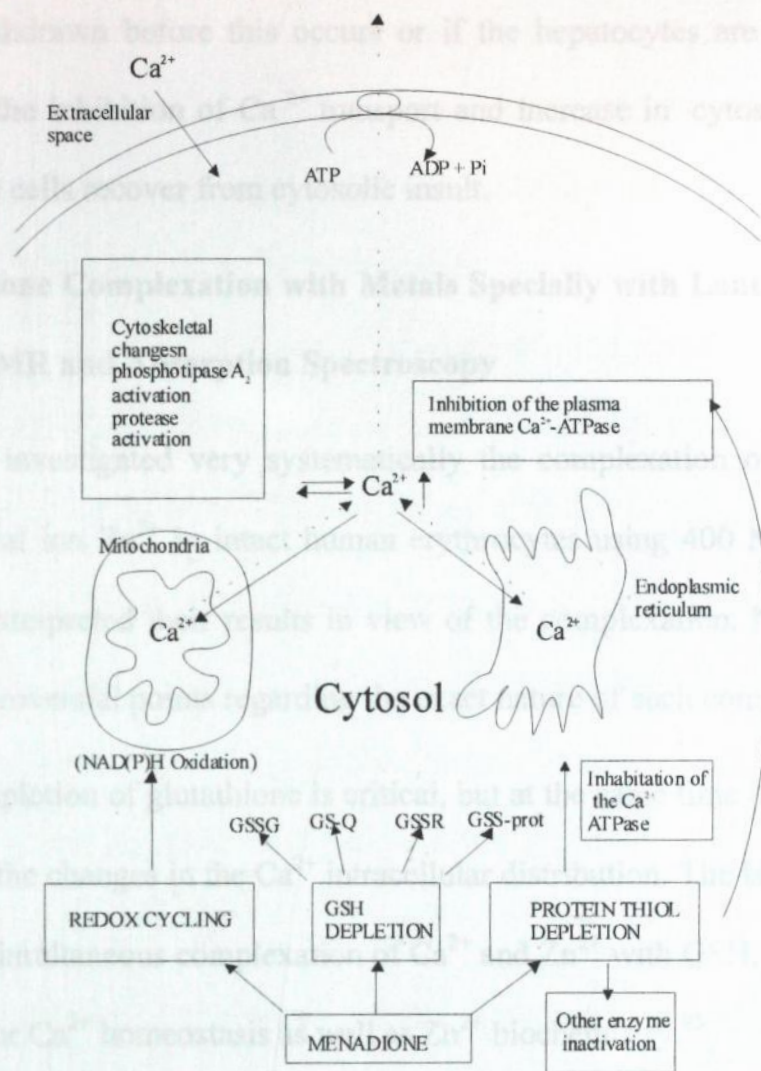


Figure 5.05 Schematic illustration of mechanism of menadione induced perturbation of intracellular thiol and Ca^{2+} hemostasis and development of cytotoxicity in hepatocytes.

Depletion of intra-cellular GSH is no doubt critical and most probably prerequisite for the development of change in intracellular Ca^{2+} distribution. When intracellular GSH is depleted and protein thiols are affected, a combination of Ca^{2+} release from intracellular stores and inhibition of Ca^{2+} concentration followed by a loss of cell viability. If the toxic

challenge is withdrawn before this occurs or if the hepatocytes are treated with thiol reducing agent the inhibition of Ca^{2+} transport and increase in cytosolic Ca^{2+} become transient and the cells recover from cytosolic insult.

5.3.4 : Glutathione Complexation with Metals Specially with Lanthanides Explored Through IR, NMR and Absorption Spectroscopy

Rabenstein has investigated very systematically the complexation of glutathione with endogenous metal ion Zn^{2+} in intact human erythrocytes using 400 MHz proton NMR. However they interpreted their results in view of the complexation. No doubt there are still several controversial points regarding the exact nature of such complexes.⁷⁰

The cytosolic depletion of glutathione is critical, but at the same time it is prerequisite for development to the changes in the Ca^{2+} intracellular distribution. The later changes can be ascribed to the simultaneous complexation of Ca^{2+} and Zn^{2+} with GSH, which in turn may be responsible for Ca^{2+} homeostasis as well as Zn^{2+} biochemistry.⁹⁵

The outstanding work of Orrenius and Bellomo have clearly shown that glutathione molecule plays dominant role in maintaining intracellular Ca^{2+} ion homeostasis needless to add such activities involved in vivo complexation of Ca^{2+} with glutathione.⁷⁹⁻⁸¹

Calcium ion one of the most abundant and essential metal ion in animal and human system, yet it is spectroscopically non-informative. Lanthanide(III) ions resemble very closely to calcium ion in ionic size, coordination characteristics, binding properties, binding affinities towards the donor sites of the biomolecules permit effective isomorphous substitution of Ca^{2+} by Ln^{2+} without altering its structure, conformation and

even the biological activities of the biomolecules. Therefore our attempt is to investigate the simultaneous coordination of two or three chemically different metal ions like Nd/Pr/Er/Eu/La/Y and Zn with glutathione, is an attempt to mimic the simultaneous coordination of Ca and Zn, taking place *in vivo* intracellularly, during Ca^{2+} homeostasis. The paramagnetic nature of Lanthanides provides 4f-4f transition signals, which are being used as SPECTRAL PROBE in following the coordination chemistry of GSH with endogenous metal ions Ca, Zn and others in *in vivo* condition.

Sakamoto and coworkers found that the bi-nuclear complexes involving Pr^{3+} Nd^{3+} and a soft metal ion (Co^{3+} , Cu^{2+} , Ni^{2+} and Zn^{2+}) to display unique selective solvation associated with the nature of lanthanide.⁹⁶⁻⁹⁸ Lanthanide ions prefer selective coordination by DMF, dioxane, water and MeOH while MeCN and pyridine initiate coordination at the Zn(II) or Cu(II) center.

The formation of double and triple helical, both homonuclear and heteronuclear complexes involving lanthanide like Eu, Tb and d-block transition metal Zn or Cu in solution involving multidentate heterocyclic units, have shown high potentiality of being building blocks with controlled magnetic and photophysical properties.⁹⁹

The design of new supramolecular devices involving double and triple helical homonuclear and heteronuclear complexes involving paramagnetic f-block metal ion and a d-block metal ion for electron transfer, charge separation, light conversion is a subject of tremendous and current interest. These show high potential of their applications as fluorescent sensors, natural, medical, analytical and bioinorganic sciences.

