

Electronic spectral studies of Pr (III) and Nd (III) with mixed ligand system

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Some biprotic acids, namely, salicylic acid, tartaric acid & lactic acid and a few amino acids like glycine and β -alanine were chosen for mixed ligand system (biprotic acids as primary ligands & amino acids as secondary ligands). These were interacted with metal ion, Pr (III) or Nd (III) in different molar ratios & their electronic absorption spectra were recorded in aqueous solution. The various energy parameters such as Slater-Codon (F_k), Racah (E^k) & Lande (ξ_{4f}) parameters & intensity parameters such as, oscillator strength (P), Judd-Ofelt parameters (Ω_λ) have been computed using partial & regression statistical methods. The bonding parameter ($b^{1/2}$) & nephelauxetic ratio (β) have also been evaluated to ascertain the covalency in the metal-ligand bond.

Keywords: Amino acids, biprotic acids, rare earth metals, mixed ligand system, energy & intensity parameters, bonding parameters, nephelauxetic ratio.

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How to site this article

Vyas A., Vyas M., Shekhawat M. S., Electronic spectral studies of Pr (III) and Nd (III) with mixed ligand system, Chemical Synthesis Letters, 2023; 01 (01):50-57

Available from:

<https://cs.l.worldscience.in/index.php/j/article/view/1/version/1>

**Introduction**

Recent decades have witnessed a growing interest in the investigations of the trivalent rare earth metal ions [especially Pr (III) and Nd (III) complexes] due to their special photo physical properties which make them useful material for molecular lighting devices, lasers, optical telecommunications, quantum dot nanocrystals, diode pumped lasers and in various bioanalytical methods [1-15]. The photo physical properties like luminescence of rare earth metals ions could be enhanced through chelation with appropriate organic ligand. Fortunately, trivalent rare earth metal ions can form stable coordination compounds or chelates (with a variety of organic ligands) exhibiting high stability & strong luminescence.

Among the rare earth metal ions, Pr (III) & Nd (III) show emission spectra which extends from the blue to the near infrared region. Although much work has done on binary chelates of metals with single ligand system like Schiff bases, crown ethers, calixarenes, podents etc, but the literature survey has indicated that little work has been done on the ternary or mixed ligand chelates involving two ligands, especially, one having a biprotic acid & other as amino acid. The earlier studies associated with the amino acids and rare earth metals [Pr (III) and Nd (III)] includes work by A. Kuliev [16] who studied spectral and thermal properties of mixed ligand complexes of Pr (III) with glycine, methionine and tartaric acid. T.D. Singh and others

[17] have conducted spectral investigation of the Nd (III) complexes with glutathione in presence and absence of Zn (II) in aquated organic solvents. Spectroscopic study of the interaction of Nd (III) with amino acids like L-aspartic acid, L-histidine, DL-malic acid and aspartame in aqueous solution was done by Soraya Jerico et.al [18]. The mixed ligand complexes of some biologically important polyamine polycarboxylic acids with Nd (III) and Pr (III) have been studied by Prashant N. Bhatt and others [19] They investigated spectral characteristics like oscillator strength, T_λ and Judd-Ofelt intensity parameters of the 4f-4f transitions through absorption spectroscopy. H. Debecca Devi and others [20] have investigated spectral parameters (energy and intensity) of Nd (III) complexes with amino acids like DL-valine, DL-alanine and β -alanine in presence and absence of $\text{Ca}^{2+}/\text{Zn}^{2+}$ in aqueous and different aquated organic solvents. Reda A Ammar et. Al [21] have determine the stability constants of mixed ligand complexes of adenine and amino acids with Ni (III) complexes by potentiometric method. However spectral investigation on mixed ligand system of biprotic acids likes salicylic acid, Tartaric acid & Lactic acid and simple amino acids like Glycine & β -Alanine still needs to be explored and hence in the current pursuit, mixed ligand system of biprotic acids and amino acids were interacted with metal ions-Pr (III) & Nd (III) in different molar ratios. The spectral studies were carried out in aqueous solution which provides information about

energy levels of different transitions, coordinating environment (symmetry) & extent of metal-ligand interaction which has been expressed in terms of energy, intensity & bonding parameters.

