

COMPARATIVE 4F-4F ABSORPTION SPECTRAL APPROACH TO STUDY THE COMPLEXATION OF PR (III) WITH GUANOSINE AND GUANOSINE TRI PHOSPHATE (GTP) IN THE PRESENCE AND ABSENCE OF CA (II)

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ABSTRACT

The interactions of Pr (III) with some selected nucleosides and nucleotides have been studied in presence and absence of Ca (II) employing the comparative absorption spectroscopy involving the 4f-4f transitions in different organic solvents. The mode of binding of Pr(III) with different ligands (i.e. Guanosine and Guanosine Tri Phosphate (GTP) were interpreted from the evaluated various spectral parameters like Slater-Condon (F_k), Racah (E^k), Lande parameter (ξ_{4f}), Nephelauxetic ratio (β), bonding parameter ($b^{1/2}$), Percentage covalency (δ). The variations in the values of intensity parameters like Oscillator strength (P) and Judd Ofelt electric dipole intensity parameters (T_λ , $\lambda= 2, 4, 6$) are being used to investigate the nature of complexation of Lanthanides with the ligands.

Key Words: Absorption Spectra, Nephelauxetic Effect, Intensity Parameters, Guano sine/ GTP

INTRODUCTION

Analysis of 4f-4f transitions has been used successfully in elucidating the structures of lanthanide complexes with ligands having varied structural features. Lanthanide co-ordination chemistry in solution have been used as PROBES to study the structural functions and biomolecular reactions (Choppin *et al.*, 1976; Williams, 1982; Bukietynska *et al.*, 1987; Holz *et al.*, 1988; Devlin *et al.*, 1988; Martin *et al.*, 1983) because of similarities in their sizes, bonding, co-ordination geometries, donor atom preference and their ability to replace Ca(II) in a specific manner. Lettvin *et al.*, (1964) had studied the similarities of the ionic radii of Ca(II) and Ln(III) ions and concluded that Ln(III) ions could be profitably used to study the interaction of Ca(II) with nerves. Birnbaum *et al.*, (1970) had well explained the usefulness of lanthanides as functional replacement for Ca(II) ions in enzymatic reactions.

Nucleosides and nucleotides, the basic building blocks of nucleic acid play important roles in all major aspects of metabolism (Zubey, 1993). Electronic spectral studies on their interaction with lanthanide ions in aquated organic medium have led to an understanding of the nature and reactivity of the biochemical reactions involving these species. Since Pr(III) resemble very closely to one of the most abundant and biologically important metal ion Ca(II). Its complexation with nucleosides and nucleotides can provide information about co-ordination characteristics of diamagnetic Ca(II) with biomolecules during biochemical reactions. Lanthanides being paramagnetic in nature have been used as spectral probes for exploring the biological roles of Ca(II) by isomorphous substitution (Indira *et al.*, 1994). Earlier researchers have used absorption difference and comparative absorption spectroscopy to investigate the co-ordinations of lanthanides with a number of organic molecules like Gluthathione, Amino acids etc. (David Singh *et al.*, 2004; Debecca Devi *et al.*, 2004; Bimola Huidrom *et al.*, 2012).

In our present work, we report mainly the quantitative spectral energy interaction paramaters and intensity parameters for the complexation of Pr(III) with Guanosine and Guanosine Tri Phosphate (GTP), in presence and absence of Ca(II) in different aquated organic solvents. It shows the sensitivity of the different pseudo hypersensitive transitions $^3H_4 \rightarrow ^3P_2$, $^3H_4 \rightarrow ^3P_1$, $^3H_4 \rightarrow ^3P_0$ and $^3H_4 \rightarrow ^1D_2$ of Pr(III). The magnitude and variations of the energy parameters like Slater-Condon (F_k), Racah (E_k), Lande spin orbit coupling parameter (ξ_{4f}), Nephelauxetic ratio (β), bonding parameter ($b^{1/2}$), Percentage covalency (δ)

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and intensity parameters like Oscillator strength (P) and Judd Ofelt electronic dipole intensity parameters (T_{λ} , $\lambda=2,4,6$) are employed to study the binding modes of Guanosine and GTP with the metals and to interpret the nature of complexation.