The present work involving absorption spectral 4f-4f transition analysis, helps in extracting significant information regarding the mode of lanthanide bonding and structure of lanthanide complexes with coordinating and biologically relevant molecules, both in crystalline states and in solutions. The simultaneous coordination of Nd and Zn with naturally occurring tripeptide glutathione, is just to mimic probable interaction of Ca and Zn with glutathione taking place intracellularly.

Biological fluid is a multi-metal, multi-ligand system, in which effective concentrations of metal complexes formed *in vivo* are interrelated and their influence on each other can be either be STIMULATIVE (where different ions involved in complexation endorse each other complexation, i.e. strengthening the complexation of other metals) or ANTAGONISTIC (where different ions compete with each other for the similar binding sites of the biomolecule and therefore canceling each others' interaction).

Glutathione with the sequence γ -L-glutamyl-L-cysteinyl-glycine, with eight potential donor sites, some of the sites like carboxylate are strong complexing ligand sites for lanthanide and calcium, because this ligand can compete effectively with solvent molecules (water or aquated organic solvents), for Ln coordination, however sites like sulphhydryl group is the most suitable donor for soft metal Ion like Zn or Cd. The borderline donor sites like peptide and amino groups can participate with either type of metal ion if required for stable chelation. Carboxylate groups like gluta and glycolic (the former is around 10.8 times more acidic than the later) are very strong ligands for lanthanide and therefore coordinate very effectively with lanthanide irrespective of the

nature of the solvent (aqueous or aquated organic solvents). In presence of metal ion like Ln(III) both glutamyl glutamic acid component and glycine component are deprotonated in presence of Ln(III) even at pH = 1 or above. Therefore it is always coordinated as charged species. The IR spectra of GSH, Ln(III) : GSH and Ln(III) : GSH: Zn(II) complexes [Figure 5.08 (a) and (b)] clearly show that the binding mode of carboxylic ligand is bidentate, The coordination of Zn(II) to sulphhydryl group is very prominent, but interesting observation is that, the sulphhydryl group band characteristic of GSH gradually reduces in its intensity and becomes very weak. This suggests that in Ln(III) : GSH complex there is a clear cut interaction of Ln(III) with cysteinyl group formed as a result of deprotonation of sulphhydryl group, this is somewhat unusual because Ln(III) is hard metal ion while sulphhydryl is soft ligand and generally such interaction is quite rare. The coordination of sulphhydryl-S to Ln(III) enhance the stability of Ln(III):GSH chelate and Ln(III):GSH:Zn(II) complex, we observe very strong Zn-S complexation which is quite understandable in view of high affinity of Zn towards sulphur donor site of the biomolecule. During heterobimetal complexation of Ln(III) and Zn with GSH, it is the Zn²⁺ ion which forms strong bond with sulphhydryl sulphur, in absence of Zn(II), i.e. Ln(III):GSH complex there is clear cut interaction of Ln(III) with GSH sulphur, inspite of the inherent mismatch the affinities of Ln(III) and sulphur.

5.4 : Interpretation of Experimental Results

5.4.1 : Absorption Spectra of the Complexes

In continuation of our interest in the thiol-disulfide interchange relation in peptides and proteins as well as quantitative transitions we are reporting here sulphur containing amino acids. In view of our continuous interest in the sulphur containing amino-acids and peptides including metalloenzymes, which involve directly or indirectly thiol disulfide interchange being explored through paramagnetic lanthanide involving 4f-4f transition as well as cyclic voltametry spectral characterization.

We are reporting here the systematic spectra and structural correlation of glutathione hetero bi- and tri- metallic complexation at pH = 4 and in different solvent compositions. Different experimental conditions like solvent variation and pH, create significantly different coordinating environment which significantly effects the binding of glutathione. The Ln(III) being a hard metal acceptor (in Pearson's scheme) and therefore will occupy hard donor sites of a biomolecule. Carboxylic groups are the strongest ligands and are ablest competitor for lanthanide coordination even in presence of water. Comparing to carboxylic group the carbonyl oxygen and sulphhydryl sulphur are much-much weaker, no doubt, certain specific experimental chemical environment may induce the participation of sulphhydryl sulfur or carbonyl oxygen. However such bonding (if it is formed) can be broken especially in presence of soft metal ion acceptor (like Zn), because neutral carbonyl group, peptide-NH, and sulphhydryl sulphur are better suited for coordination soft metal ion like Zn, Cd, Hg, and even Cu or Ni.

As discussed in detail in introduction and early part of this chapter about the activities glutathione and its role in human metabolism, especially Ca(II) ion metabolism, the interaction glutathione both reduced (GSH) and oxidized (GSSG) with Ca(II) and also with Zn(II) within the cell most probably play predominant role in Ca(II) homeostasis. Zn(II) ion occurs intracellular and sometimes extracellularly also, is known to form very stable complex *in vivo*. Therefore Ca(II) and Zn(II) ions within the cell *in vivo* may involve hetero bimetallic simultaneous complexation with GSH and may therefore be responsible directly or indirectly in controlling the level of GSH intracellular and sometimes in extracellular, and therefore affecting a large number of biological activities.

The comparative absorption spectra of Ln(III), Ln(III):GSH, Ln(III):GSH:Ca and Ln(III):GSH:Zn in aquated organic solvents (DMF+Water, MeCN+Water, Dioxane +Water) shown in Figures 4.01 – 4.10, clearly show that the addition of GSH to Ln(III) both in water and aquated organic solvents contribute towards enhance intensification of 4f-4f bands. This clearly suggests that GSH behaves as a good ligand for hard metal ion like Nd(III) both in aqueous and as well as aquated organic solvents. The values of inter electronic repulsion and spin orbit interaction parameters along with experimentally determined nephelauxetic parameters gave clear indication about the substantial ionicity of Ln(III):GSH binding. This is clear matched the high solubility of Ln(III):GSH complex in water. The shapes of the observed multiplet to multiplet electronic transition manifolds and overall absorption spectral pattern has been four quite similar to

that shown by Ln(III) aquo ion and therefore suggesting almost similar nonacoordinated environment around in Ln(III):GSH complex.