Experimental

(a) Preparation of sample solutions:

Pr (III) & Nd (III) acetates (IREL, India) have been used for the preparation of metal-ion solutions (0.01 M) in double-distilled water which were duly standardized by the conventional methods [22]. The sample solutions were prepared in different molar-ratio [M: L₁:L₂] viz., 2:0.5:0.5, 2:0.7:0.7, 2:1:0.5 etc., where M=Pr (III) or Nd (III), L₁=primary ligand-biprotic acid & L₂=secondary ligand - amino acid. The electronic absorption spectra of these sample solutions have been recorded on a double beam spectrophotometer Systronic-119 in the range of 350-900 nm.

(b) Evaluation of Spectroscopic Parameters:

The recorded spectra have been analysed and interpreted in terms of the various electronic spectral parameters (energy, intensity & bonding) which give useful information regarding spin-orbital interactions, inter electronic repulsion, nephelauxetic effect & bonding in the complexes. The values these have been calculated by using partial & multiple regression methods involving the various theories given by Slater-Condon [23], Racah [24-26], Slater [27], Wybourne [28], Dieke [29] & Judd-Ofelt [30-31]. The various energy parameters like Slater-Condon (F_k) & Lande (ζ_{4f}) factors have been calculated using following equation (1.1-1.3) as proposed by Wong [32-33].

$$E_j(F_k, \zeta_{4f}) = E_{oj}(F_k, \zeta_{4f}) + \sum_{k=2,4,6} \frac{\partial E_j}{\partial F_k} \Delta F_k + \frac{\partial E_j}{\partial \zeta_{4f}} \Delta \zeta_{4f} \quad \dots 1.1$$

$$[F_k = F_k^0 + \Delta F_k]_{k=2, 4, 6} \quad \dots 1.2$$

$$\zeta_{4f} = \zeta_{4f}^0 + \Delta \zeta_{4f} \quad \dots 1.3$$

The energy and other spectroscopic parameters for different peaks observed during experimental studies have been summarized in Table-1.3 and 1.4 for Pr (III) & Nd (III) chelates corresponding to [M:L₁:L₂=2:0.5:0.55] molar ratios. The bonding parameter (b^{1/2}) & nephelauxetic ratio (β) were calculated by following relations

$$\beta = \frac{F_k^c}{F_k^f} \quad \text{and} \quad b^{1/2} = \left[\frac{(1-\beta)}{2} \right]^{1/2} \quad \dots 1.4$$

and the values of these calculated for [M:L₁:L₂ ratios=2:0.5:0.5] for both the metal ion [Pr(III) and Nd(III)] system have been tabulated in Table-1.4. The oscillator strength of each band has been computed using following equation(1.5),

$$P_{obs} = 4.6 \times 10^{-9} \times \epsilon_{max} \times \Delta \nu_{1/2} \quad \dots 1.5$$

where Δν_{1/2} is half band width & ε_{max} is molar extinction coefficient. The solution spectra have been analysed by resolving each band into gaussian curve shape to enable evaluation of oscillator strength. The bands for different transitions have been identified by comparing the values of energies with corresponding energy level in free metal-ion. The oscillator strength values besides several minor interactions are composed of prominently three main parameters known as Judd-Ofelt parameters Ω_λ (λ=2, 4, 6). The Judd-Ofelt equation for experimentally observed oscillator strength is given by,

$$P_{exp} = \Omega_2 \nu [U^2]^2 + \Omega_4 \nu [U^4]^2 + \Omega_6 \nu [U^6]^2 \quad \dots 1.6$$

where, ν is energy of the band (cm⁻¹) & Ω₂, Ω₄ & Ω₆ are Judd-Ofelt intensity parameters. The values of energy and oscillator strength of absorption band and their intensity parameters are listed in Table-1.1 & 1.2 for Pr (III) & Nd (III) metal-chelates having [M:L₁:L₂=2:0.5:0.5 ratio].

Results & discussions:

The absorption spectra of the Pr (III)-metal chelates show four bands corresponding to the four transitions from the ground state (³H₄) to various excited state (¹D₂, ³P₀, ³P₁, ³P₂), & the Nd (III)-metal chelates show ten bands originating from the ground state ⁴I_{9/2} to various excited states (⁴F_{3/2}, ⁴F_{5/2}, ⁴F_{7/2}, ⁴F_{9/2}, ⁴G_{5/2}, ⁵G_{7/2}, ²G_{9/2}, ⁴G_{11/2}, ²P_{1/2}) in the visible region. The bands for different transitions have been identified by comparing the values of energies with corresponding value in a free metal-ion. The spectra have been analyzed and the various parameters have been evaluated. The values of these parameters for Pr (III) & Nd (III)-metal chelates have been summarized in Table -1.3 & 1.4, respectively, in different metal-ligands molar-ratio.