MATERIALS AND METHODS

Materials

Pr (III) nitrate of 99.9 % purity was purchased from M/S Indian Rare Earth Ltd., nucleoside and nucleotide from SISCO Pvt. Ltd. Mumbai. The solvents used are CH_3CN , CH_3OH , DMF and dioxane of AR grade from Qualigens. The solutions of Pr(III), adenosine, adenosine tri phosphate, Ca(II) salts were prepared in different solvents with the concentration 10^{-2} M. For the present study Pr (III): ligand was kept at 1:1 molar ratio and the multimetal complexation like Pr(III):ligand:Ca(II) was also kept at 1:1:1 molar ratio. The absorption spectra were recorded at pH_4 on a Perkin-Elmer Lamda 35 UV-Visible spectrophotometer with high resolution and expansion of scale in a water jacketed cell holder in the region 400-1000 nm. The temperature for recording of all spectra was maintained at 298K using water-circulating thermostat model DS-G-HAAKE.

Methods

Theoretical background.

For spectra of lanthanides complexes, the energy of the bands arises due to forbidden transitions within the $4f^N$ configurations. They are assigned in terms of the intensity distribution of the observed bands. Interest in the intensities of lanthanides 4f-4f transition spectra can be said to have begun with a paper by (Van Vleck JH, 1937), in which it was known whether the sharp lines in the spectra of trivalent were due to $4f^N$ transition or $4f^{N-1} \rightarrow 5d$ transition. (Carnall *et al.*, 1968) has successfully applied the Judd Ofelt theory for the assignments in case of Ln(III) aquo-ions.

The Nephelauxetic effect (Peacock, 1964; Jorgensen *et al.*, 1964; Choppin *et al.*, 1976), a measure of covalency has been interpreted in terms of Slater Codon and Racah parameters by the measure of free ion and complex ion (Misra, 1985 and Misra, 1990).

$$\beta = \frac{F_k^C}{F_k^f} \text{ or } \frac{E_c^K}{E_f^K} \quad (1)$$

Where F_k ($k=2, 4, 6$) is the Slater-Condon parameter and E^k is the Racah parameters for complex and free ions respectively. The bonding parameter ($b^{1/2}$) is inter-related to Nephelauxetic effect as,

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

The percent covalency parameter (δ) representing the Nephelauxetic effect was given by the relation

$$\delta = \left(\frac{1-\beta}{\beta} \right) \times 100 \quad (3)$$

In the electronic transition of 4f-4f, the energy, E_{so} arises from the most important magnetic interactions, while the spin orbit interactions may be written as

$$E_{so} = A_{so} \xi_{4f} \quad (4)$$

Where A_{so} is the angular part of spin-orbit interaction and ξ_{4f} is the radial integral and is known as Lande's parameter. By first order approximation the energy E_j of the j th level is given by (Wong EY, 1963) as

$$E_j(F_K, \xi_{4f}) = E_{oj}(F_K^0, \xi_{4f}) + \frac{\partial E_j}{\partial F_K} \Delta F_K + \frac{\partial E_j}{\partial \xi_{4f}} \Delta \xi_{4f} \quad (5)$$

Where E_{oj} is the zero order energy of the j th level. The value of F_k and ξ_{4f} are given by

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$$F_k = F_k^0 + \Delta F_k$$

$$\xi_{4f} = \xi_{4f}^0 + \Delta \xi_{4f} \quad (6)$$

The difference between the observed E_j and the zero order values, ΔE_j is evaluated by

$$\Delta E_j = \sum_{k=2,4,6} \frac{\partial E_j}{\partial F_k} \Delta F_k + \frac{\partial E_j}{\partial \xi_{4f}} \Delta \xi_{4f} \quad (7)$$

By using the zero order energy and partial derivatives of Pr (III) ion given by Wong, the above equation can be solved by least square technique and the value of ΔF_2 and $\Delta \xi_{4f}$ can be found out. From these the value of F_2 and ξ_{4f} are evaluated using relation (6).

The calculation of the band intensities is based upon the theoretical treatment derived by Judd and Ofelt (Ofelt GS, 1962). They considered the transitions are essentially electric dipole in character and the oscillator strength corresponding to the induced electric dipole transition $\psi J \rightarrow Z \psi' J'$ as given by:

$$P = V \sum_{\lambda=2,4,6} T_\lambda \langle f^n \psi J || U^{(\lambda)} || f^n \psi' J' \rangle^2 \quad (8)$$

Where $U^{(\lambda)}$ is the unit tensor operator of the rank which connect the initial $\langle f^n \psi J |$ and the final $| f^n \psi' J' \rangle$ state through three phenomenological parameters T_λ ($\lambda=2, 4, 6$) called Judd-Ofelt parameters. These parameters are related predominantly to the radial part of the $4f^n$ wave function. The wave functions of perturbing configuration of which the nearest is $4f^{n-1}5d$.