A look at the table listing energy interaction Slater Condon inter-electronic repulsion Slater Condon (F_k), Lande spin orbit coupling constant (ξ_{4f}), nephelauxetic ratio (β), bonding parameter ($b^{1/2}$) and percent covalency (δ) parameter reveal that addition of GSH to Nd(III) brings about lowering in inter-electronic repulsion (F_k) and spin orbit interaction ξ_{4f} parameters, as a result of long wave shift of the bands. The complex formed between Ln(III) and GSH, in different solvents (DMF, MeCN, MeOH and Dioxane) also exhibited parallel nephelauxetic effect, as compared to Ln(III) aquo ion. Absolute values of nephelauxetic effect (β)covalency (δ) and bonding parameters (b) clearly suggest that aquated organic solvents also involve Ln(III) : GSH interaction predominantly ionic, no-doubt when we compare amplitude of nephelauxetic effect observed in Ln(III) : GSH (in nona-coordinated Ln(III) species) with nona coordinate haloacetate¹⁰⁰ and amino acid derivatives^{101,102}, we find much greater nephelauxetic effect in Ln(III) : GSH complexes.

It is understandable in view of the involvement of glutathione molecule substantially even in the inner sphere of coordination in aqueous medium contradictory to the involvement of both haloacetate and aminoacid moiety, In predominately outer sphere of lanthanide coordination. The increase in covalency in general is accompanied by increase in the magnitude of T_λ parameters. It should be noted that the covalency is not the sole factor, which influence T_λ intensity parameters. nephelauxetic effect, which caused by the

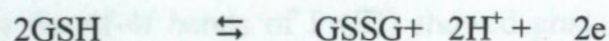
lowering of the excited state of the ion by surrounding ligand field. The change in T_λ parameters in absence of substantial nephelauxetic effect as found in present series of complexes shows that the non symmetrical part of the field has major influence on T_λ parameters. The different potential donor coordinating sites of glutathione (GSH) are responsible for the distortion of the polyhedron, mainly of "O" around Ln(III), lowers the sites symmetry and increasing the probability of the 4f -4f transition. Using the Judd-Ofelt theory, this picture can be interpreted through following equation,

$$T_\lambda = \chi \left[\frac{8\pi^2 m}{3h} \right] (2\lambda + 1) \sum_{p,t} |A_{t,p}| \xi^2(t, \lambda) \quad (17)$$

The $A_{t,p}$ (t, odd) are odd parity terms in crystal field expansion depending on site symmetry of the ion in given matrix. The quantity $\xi^2(t, \lambda)$ contains integrals involving radial part $4f^n$ wave function and excited opposite parity electronic state wave function $\xi^2(t, \lambda)$ is a measure of symmetric part of ligand field (amount of covalency) and appears to vary slightly in these complexes. However T_λ parameters vary with the change of solvent, hence the quantity $\xi^2(t, \lambda)$ which is not dependent on the nature of the coordinating ligand does not appear to be a factor contributing effectively to the changes in T_λ . The equation shows that the remaining quantity which appears to be responsible for the variation of T_λ parameters, is the asymmetric part of the ligand field expansion. The $A_{t,p}$ (t, odd) arising mainly from distortion of geometry around lanthanide ion.

5. 4. 2 : Binding of Ln(III) with GSH in Presence or Absence of Zn(II)

Glutathione (GSH) being multidentate ligand with some coordinating sites suitable for hard metal ion like Nd(III), while some being sites preferably opt for soft metal ions like Zn (II), as well as Cu(II) or Cd(II). Hence we thought it proper to investigate the ligating behaviour of this ligand with metal ion like Ln(III) or metals like Ln(III) and Zn(II) facilitated by the utility of comparative absorption and absorption difference spectroscopy involving electronic dipole multiplate to multiplate transition manifolds as PROBE. The sulphhydryl group of GSH has been reported to be oxidized and its oxidation is catalyzed even by the trace of metal ion like Fe(II), Co(II), and Cu(II) interestingly. Our studies have also shown that lanthanide ions also induce such catalytic conversation of GSH in to GSSG through complex formation.



Our preliminary studies have shown that Cu(II) catalyzed oxidation generally increases with pH, this suggests the involvement of deprotonated sulphhydryl group. The rate of oxidation has been found to increase with the concentration of metal ion. Naturally the metal catalyzed oxidation will involve therefore the formation of GSH complexes, which are reactive species. It has been found that Cu(II) oxidizes sulphhydryl group directly by the mechanism involving the formation of inner sphere complex Proton NMR spectroscopy of GSH and EPR measurements of Cu(II) has shown that, addition of Cu(II) caused only little broadening of GSH resonance indicative of little, if any binding under acidic medium However, at pH>8 the addition Cu(II) to GSH SOLUTION first caused

the, broadening of ^1H resonance from cysteine. residue are preferentially attached while γ -glutamyl- αCH resonance could be detected only at considerably higher pH. All these factors point towards the sulphhydryl and deprotonated peptide nitrogen of cysteinyl residue are preferentially attacked while γ -glutamyl group is involved at the later stage. Since no attempt has earlier been made to explore the relative and preferential binding capability of different binding sites of GSH in presence of both hard metal ion and soft metal ion. We thought worthwhile to utilize the comparative absorption and absorption difference spectrophotometry along with the variation and magnitude of various spectral parameters to explore the simultaneous coordination of Nd(III) and Cu(II) to GSH.

The addition of Zn(II) to Pr(III) : GSH gave significant changes in the energies, shift and oscillator strength of $^3\text{H}_4 \rightarrow ^3\text{P}_2$, $^3\text{H}_4 \rightarrow ^3\text{P}_2$, $^1\text{D}_2$ ps eudohypersensitive 4f-4f bands. Slowly the 4f-4f bands of Pr(III) showed gradual increase in the intensity along with significant long wave shift (Figures 4.01 – 4.05), which indicated that addition of Zn(II) to Pr(III) : GSH strengthened the binding of Pr(III) : GSH.

The intensities of 4f-4f bands showed gradual change In the intensity with time, the d-d band intensity decreased while the intensity of 4f-4f bands increased with time, this is understandable in view of the auto oxidation of GSH to GSSG, catalyzed by Zn(II) and complexation with lanthanide. In order to understand more about this complexation, We have tried to isolate this complex from the reaction of Pr(III) : GSH : Zn(II) in 1:1:1 stoichiometry. The reaction gave greenish crystalline solid, which initially was highly soluble in water but slowly it lost its solubility and became insoluble in most of the

inorganic solvents. This low solubility of the isolated complex indicates the highly polymeric nature of the complex. Most probably the structure involving octacoordinated Pr(III) and Zn(II) six coordinated preferably highly distorted octahedral stereochemistry. As time passes the association of this kind of species finally appears to lead to the formation of highly polymeric Zn(II):GSSG cluster with enclosed Pr(III) ion.