The spectral or photo-physical properties of rare earth metal chelates depend upon intra-configurational transitions that take place through magnetic dipole, induced electric dipole or electric quadrupole transitions (governed by Laporte & spin-multiplicity rule). The magnetic dipole transitions are spectroscopically allowed but their intensity is independent of surrounding matrix, on the other hand induced electric dipole transitions are spectroscopically forbidden but in a coordinating environment these become allowed as asymmetric ligand field mixes the electronic states with opposite parity within 4fⁿ configuration. The theoretical method for energy calculation of different 4fⁿ transitions was initially developed by Slater & Codon [17,21] but it could not be applied to configurations higher than 4f². Later on Racah [24-26] developed a tensor-operated method which was extended by Judd³⁰, Wybourne [28] Dieke [29] & others. Here interactions among 4f electrons were expressed in term of Slater-Codon (F_k), Racah (E^k) & Lande (ζ_{4f}) parameters. These parameters are collectively referred to as energy parameters. Judd [30] & Ofelt [31]

independently developed a theory for calculating induced electric dipole matrix elements and the effect of the coordinating environment on the intensity of spectral peaks were expressed in terms of the Judd-Oflet intensity parameters (Ω_λ , $\lambda=2,4,6$). The intensity parameters along with nephelauxetic effect (β) & bonding parameter ($b^{1/2}$) are indicative of covalency in a metal-ligand bond. Thus, the study of these parameters (energy, intensity & bonding) provides useful information regarding coordination & bonding in rare earth metal chelates.

(1) Energy parameters

(a) Racah Parameter (E^k) & Slater-Condon Parameter (F_k):

The Racah parameters can be expressed as the linear combination of Slater-Condon parameter (F_k). The Racah parameters may be calculated by the following relations [28-35].

$$E^1 = (70 F_2^2 + 231 F_4 + 2002 F_6) / 9 \quad \dots(1.7a)$$

$$E^2 = (F_2 - 3F_4 + 7F_6) / 9 \quad \dots(1.7b)$$

$$E^3 = (5 F_2 + 6 F_4 - 91 F_6) / 3 \quad \dots(1.7c)$$

The trend of values both Racah parameters (E) & the Slater-Condon (F_k) is same for all the metal chelates and were found to be $E^1 > E^3 > E^2$ and $F_2 > F_4 > F_6$ which is in conformity with the earlier findings [36-37].

On chelation, the values of F_2 parameter reduces in the range of 2.85-3.70% for the Pr(III) metal-chelates as compared to the free/aquo ion value & in the range of 1.15-3.30% for the Nd(III) metal-chelates. This suggests that interaction of the 4f-orbital of the metal ion with the ligand orbitals decreases in the order Pr (III) > Nd (III). The values of F_2 parameters for the metal ions have been calculated by using the empirical relation [38].

$$F_2 = 12.4 (Z-34).$$

The F_2 values calculated from this empirical relation were found to be 310.00 & 322.48 for the Pr (III) & Nd (III)-metal chelates, respectively, which are less than 1% of the computed values obtained from the observed spectra. The ratio F_4/F_2 for Pr (III) metal chelates is 0.1381, but for Nd (III)-metal chelates varies from 0.1560 to 0.1611, respectively. These values are slightly higher than those calculated by assuming 4f-wave function to be hydrogenic [39] wave function (~ 0.138) or by Hartee-Fock methods [40] (~ 0.130). The F_6/F_2 ratio for Pr (III) chelates have been found to be 0.0151 & for the Nd (III) chelates it varies from 0.1390 to 0.0183 which are nearly equal to that of hydrogenic wave function [41] (~ 0.0151). This justifies the approximation made in the case of Pr (III) chelates. In the case of Pr (III) chelates the number of levels observed is just equal to the number of parameters to be evaluated, so only F_2 & ζ_{4f} have been calculated and values of the F_4 & F_6 are calculated in term of F_2 by the relations

$$F_4 = 0.1380 F_2 \text{ \& } F_6 = 0.0151 F_2.$$

From these equations it is clear that the ratio F_4/F_2 & F_6/F_2 are respectively equal to 0.1380 & 0.0151 & remains constant.