The measured intensity of an absorption band is related to the probability (P) for the absorption of radiant energy (oscillator strength) by the expression:

$$P = (4.32 \times 10^{-9}) \int \epsilon_{\max}(\nu) d\nu \quad (9)$$

Where ϵ_{\max} is the molar extinction coefficient and ν is the energy of the band in cm^{-1} . The calculated oscillator strength can be expressed in terms of T_λ parameters as

$$\frac{P_{\text{cal}}}{\nu} = [U^{(2)}]^2 \cdot T_2 + [U^{(4)}]^2 \cdot T_4 + [U^{(6)}]^2 \cdot T_6 \quad (10)$$

The transition energies and the intra configurational $U^{(\lambda)}$ matrix elements are used for the intensity analysis.

RESULTS AND DISCUSSION

For praseodymium complex, four transitions (3P_2 , 3P_1 , 3P_0 , and 1D_2) have been observed, originating from the symmetry forbidden 3H_4 ground level, in the 400-600 nm spectral regions. The energy parameters of these transitions are shown in Table 1. The 4f-4f transitions $^3H_4 \rightarrow ^3P_2$, $^3H_4 \rightarrow ^3P_1$, $^3H_4 \rightarrow ^3P_0$, $^3H_4 \rightarrow ^1D_2$ of Pr(III) do not obey selection rule and so they are considered non-hypersensitive transition. Yet, they have been found to exhibit substantial sensitivity towards even minor co-ordination changes around Ln(III), due to the difference in the binding behaviour and changes in the immediate co-ordination environment and referred these transitions as ligand mediated pseudo-hypersensitive transitions (Blasse *et al.*, 1966; Bruber *et al.*, 1968 and Peacock, 1970). Misra (Misra *et al.*, 1991; Devi *et al.*, 1997 and Abdi *et al.*, 1992) studied the high sensitivity of $^3H_4 \rightarrow ^3P_2$, $^3H_4 \rightarrow ^3P_1$, $^3H_4 \rightarrow ^3P_0$ and $^3H_4 \rightarrow ^1D_2$ transitions of Pr(III) and transition of Nd(III) chelates in their complexes with ligands having widely different binding characteristics. They have found that the nature of the co-ordinating sites, chelating power of the ligand and nature as well as the geometry of the complex species induced unusual sensitivity to this pseudo-hypersensitive transition. Karraker (Karraker, 1967 and Karraker, 1969) studied the hypersensitive transition correlating with the co-ordination number of lanthanide ions. As such the interaction of Guanosine and GTP with Pr(III) in different aquated organic solvents like DMF, CH_3OH , CH_3CN , Dioxane have been investigated, which gives results of the shape, energy and oscillator strength of

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pseudo-hypersensitive transition that correlates with co-ordination number. The comparative absorption spectra of Pr(III), Pr(III):Guanosine, Pr(III): Guanosine: Ca(II) are shown in Figure1 and Figure 2 shows that of Pr(III), Pr(III): GTP, Pr(III): GTP: Ca(II). From the figures it is clearly seen that the addition of ligands (Guanosine/GTP) to Pr(III) ions enhances the intensities of the different 4f-4f transitions i.e. there is a red shift in all the energy bands. Also the intensities of the different 4f-4f increases when Ca(II) ion is added to the solution. As a consequence, we have observed noticeable increase in the magnitude of Judd-Ofelt intensity parameters (T_{λ}). These suggest the binding of Guanosine/ GTP to Pr(III) in solution state. The intensification of bands is interpreted in terms of increased interaction of 4f orbitals of Pr(III) with ligand orbitals. The intensification of bands especially ${}^3H_4 \rightarrow {}^3P_2$ transition can be correlated with the lowering of the co-ordination number and shortening of metal-ligand distance.