We have shown that some of the $4f - 4f$ transitions which do not obey selection rules yet show remarkable sensitivity towards minor coordination changes around lanthanide. We have coined the term LMP. These days the term hypersensitive has been generalized. The main contribution of the present work is even in the hetero metal complexation of GSH with metals like Pr/Nd in presence and absence of Zn and Ca in water and aqated organic solvents at $\text{pH} = 4$. The ligand is same but the experimental conditions are different, therefore the changes induce in the immediate coordination environment around Pr/Nd due to varying ligating behavior GSH by solvent change and stoichiometry of mixed solvents. We have shown the intensities and oscillator strength of all the observed $4f - 4f$ transitions, which significantly changes. These changes are also reflected through the values and there variation in Judd - Ofelt intensity parameters (T_λ , $\lambda=2,4,6$). We are also showing through our study the energy interaction parameter i.e. Slater Condon (F_K), Lande spin orbit coupling constant (ξ_{4f}), nephelauxetic ratio (β), bonding parameter ($b^{1/2}$) and percent covalency (δ). The changes in the energy interaction and intensity parameter determined from the observed absorption spectra of hetero metal complexation of GSH with Pr/Nd and Ca/Zn.

5.4.5 : ^1H NMR Spectral Analysis of GSH, Ln(III) : GSH and Ln(III):GSH:Zn(II)

and 3.45 ppm in the Nd(III):GSH:Zn(II) complex (Figure 5.07) with a coupling constant of 6.35 Hz. This shows that the presence of Zn(II) strengthens the binding of the

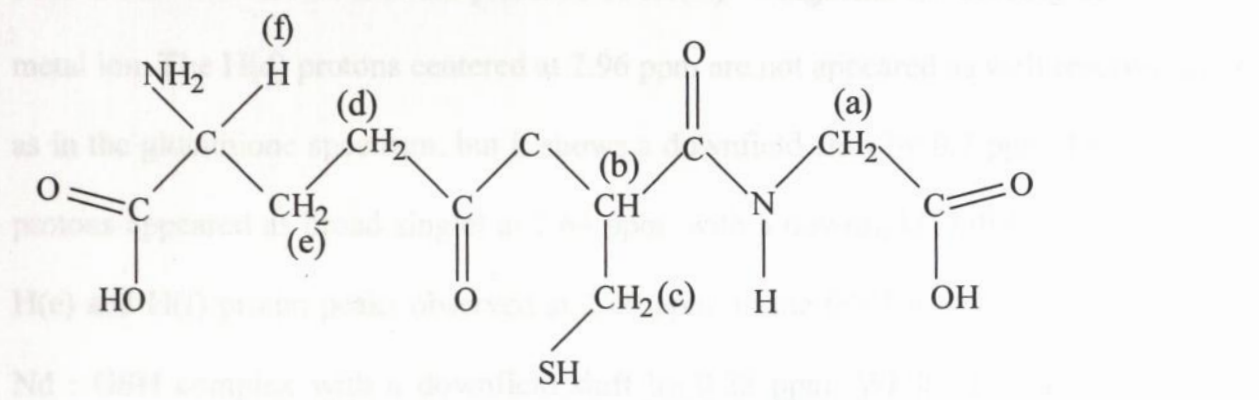


Figure 5.06 Structural Formula of Glutathione

The ^1H spectrum of the Nd(III) : GSH complex (Figure 4.10) gives evidence of the interaction of glutathione (GSH) with Nd(III) ion. Table 4.02 clearly shows the shifts in the proton peaks. All the peaks are showing a down field shift in the Nd : GSH complexes. The H(a) proton peak observed at $\delta_{3.98}$ in the ligand (GSH) spectrum is shifted to $\delta_{4.37}$ in the complex. The triplet H(b) proton (Figure 4.10) peaks centered at $\delta_{3.83}$ in the ligand to shifted to $\delta_{4.19}$. Interestingly H(c) proton peak also shows a down field shift which indicates the weak interaction of sulphur with Nd(III) ion. Similarly other proton peaks of the complex are also showing down field shift the H(e) and H(f) proton peaks are slightly broadened due to the paramagnetic nature of the complex. In the ^1H spectrum of the Nd(III)-GSH-Zn complex, the H(a) proton peak is shifted from 4.00 ppm to 4.32 ppm. The peak is slightly broadened and can be accounted for 3H, which indicates that the CH proton (b) is merged with these protons. The doublet H(c) proton

peaks observed at 2.97 ppm and 2.91 ppm in the ligand spectrum are shifted to 3.21 ppm and 3.15 ppm in the Nd(III):GSH:Zn(II) complex (Figure 5.07) with a coupling constant of 6.35 Hz. This shows that the presence of Zn(II) strengthens the binding of S with the metal ion. The H(d) protons centered at 2.96 ppm are not appeared as well resolved triplet as in the glutathione spectrum, but it shows a downfield shift by 0.7 ppm. H(e) and H(f) protons appeared as broad singlet at 2.64 ppm. with a downfield shift by 0.57 ppm. The H(e) and H(f) proton peaks observed at 2.20 ppm. in the GSH is shifted to 2.42 ppm. in Nd : GSH complex with a downfield shift by 0.22 ppm. While H(e) and H(f) proton peaks observed at 2.64 ppm. in the Nd(III):GSH: Zn(II) complex showing a downfield shift by 0.44 ppm. This increase in the value gives evidence of the involvement of Zn(II) in complexation with glutathione (GSH) and Nd(III) ion.