(b) Lande (ζ_{4f}) Parameter:

The spin-orbit coupling constants, Lande parameter (ζ_{4f}), for the aquo metal ion is given by [42] -

$$\zeta_{4f} = 142 (Z-7648).$$

The simple calculation gives the 748.14 & 497.00 value of ζ_{4f} , for Pr (III) & Nd (III) aqua ion, respectively. The observed values lie between 686.51 & 681.42 cm^{-1} for the Pr. (III) and 497.80, & 499.07 cm^{-1} , for the Nd (III)-chelates, respectively, which are in close agreement with the empirical values. The energy (E_{cal}) of various observed transitions for Pr (III) & Nd (III) chelates have been calculated using the computed values of F_k & ζ_{4f} parameters & are summarized in Table 1.3 and 1.4. The $\sigma_{\text{r.m.s}}$ deviation of the calculated & observed energy values are in ranges of 1.32- 1.65 $\times 10^{-6}$ for Pr (III)-chelates & for the Nd (III)-chelates it is 0.76 - 0.91 $\times 10^{-6}$ & the small value of $\sigma_{\text{r.m.s}}$ deviation shows validity of the Judd-Ofelt theory and the calculations made.

Finally, the reduction in the values of F_k & ζ_{4f} with respect to free aquo ion is evidence for the chelation. The lowering of these values further indicates the expansion of the metal orbitals on chelation. But this lowering is not significant with change in metal-ligands stoichiometries, thereby showing ligands have little effect on the spectral pattern & points towards outer sphere chelation [43] & the covalence of metal-ligand bond. The lowering in ζ_{4f} values is more than that of the F_k values on chelation.

(2) Intensity parameters:

Oscillator strength (P) & Judd-Ofelt (Ω_λ) Parameters:

The oscillator strength value is a measure of intensity & degree of allowance of a specific electronic transition and these values show the marked dependence on the cations environment. The oscillator strength is highest for the transition, $^3\text{H}_4 \rightarrow ^3\text{P}_2$ suggesting it to be a hypersensitive transition for the Pr (III) chelates, and $^4\text{I}_{9/2} \rightarrow ^4\text{G}_{5/2}^*$ appears to be hypersensitive transition in the Nd (III) chelates. The value of oscillator strength for hypersensitive transition is highest for all the metal-chelates whenever the primary ligand is tartaric acid & secondary ligand is glycine. And the effect of secondary ligand is also clear from the data, the values of interelectronic shows more decrease for glycine than for β -alanine. The decrease in the value of ζ_{4f} , as compared to free ion clearly suggest the decrease in spin-orbit interaction as also evident by the general red shift in case of all the metal chelates. The value of nephelauxetic ratio (β) is less than one indicating that interaction is not merely ionic but there is some sort of mixing of metal-ligand orbitals.

The intensity of the observed bands have been given in terms of the oscillator strength (P) & the Judd-Ofelt parameters Ω_λ (Ω_2 , Ω_4 & Ω_6) for all the metal – chelates & have been computed by using values of the oscillator strength. The matrix elements $U^{(\lambda)}$ were taken as given by Carnell [44]. Out of these three parameters, Ω_2 parameters shows high sensitivity towards co-ordination while Ω_4 & Ω_6 have been found to exhibit more sensitivity towards symmetry changes around the metal-ion. The values of the intensity parameters for all the metal-chelates have been summarized in Tables 1.1 & 1.2. The value of Ω_4/Ω_6 ranges from 0.151 to 0.301 for Pr (III)-chelates & 0.184 to 0.825 for Nd(III)-metal chelates, respectively, indicating similar symmetry of stereo environment around these metal-ions is through oxygen & nitrogen donor atom.

(3) Bonding parameters:

Nephelauxetic (β) & Bonding ($b^{1/2}$) Parameters:

The data summarized in Tables – 1.3 & 1.4 reveal that the values of nephelauxetic ratio for the Pr (III) & Nd (III) chelates are in the range of 0.963 to 0.967 & 0.960 to 0.970, respectively. From these values it has been found that the nephelauxetic ratio (β) for the chelates of Pr (III) & Nd (III) follows the order Pr-SG > Pr-S β > Pr-T β > Pr-TG & Nd-LG < Nd-L β < Nd-TG < Nd-S β < Nd-SG, respectively. Similarly bonding parameter ($b^{1/2}$) values for Pr (III) & Nd(III) chelates have been found between 0.136 to 0.131 & 0.122 to 0.137, respectively. These values for Pr (III) & Nd (III) chelates follows the order Pr-SG < Pr-LG < Pr-T β < Pr-TG & Nd-SG < Nd-T β < Nd-SG < Nd-TG < Nd-LG, respectively. Both the nephelauxetic (β) & bonding ($b^{1/2}$) parameters indicate that the covalency in metal-ligand bond is the highest in the Pr-TG chelate among all the Pr (III) and the lowest is in the Nd-TB chelate among all the Nd (III) chelates.

Based on these data it may be concluded that in all the chelates, the metal - ligand bond is not merely ionic but there is covalency up to some extent. The order of covalency, on the basis of these data, in all the metal-chelates with these ligands, is as follows Pr-TG > Pr-T β > Pr-S β > Pr-SG & Nd-LG > Nd-L β > Nd-TG > Nd-SG > Nd-T β . These data also suggests that, in the present case, in all the chelates, It is interesting to point out that the covalency decreases as the atomic number of rare earth metal ion increases. Thus the order of covalency in complexes will be Pr (III) > Nd (III).

Electronic Absorption Spectra of Pr (III) Complexes

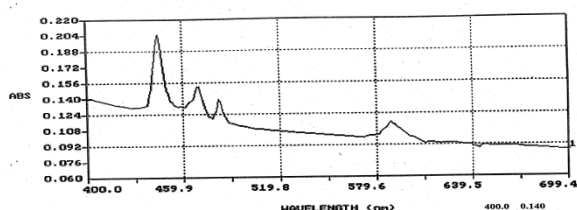


Fig.1 Absorption spectra of Praseodymium: Tartaric acid: Glycine [2:0:0.5:0.5]

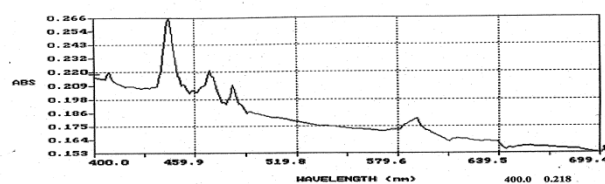


Fig.2 Absorption spectra of Praseodymium: Tartaric acid: β -alanine [2:0:0.5:0.5]

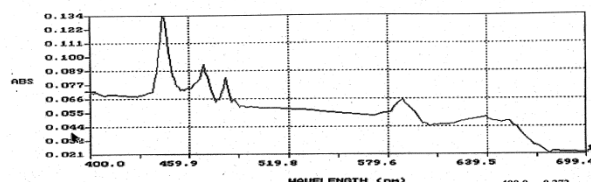


Fig.3 Absorption spectra of Praseodymium: Lactic acid: Glycine [2:0:0.5:0.5]

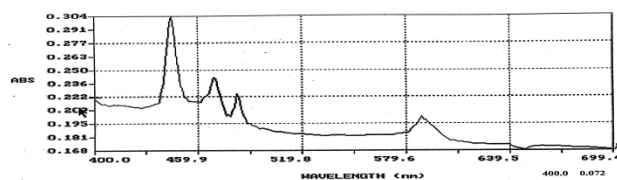


Fig.4 Absorption spectra of Praseodymium: Lactic acid: β -alanine [2:0:0.5:0.5]

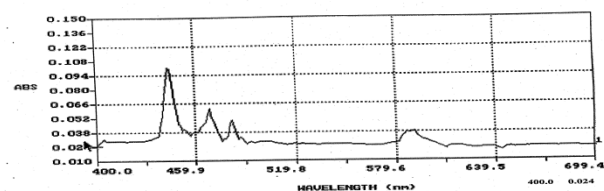


Fig.5 Absorption spectra of Praseodymium: Salicylic acid: β -alanine [2:0:0.5:0.5]

Electronic Absorption Spectra of Nd (III) Complex

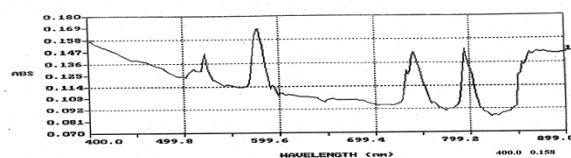


Fig.6 Absorption spectra of Neodymium: Tartaric acid: Glycine [2:0:0.5:0.5]