Table 5.02 ¹H NMR δppm for protons of GSH in different complexation states :

Compound	a	b	c	d	e and f
GSH	3.98	3.77	2.97	2.64	2.20
		3.83	2.91	2.57	
		3.90		2.49	
Ln(III):GSH	4.37	4.19	2.98	2.84	2.61
				3.12	
Ln(III):GSH:Zn	4.32		3.21	2.96	2.64
			3.15		

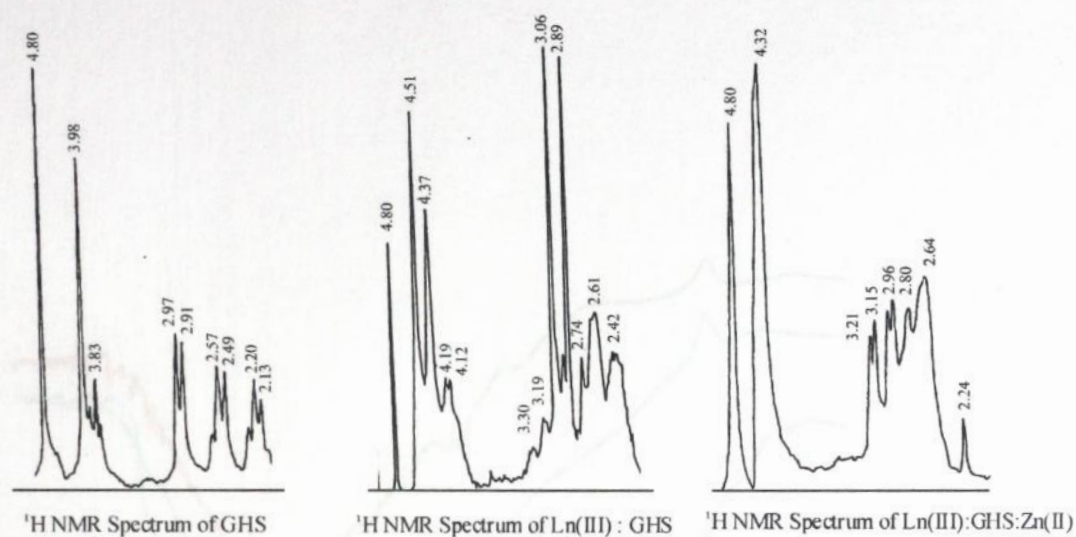


Figure 5.07 ¹H NMR Spectra of GSH in different complexation state

5.4.7 Infrared Spectral Analysis of the GSH, Ln(III) : GSH, Ln(III):GSH:Zn(II) complexes:

Preliminary infrared spectral studies have been made to find out the important structural features of Ln(III):GSH complexes. The spectra is quite complicated because of the presence of several functional groups and hence to extract any quantitative information regarding the complexes will be misleading.

Two important information which could provide by our IR spectra :

- (i) regarding the changes taking place in the sulphhydryl (SH) group of the biomolecule, when it undergoes complexation, and
- (ii) the carboxylic group attachment to lanthanide.

Sulphydryl Group:

The IR spectrum of the glutathione (GSH) shows a stretching frequency due to sulphydryl(SH) group occurring as a sharp intense band around 2523 cm^{-1} the addition of Nd(III) to glutathione clearly leads to its deprotonation, in all probability, it induces the formation of lanthanide(III) - sulphur bond. This looks little but surprising in view of the hardness of the Ln(III) ion which generally do not prefer sulphur for coordination, but the IR spectra (Figure 5.08) shows that without doubt deprotonation of sulphydryl group occurs even at pH 5.00 at which the complexes are being synthesized.

The IR spectra in the $800 - 200\text{ cm}^{-1}$ region show the appearance of new bands, and some of these can be ascribed to Nd - S. The addition of Ca(II) or Zn(II) to lanthanide(III) : GSH complex enhances the deprotonation tendency. the Ca(II)- or Zn(II) - S bands can be expected in the region $800 - 200\text{ cm}^{-1}$ which we could not resolve. The carboxylic group frequencies as well as carbonyl group frequencies are highly sensitive when the complex has metal ion like lanthanide(III). This is clearly visible in the IR spectrum. The carbonyl (CO) stretching frequency occurring at 1715 cm^{-1} in the ligand (GSH) spectrum is shifted to the lower field at around 1680 cm^{-1} in Ln(III) : GSH complex and showing a shift at 1675 cm^{-1} and 1630 cm^{-1} in Ln(III): GSH: Zn(II) complex, indicating the involvement of CO group in binding with the lanthanide ion.

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CHAPTER NO. VI

SUMMARY AND CONCLUSION

The biological fluids are basically multimetal-multiligand system with abundance of organic and inorganic species present in micro, sub-micro and mili-molar concentration with fluctuating lipophilicity and lipophobicity in widely divergent physiological pH. These multidimensional characteristics of the biological fluids provide platforms for a number of TEMPLATE synthesis, homogeneously catalyzed transformations, redox reactions, influx and efflux of ionic and molecular species both intra- and extra-cellularly. Thus these immensely important biological fluids are essentially multimetal-multiligand systems, where a number of endogenous metal ions compete with the coordinating sites of multidentate macromolecular metabolites and multidonor sites also experience strong competition for different metal sites. Thus the binding of metal to a particular donor site of the biomolecule depends upon a number of factors like donor capability, structure, conformation, orientation, physiological pH, presence of similar type of metal ions and their relative abundance. It is considered therefore worthwhile to study the simultaneous coordination of two or three different metal ions with a multidentate biological molecule with immense biological relevance. We have chosen a very important polypeptide glutathione reduced(GSH) which in its reduced form is a

tripeptide with active carboxylate groups, a sulphhydryl group and peptide groups, which has total eight potential donor binding sites for endogenous metal ion complexation.

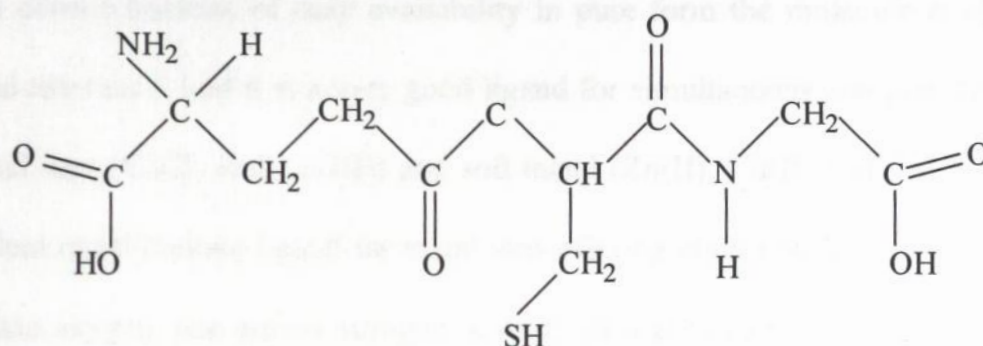


Figure 6.01 Structural Formula of Glutathione

Glutathione, in oxidized form disulphide group, formed as a result of oxidation of oxidation of two glutathione sulphhydryl groups, leading to the formation of a hexapeptide. The coordination chemistry of glutathione reduced i.e. GSH and oxidized i.e. GSSG and its binding with metal ions serves as MODEL SYSTEM for binding of metal ions with proteins and macromolecular polypeptides. The coordination chemistry of glutathione, not only is of interest as it serves as an indicator for the chemistry of thiol-sulphide interchange reactions, as well as in understanding toxicology of several metals, but it is equally relevant in understanding large number of biological functions.