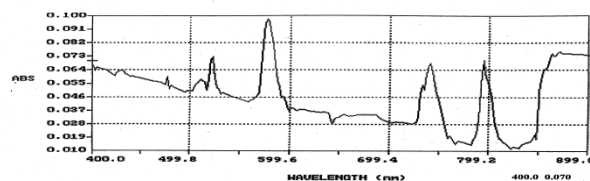


Fig.7 Absorption spectra of Neodymium: Tartaric acid: β -alanine [2:0:0.5:0.5]

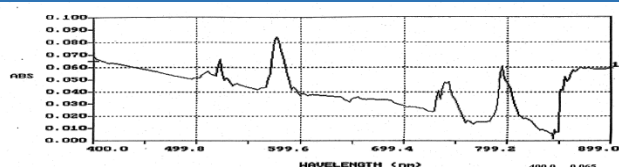


Fig.8 Absorption spectra of Neodymium: Lactic acid: Glycine [2:0:0.5:0.5]

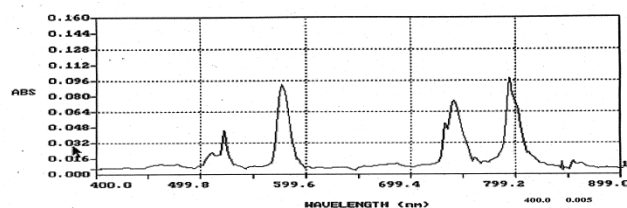


Fig.9 Absorption spectra of Neodymium: Lactic acid: β -alanine [2:0:0.5:0.5]

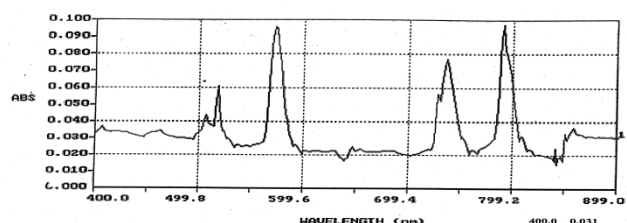


Fig.5 Absorption spectra of Praseodymium: Salicylic acid: β -alanine [2:0:0.5:0.5]

Conclusion:

For all the Pr (III)&Nd (III) metal-chelates, the value of interelectronic repulsion parameters especially, the Slater & Condon decreases from free ion value indicating complexation (Table 1.1 & 1.2). Among all the Pr (III)&Nd (III) metal-chelates, the decrease is more pronounced for group of Pr (III)&Nd (III) metal-chelates consists of tartaric acid as primary ligand & glycine or β -alanine as secondary ligands, respectively, probably due to more effective coordination sites provided by the two adjacent -COOH groups in tartaric acid as compared of group of Pr (III) & Nd (III) metal-chelates consists lactic acid or salicylic acid as primary ligands & , glycine or β -alanine as secondary ligands, respectively. The effect of secondary ligand is also clear from the data, the values of interelectronic shows more decrease for glycine than for β -alanine. The decrease in the value of, Lande parameter ζ_{4f} , as compared to free ion clearly suggest the decrease in spin-orbit interaction as also evident by the general red shift in case of all the metal chelates. The value of nephelauxetic ratio (β) is less than one indicating that interaction is not merely ionic but there is some sort of mixing of metal-ligand orbitals, i.e.covalent.

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Table1.1

Oscillator strength and Judd-Oflet parameter of Pr (III) ion with different ligands

M:L ₁ :L ₂	Energy And Oscillator Strength	Energy Levels				rms(σ)	Judd-Oflet Intensity Parameters			
		¹ D ₂	³ P ₀	³ P ₁	³ P ₂		T ₂ X10 ⁹	T ₄ X10 ⁹	T ₆ X10 ⁹	T ₄ /T ₆
Pr:T:G (2.0:0.5:0.5)	E _{exp} (cm ⁻¹)	16954	20741	21378	22512	1.32 x 10 ⁻⁶	-11.513	0.614	3.325	0.184
	P _{exp} x 10 ⁶	3.940	3.830	4.980	12.470					
	P _{cal} x 10 ⁶	3.907	2.940	4.005	12.430					
Pr:T:β (2.0:0.5:0.5)	E _{exp} (cm ⁻¹)	16972	20769	21378	22533	1.41 x 10 ⁻⁶	-8.251	0.831	3.170	0.263
	P _{exp} x 10 ⁶	3.599	3.540	4.730	10.212					
	P _{cal} x 10 ⁶	3.550	3.124	4.330	10.090					
Pr:L:G (2.0:0.5:0.5)	E _{exp} (cm ⁻¹)	17024	20794	21378	22564	1.47 x 10 ⁻⁶	-10.796	0.989	3.101	0.318
	P _{exp} x 10 ⁶	3.500	3.390	4.570	10.109					
	P _{cal} x 10 ⁶	3.480	3.380	4.349	9.199					
Pr:L:β (2.0:0.5:0.5)	E _{exp} (cm ⁻¹)	17024	20794	21378	22533	1.65 x 10 ⁻⁶	-7.584	0.7301	2.888	0.252
	P _{exp} x 10 ⁶	3.309	3.125	4.350	10.101					
	P _{cal} x 10 ⁶	3.247	3.120	4.140	9.100					
Pr:S:G (2.0:0.5:0.5)	E _{exp} (cm ⁻¹)	17041	20821	21378	22564	1.42 x 10 ⁻⁶	-8.126	0.950	3.185	0.298
	P _{exp} x 10 ⁶	3.380	3.270	4.430	10.065					
	P _{cal} x 10 ⁶	3.290	3.200	4.132	9.050					
Pr:S:β (2.0:0.5:0.5)	E _{exp} (cm ⁻¹)	16973	20796	21381	22595	1.62 x 10 ⁻⁶	-7.540	0.938	3.176	0.285
	P _{exp} x 10 ⁶	3.370	3.185	4.146	9.880					
	P _{cal} x 10 ⁶	3.192	3.175	4.035	9.800					

T=Tartaric acid, S=Salicylic acid, L=Lactic acid, G=Glycine, β= β-alanine

Table1.2
Oscillator strength and Judd-Oflet parameter of Nd(III) ion with different ligands

M: L ₁ :L ₂	Energy And Oscillator Strength	Energy Levels										rms(σ)	Judd-Oflet Intensity Parameters			
		⁴ F _{3/2}	⁴ F _{5/2}	⁴ F _{7/2}	⁴ F _{9/2}	⁴ G _{5/2} *	⁵ G _{7/2}	² G _{9/2}	⁴ G _{9/2}	⁴ G _{11/2}	² P _{1/2}		T ₂ X10 ⁹	T ₄ X10 ⁹	T ₆ X10 ⁹	T ₄ /T ₆
Nd: T: G (2.0:0.5:0.5)	E _{exp} (cm ⁻¹)	11526	12486	13286	14739	17381	19426	19694	21412	21522	23134	0.79 x 10 ⁻⁶	0.544	0.278	0.724	0.384
	P _{exp} x 10 ⁶	1.283	4.919	4.617	0.420	11.358	3.424	1.987	0.613	0.759	1.115					
	P _{cal} x 10 ⁶	1.185	4.417	4.297	0.452	10.880	2.170	0.281	1.038	0.157	0.245					
Nd: T: β (2.0:0.5:0.5)	E _{exp} (cm ⁻¹)	11507	12484	13283	14735	17377	19420	19688	21404	21517	23125	0.76 x 10 ⁻⁶	0.536	0.274	0.728	0.377
	P _{exp} x 10 ⁶	1.262	4.872	4.576	0.402	11.272	3.373	1.922	0.563	0.703	1.059					
	P _{cal} x 10 ⁶	1.185	4.405	4.282	0.450	10.833	2.165	0.280	1.037	0.156	0.246					
Nd: L : G (2.0:0.5:0.5)	E _{exp} (cm ⁻¹)	11523	12501	13302	14758	17400	19449	19717	21439	21548	23166	0.91 x 10 ⁻⁶	0.540	0.194	0.616	0.315
	P _{exp} x 10 ⁶	1.027	3.692	4.475	0.398	10.842	3.322	1.915	0.581	0.722	1.063					
	P _{cal} x 10 ⁶	0.901	3.627	3.618	0.379	10.229	1.531	0.231	0.848	0.129	0.171					
Nd : L : β (2.0:0.5:0.5)	E _{exp} (cm ⁻¹)	11529	12508	13310	14769	17410	19463	19730	21457	21561	23186	0.88 x 10 ⁻⁶	0.535	0.195	0.614	0.317
	P _{exp} x 10 ⁶	1.010	3.654	4.435	0.380	10.759	3.273	1.852	0.534	0.668	1.010					
	P _{cal} x 10 ⁶	0.903	3.619	3.606	0.378	10.185	1.533	0.230	0.847	0.129	0.172					
Nd : S : G (2.0:0.5:0.5)	E _{exp} (cm ⁻¹)	11520	12516	13325	14781	17387	19415	19710	21401	21589	23181	0.85 x 10 ⁻⁶	0.537	0.095	0.613	0.159
	P _{exp} x 10 ⁶	1.035	3.527	4.284	0.369	10.527	3.189	1.818	0.541	0.673	0.996					
	P _{cal} x 10 ⁶	0.629	3.314	3.542	0.364	9.935	1.529	0.201	0.711	0.117	0.811					
Nd : S : β (2.0:0.5:0.5)	E _{exp} (cm ⁻¹)	11523	12518	13328	14785	17391	19421	19715	21409	21594	23189	0.83 x 10 ⁻⁶	0.525	0.092	0.608	0.151
	P _{exp} x 10 ⁶	1.010	3.471	4.224	0.348	10.452	3.122	1.747	0.491	0.617	0.936					
	P _{cal} x 10 ⁶	0.627	3.291	3.514	0.361	9.901	1.523	0.200	0.708	0.116	0.815					