Quantitative absorption spectral analysis involving 4f—4f transition absorption difference and comparative absorption difference spectroscopy has been used by us as PROBE to follow the simultaneous coordination of two or three chemically different metals in tri-nuclear simultaneous coordination of glutathione reduced GSH mainly and

in part the complexation involving oxidized glutathione GSSG in aqueous and in aquated organic solvents at different pH is an attempt to MIMIC the *in vivo* complexation of the GLUTATHIONE (GSH) with endogenous metal ions like Ca(II) and Zn(II). Glutathione has been chosen because of easy availability in pure form the molecule is of immense biological relevance, and it is a very good ligand for simultaneous complexation by both hard metal ions [Ca(II) and Ln(III)] and soft metal (Zn(II), Cd(II) and Cu(II)] ions. It is an excellent multi-dentate ligand for metal ions offering eight potential binding sites two carboxylate oxygen, one amino nitrogen, a sulphhydryl group and two amine groups. The structure of glutathione is such that all its potential binding sites cannot be coordinated to the same metal ions and therefore the coordination chemistry of this multidentate biomolecule is characterized by the formation of protonated and polynuclear species.

The 4f electrons of lanthanides yield three types of transitions:

- i) Internal 4f—4f transitions, which give rise to sharp narrow bands of comparatively weak intensities such transitions are Laporte-forbidden in nature.
- ii) Allowed $4f^n - 4f^{n-1}(n-1)d$ which are relatively broad and intense.
- iii) Broad and often very intense $4f^n - \lambda^{-1} f^{n+1}$ electron transfer bands generally occurring in the ultraviolet region (λ^{-1} represents a hole in the orbital concentrated mainly on ligands).

The presence of internal 4f electron transition spectra in the accessible spectral region for the most of the lanthanides and the sensitivities of such transitions towards immediate coordination environment, makes quantitative absorption spectroscopy involving 4f-4f transitions a powerful tool in the investigation of coordination chemistry and biochemistry of lanthanides specially in solutions.

The electrostatic CFT model provides lot of information yet cannot lead to a complete understanding of lanthanide absorption spectra, as it does not take into consideration the contribution from covalency as a result of nephelauxetic effect arising from the decrease in the inter-electronic repulsion and spin orbit interaction parameters. The increased nephelauxetic effect contributes towards the shortening of the metal-ligand distances and hence has direct effect on the coordination number and geometry of the complex molecules.

The ground state for Nd^{3+} ion is $^4I_{9/2}$. Since coulombic and spin orbit coupling represent major interaction between equivalent 4f electrons, the second order configuration interaction should be included for highly accurate spectral work. To do this one requires the inclusion of higher energy configurations into ground state configuration via electrostatic repulsion terms. For the atom with N-electrons, and the Ze nuclear charge, the non-relativistic Hamiltonian can be written as,

$$H = \sum_{i=1}^N \frac{p_i^2}{2m} - \sum_{i=1}^N \frac{Ze^2}{r_i} + \sum_{i < j}^N \frac{Pe^2}{K r_{ij}}$$

Where the first term represents the kinetic energy of all the electrons, the second term represents the nuclear electrical field and the third term describes the repulsive coulombic potential between pairs of electrons.

The central field Hamiltonian,

$$H_{CF} = \sum_{i=1}^N \frac{p_i^2}{2m} + U_{(n)}$$

The energy levels are found to be highly degenerate, however by the inclusion of covalency and perturbing effect, the degeneracy may be lifted. The important perturbation of f electrons can be evaluated as:

$$H - H_{CF} = \sum_{i=1}^N \left[\frac{Ze^2}{2m} - U_{(n)} \right] + \sum_{i < j} \frac{e^2}{r_{ij}}$$

The energy levels of electrostatic interactions are generally written in terms of Slater integrals.

$$F^k = e^2 \int_{r_<}^{r_>} \frac{r_<^k}{r_>^{k+1}} [R_{4f}(r_i)R_{4f}(r_j)]^2 dr_i dr_j$$

Where $r_<$ and $r_>$ are the smaller and larger radius r_i and r_j , k and R must be even and $k \leq 2l$

The area under the absorption band is a better measure of the intensity of the absorption band than the molar absorptivity at the peak maximum, because it is the same for the resolved, partly resolved or even unresolved band. The area under the curve determined by integrating

the peak, which is equivalent to the calculation of the integral. The oscillator strength of the

$$\int \epsilon(\bar{\nu}) d\bar{\nu}$$

where $\bar{\nu}$ is the wave number

The integrated molar absorptivity can be seen as the sum of $\epsilon(\bar{\nu})$ values over whole absorption band, instead of molar absorptivity, the dipole strength D or the Oscillator strengths P are reported. The molar absorptivity $\epsilon(\bar{\nu})$ at a wave number $\bar{\nu}$ is related to the dipole strength by.

$$\epsilon(\bar{\nu}) = \frac{8\pi^2}{hc} \cdot \frac{N_A}{2303} \int f(\bar{\nu}) \bar{\nu} d\bar{\nu}$$

$$\epsilon(\bar{\nu}) = \frac{8\pi^2}{hc} \cdot \frac{N_A}{2303} \int f(\bar{\nu}) \bar{\nu} D'$$

where

N_A — Avogadro number = 6.02214×10^{23} $f(\bar{\nu})$ — line shape function

h — Planck Constant = 6.62554×10^{-27} ergs D' — Dipole strength

c — Velocity of light = 2.997925×10^{10} cm/s

The oscillator strength P of a 4f — 4f transition can be given by,

$$P = \frac{8\pi^2 m_e c^2}{h e^2} \cdot \frac{2303 hc}{8\pi^2 N_A} \int \epsilon(\bar{\nu}) d\bar{\nu}$$

$$= \frac{2303 m_e c^2}{N_A \pi e^2} \int \epsilon(\bar{\nu}) d\bar{\nu}$$

$$P = \frac{2.303 \times (9.10904 \times 10^{-28}) \times (2.997925 \times 10^{10})^2}{(6.02214 \times 10^{23}) \times 3.14159 \times (4.803 \times 10^{-10})^2} \int \epsilon(\bar{\nu}) d\bar{\nu}$$

$$P = 4.32 \times 10^{-9} \int \epsilon(\bar{\nu}) d\bar{\nu}$$

Above is the simplest representation of oscillator strength. The oscillator strength of the induced electric dipole transition is related to the energy of transition (σ) square of the matrix element of unit tensor operator $U^{(\lambda)}$, connecting initial $\langle f^N \psi J$ and final $|f^N \psi' J'$ through three phenomenological parameters T_λ or \mathfrak{T}_λ ($\lambda = 2, 4, 6$). These parameters are related to the radial wave function of the state, and the ligand field parameters that characterize the environmental field (Carnall et al 1965).