Table 1.3

Computed values of (F_k), (ζ_{4f}), (E^k) (β) and ($b^{1/2}$) parameters of Pr (III) chelates in various metal-ligand stoichiometries

M:L ₁ : L ₂	Racah Parameter (cm ⁻¹)			Slater-Condon Parameter (cm ⁻¹)			Lande Parameter (cm ⁻¹) ζ_{4f}	Nephelauxetic ratio β	Bonding Parameter $b^{1/2}$
	E ¹	E ²	E ³	F ₂	F ₄	F ₆			
Pr:T:G (2.0:0.5:0.5)	4565.046	23.880	461.548	310.932	42.924	4.698	685.548	0.963	0.136
Pr:T:β (2.0:0.5:0.5)	4565.760	23.891	461.619	310.933	42.928	4.699	686.519	0.965	0.132
Pr:L:G (2.0:0.5:0.5)	4564.302	23.879	461.534	310.923	42.923	4.698	681.428	0.965	0.132
Pr:L:β (2.0:0.5:0.5)	4564.641	23.883	461.608	310.973	42.930	4.699	685.880	0.967	0.129
Pr:S:G (2.0:0.5:0.5)	4566.593	23.887	461.699	311.034	42.938	4.700	685.226	0.966	0.131
Pr:S: β (2.0:0.5:0.5)	4571.903	23.915	462.241	311.034	42.989	4.705	685.542	0.967	0.129
Free Aqua ion	322.090	44.460	4.867	741.000	4729.000	24.740	748.140		

T=Tartaric acid, S=Salicylic acid, L=Lactic acid, G=Glycine, β= β-alanine

Table 1.4

Computed values of (F_k), (ζ_{4f}), (E^k) (β) and ($b^{1/2}$) parameters of Nd (III) chelates in various metal-ligand stoichiometries

M:L ₁ : L ₂	Racah Parameter (cm ⁻¹)			Slater-Condon Parameter (cm ⁻¹)			Lande Parameter (cm ⁻¹) ζ_{4f}	Nephelauxetic ratio β	Bonding Parameter $b^{1/2}$
	E ¹	E ²	E ³	F ₂	F ₄	F ₆			
Nd : T : G (2.0:0.5:0.5)	322.782	56.101	5.011	829.812	5065.280	21.062	498.157	0.974	0.1124
Nd : T : β (2.0:0.5:0.5)	322.852	56.147	5.014	829.915	5067.602	21.056	498.277	0.974	0.1119
Nd : L : G (2.0:0.5:0.5)	323.490	56.209	5.031	831.880	5077.955	21.119	498.951	0.976	0.1076
Nd : L : β (2.0:0.5:0.5)	323.559	56.255	5.034	831.984	5080.289	21.114	499.072	0.977	0.1071
Nd : S : G (2.0:0.5:0.5)	325.293	54.846	5.079	844.188	5067.711	21.812	497.768	0.982	0.0941
Nd : S : β (2.0:0.5:0.5)	325.338	54.893	5.081	844.309	5069.645	21.802	497.889	0.982	0.0937
Free Aqua ion	331.159	50.714	5.154	884.000	5024.000	23.900	497.000		

T=Tartaric acid, S=Salicylic acid, L=Lactic acid, G=Glycine, β= β-alanine