$$P = \sum_{\lambda=2,4,6} \mathfrak{T}_\lambda \sigma \langle f^N \psi J \| U^{(\lambda)} \| f^N \psi' J' \rangle^2$$

Judd used T_λ parameters instead \mathfrak{T}_λ , used by Carnall et al,

$$T_\lambda = \mathfrak{T}_\lambda (2J + 1)^{-1}$$

$$P = \sum_{\lambda=2,4,6} T_\lambda \langle f^N \psi J \| U^{(\lambda)} \| f^N \psi' J' \rangle^2 (2J + 1)^{-1}$$

For calculating matrix elements U the eigen vectors were of the form,

$$f^N \psi = \sum_{\alpha^{SL}} \xi^{\alpha^{SL}} | \alpha^{SL} J \rangle$$

and can be calculated by diagonalizing the complete energy matrices.

In order to define energy interaction parameters, we have to calculate four terms F_2, F_4, F_6 and ξ_{4f} , since we have been using five main multiplet to multiplet transition manifolds for our calculation and therefore the above four terms can be solved using following equation.

$$E_{oj} = \sum_{k=2,4,6} \frac{\delta E_j}{\delta F_k} \Delta F_k + \frac{\delta E_j}{\delta \xi_{4f}} \Delta \xi_{4f}$$

By considering F_k 's and ξ_{4f} as empirical parameters derived from least square fit of the experimental energy levels of Nd(III) ion, which is either free or complexed. Solutions of the equations taking into account the reported values given by Wong, for F_2^0 , F_4^0 , F_6^0 and ξ_{4f}^0 gave parameters for Slater Condon integrals. In our complexes, we expected the metal ion radius expanded and thus lowering the values F_k and ξ_{4f} parameter than the values F_k^0 and ξ_{4f}^0 . This would give β value less than unity (i.e. nephelauxetic effect $1-\beta$) and values of bonding parameter (b) positive, we have used partial and multiple regression method and the values for zero order energies, and the partial derivatives (Wong's values) and computed F_k ($k = 2, 4, 6$) and ξ_{4f} parameters and determined values for β , b and δ all nephelauxetic bonding and covalency parameters.

$$E_{\text{obs}} = E_{\text{oj}} + \frac{\delta E_j}{\delta F_2} \Delta F_2 + \frac{\delta E_j}{\delta F_4} \Delta F_4 + \frac{\delta E_j}{\delta F_6} \Delta F_6 + \frac{\delta E_j}{\delta \xi_{4f}} \Delta \xi_{4f}$$

Dividing the above equation by we get

$$\frac{E_{\text{ob}} - E_{\text{oj}}}{\delta E_j / \delta \delta_2} = F_2 + \frac{\delta E_j / \delta \delta_4}{\delta E_j / \delta \delta_2} \Delta F_4 + \frac{\delta E_j / \delta \delta F}{\delta E_j / \delta \delta_2} \Delta F_6 + \frac{\delta E_j / \delta \delta_{4f}}{\delta E_j / \delta \delta_2} \Delta \xi_{4f}$$

We evaluate four intensity parameters P , T_2 , T_4 , T_6 and four energy interaction parameters F_2 , F_4 , F_6 and ξ_{4f} by employing partial multiplet regression method using least square fit procedure (discussed in detail in chapters 2).

The ${}^4I_{9/2} \rightarrow {}^4G_{5/2}$ transition of Nd^{3+} is universally acceptable as HYPERSENSITIVE. Birnbaum and coworkers utilized significant changes in the shape of intensity and oscillator strength of hypersensitive ${}^4I_{9/2} \rightarrow {}^4G_{5/2}$ transition of Nd(III) as a spectral probe in exploring

the binding of Nd(III) with bovine serum albumin by employing absorption difference spectrophotometry involving 4f — 4f transitions. This transition showed marked variation and extreme sensitivity towards even minor coordination changes around Nd(III). Bukietynska and Mondry used oscillator strength of hypersensitive transition as a MARKER band and the magnitude and variation of Judd - Ofelt electric dipole intensity parameters (T_x) in diagnosing the involvement of amino carboxylic group in the inner sphere of coordination.

The transitions other than the hypersensitive transition were generally considered to be almost insensitive and hence of little relevance. During the course of our studies involving spectra of Pr(III) and Nd(III), we have found that the complexes formed by variety of ligands with widely different binding characteristics induced substantial sensitivity to the nonhypersensitive transitions (earlier considered insensitive). The transition ${}^3H_4 \rightarrow {}^3P_2, {}^3P_1, {}^1D_2$ in Pr(III) and ${}^4I_{9/2} \rightarrow {}^4G_{7/2}, {}^4G_{7/2}$ of Nd(III) are such transitions which do not follow selection rules and as such cannot be considered as hypersensitive transition. but showed wide variation of their oscillator strength and high sensitivity by the complexes of Nd(III) formed by even structurally related ligands. We have given the name 'Ligand Mediated Pseudohypersensitivity' (LMP) for such observations and referred these nonhypersensitive transitions as pseudohypersensitive.

In the present thesis, we have used absorption difference and comparative absorption spectrophotometry as probe in extracting information regarding the binding modes of glutathione reduced (GSH) in different solvents towards Ln(III), in presence and absence of soft metal ions like Zinc(II).

Literature suggests that, only a little attempt has been made to follow lanthanide complexation kinetics with biomolecules, using 4f — 4f transition spectra. The present thesis describes a systematic approach for determining the rate of the multi-metal complexation of glutathione using comparative absorption and absorption difference spectroscopy. Both hypersensitive and pseudohypersensitive transitions are used as MARKER for determining the rate constant and formation constant.

The complexation of Ln(III): GSH and Ln(III) : GSH : Zn(II), were studied in different organic as well as aquated organic solvents at different pH. The probable structures of the complexes have been established by elemental analysis, IR, ¹H NMR spectra as well as by molecular modeling experiments. The structures are given as Fig. 5.07 and 5.08

The thesis has been divided into six chapters.

1. Introduction : This chapter introduces the theme of the work, the biological importance of glutathione and the importance of lanthanides as a structural and functional probes in following several biochemical reactions.

2. Review : Review on the earlier works of lanthanide coordination chemistry, related to Ln(III) complexation with biologically important ligand

3. Experimental : The second chapter enumerates the experimental procedure, analytical methods and preparatory techniques adapted during the present course of investigation. This chapter briefly describes the absorption spectral characteristics of trivalent lanthanide ions and the various parameters, which define the energy and intensities of 4f — 4f transitions.

Partial and multiple regression analysis used for computing the spectral parameters have also been discussed in this chapter.

4. Tables and Figures : In this chapter computed and observed values of oscillator strength, Judd-Ofelt parameters, ratios of intensity parameters, the energy interaction Slater-Condon, spin orbit interaction, nephelauxetic, bonding, covalency parameters and r.m.s. values for energy are tabulated for Nd(III) : GSH, Nd(III) : GSH Zn(II) and its kinetics. This chapter also includes representation for comparative absorption spectra of various systems which displays the effect of solvent stoichiometry, nature of the solvent, pH and presence and absence of the Zn(II).

5. Results and Discussion : This chapter presents the theoretical aspect of both energy level and intensity analysis of the absorption spectra. The origin of intra 4f-4f transitions and the variation of spectral parameters in the nature of metal - ligand bond, coordination number and the involvement of metal 4f orbitals in bonding are also discussed briefly. This chapter also represents the important observations and results obtained from the study of absorption difference and comparative absorption spectrophotometry involving 4f-4f transitions as probe in understanding the mode of binding of glutathione with Ln(III) are given in detail. The comparative absorption spectra of Ln(III) : GSH : Zn(II) in different aquated organic solvents and at pH = 4 clearly show that the addition of GSH in aqueous and nonaqueous solvents contribute towards high intensification of 4f - 4f bands of Ln(III). The values of different parameters indicate the substantial ionicity of Ln(III) : GSH bonding which matches with high solubility of Ln(III) : GSH complex in water. The addition of soft metal ion like Ca(II) or Zn(II) to the Ln(III) : GSH in 1:1:1 stoichiometry contributes towards substantial

enhancement in intensities of pseudohypersensitive and hypersensitive transitions of Ln(III). This clearly reflects the parameters have been found to be significantly more than for Ln(III) : GSH and Ln(III) : aquo ion, is a strong indication for the inner sphere complexation of the ligand. Finally, the binding modes were assumed on the basis of IR and ^1H NMR and the results obtained from 4f – 4f absorption spectral analysis.

APPENDIX

APPENDIX

SEMINAR ON THE HISTORY OF THE CONFERENCE

APPENDIX

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APPENDIX - 1

SEMINARS/SYMPOSIUM/CONFERENCES ATTENDED :

- (i) Presented a paper entitled, "Studies of 4f-4f Transition Spectra of Pr(III) with Glutathione in presence and absence of Zn(II) in different aquated organic solvents" in the "Twenty First Conference of Indian Council of Chemists", Rani Durgavati University, Jabalpur (M.P.), October 24-26, 2002.
- (ii) Presented a paper entitled, "Studies of 4f-4f Transition Spectra of Pr(III) with Glutathione in presence and absence of Zn(II) in different aquated organic solvents" in "Twenty First Conference of Indian Council of Chemists" Rani Durgavati University, Jabalpur (M.P.) 24th -26th October, 2002.
- (iii) Presented a poster paper entitled, "Simultaneous Interaction of two Dissimilar Metal Ions Praseodymium(III) and a Soft Metal Ion Zn(II) or a Hard Metal Ion Ca(II) with Tripeptide Glutathione(Reduced) in Different Aquated organic Solvents : An Absorption Spectral Study" in the "International Symposium on Spectroscopy, Structure and Dynamics", December 12-13, 2002, Indian Association for the Cultivation of Science, Jadavpur, Kolkata
- (iv) "Absorption Spectral Study for the Simultaneous Complexation of Pr(III): Glutathione Reduced(GSH) in Presence and Absence of Zn(II) and Mg(II) at different Aquated Organic Solvents at different pH" in "6th CRSI National Symposium, I.I.T., Kanpur, February 6-8, 2004.
- (v) Participated in the "Awareness Workshop on "The Facilities of IUC for DAEF at Indore", held during February 20-21, 2004, IIT, Guwahati.

N. Rajanathan Singh

Asian Journal of Chemistry, 16(1) (2004) 412

APPENDIX - II

LIST OF PUBLICATIONS :

1. Comparison of energy interaction parameters for the complexation of Pr(III) with glutathione reduced(GSH) in absence and presence of Zn(II) in aqueous and aquated organic solvents using 4f-4f transition spectra as PROBE
Th. David Singh, Ch. Sumitra, N. Yaiphaba, H. Debecca Devi, M. Indira Devi and N. Rajmuhon Singh
Spectrochimica Acta, **61(6)**(2005)1219.
2. Spectral study of the complexation of Nd(III) with glutathione reduced (GSH) in the presence and absence of Zn(II) in aquated organic solvents
Th David Singh, Ch Sumitra, N. Rajmuhon Singh and M. Indira Devi
Journal of Chemical Sciences,**116(6)** (2004)303.
3. Simultaneous interaction of two dissimilar metal ions praseodymium(III) and a soft metal ion Zn(II) or a hard metal ion Ca(II) with tripeptide glutathione (reduced) in different aquated organic solvents : An absorption spectral study”
Th. David Singh, N. Mohondas Singh, N. Yaiphaba, H. Debecca Devi, Ch. Sumitra., T. Kriyananda, M. Indira Devi and N. Rajmuhon Singh
Chem. & Environ. Res, **12(3&4)**(2003)295
4. An absorption spectral study of 4f-4f transitions for the interaction of Pr(III) with different amino acids in aqueous and aquated organic solvents
H. Debecca Devi, **Th. David Singh**, N. Yaiphaba, Ch. Sumitra , M. Indira Devi and N. Rajmuhon Singh
Asian Journal of Chemistry,**16(1)** (2004)412