Table 1: Hypersensitive transition of some of the Ln (III)

Metal ion	Transition	Approximate wave Number ($\times 10^5 \text{ cm}^{-1}$)
Pr ³⁺	${}^3H_4 \rightarrow {}^3F_2$	5.2
Nd ³⁺	$I_{5/2} \rightarrow {}^4G_{5/2}$	17.3
Pm ³⁺	${}^5I_4 \rightarrow {}^5G_3, {}^5G_2$	18.0
	${}^6H_{5/2} \rightarrow {}^4F_{3/2}, {}^4G_{1/2}$	6.4
Sm ³⁺	${}^7F_1 \rightarrow {}^5D_1$	18.7
	${}^7F_0 \rightarrow {}^5D_2$	21.5
	${}^7F_2 \rightarrow {}^5D_0$	16.3
Gd ³⁺	${}^6S_{7/2} \rightarrow {}^6P_{7/2}, {}^6P_{5/2}$	32.5
Dy ³⁺	${}^6H_{15/2} \rightarrow {}^6F_{11/2}$	7.7
Ho ³⁺	${}^5I_3 \rightarrow {}^5G_6$	22.1
	${}^5I_3 \rightarrow {}^3H_6$	27.7
Er ³⁺	${}^4I_{15/2} \rightarrow {}^2H_{11/2}$	19.2
	${}^4I_{15/2} \rightarrow {}^2G_{11/2}$	16.4
Tm ³⁺	${}^3H_6 \rightarrow {}^3F_4$	5.9
	${}^3H_6 \rightarrow {}^3H_4$	12.7
	${}^3H_6 \rightarrow {}^3H_{4s}$	21.3

For spectral studies on the structures of co-ordination compounds of lanthanide in solution, any evidence of the relationship between the nephelauxetic band shift and the structures is of special interest. Jorgensen and Ryan (Jorgensen *et al.*, 1996) noticed the dependence of nephelauxetic effect on the co-ordination number of lanthanides in solution and suggested that shortening in the metal-ligand bond distance occurs with decrease in the co-ordination number. To interpret the correlation and analysis of the relationship between nephelauxetic effect and geometry, energy parameters have been derived and evaluated for complex compounds using the angular overlap model, the value of 'n' is proportional to the nephelauxetic effect as,

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$$n = \left[\frac{1 - \beta^{1/2}}{\beta^{1/2}} \right] \quad (11)$$

It may also be expressed as

$$n = \frac{H_L^2}{(H_M - H_L)} (S * R)^2 N \quad (12)$$

where, N is the co-ordination number, H_M and H_L are coulomb integrals of atomic orbitals, S is the overlap integral, R is the radius of the orbit. For compounds with ligands co-ordinated through identical donor atoms, the term of equation (12) is a constant and becomes

$$n = \text{constant} (S * R)^{2N} \quad (13)$$

Table2: Computed value of energy interaction Slater Condon F_k (cm^{-1}), Racah (E^k) Spin orbit interaction ξ_{4f} (cm^{-1}), Nephelauxetic ratio (β), bonding ($b^{1/2}$) and covalency (δ) parameters of Pr (III), Pr (III): L, Pr (III): L: Ca (II), at 298K (pH4) are given below (L= Guanosine, GTP)

system	F_2	F_4	F_6	ξ_{4f}	E^1	E^2	E^3	β	$b^{1/2}$	δ
1.solvent:CH₃CN, L= Guanosine										
Pr(III)	309.27	42.66	4.667	721.39	3509.46	23.74	614.46	0.945	0.164	5.717
	75	82	1	76	71	92	67	9	4	0
Pr(III):L	309.12	42.66	4.666	721.18	3509.46	23.74	614.45	0.946	0.164	5.749
	32	45	8	72	63	27	76	5	5	2
Pr(III):L:Ca	309.10	42.66	4.666	721.02	3509.45	23.74	614.42	0.946	0.164	5.764
(II)	59	21	5	25	98	14	32	6	7	6
L= GTP										
Pr(III)	309.27	42.66	4.667	721.39	3509.46	23.74	614.46	0.945	0.164	5.717
	75	82	1	76	71	92	67	9	4	0
Pr(III):L	309.22	42.65	4.666	721.39	3509.38	23.74	614.46	0.950	0.168	5.752
	42	50	9	24	13	42	15	1	0	1
Pr(III):L:Ca	309.21	42.64	4.666	721.39	3509.18	23.73	614.44	0.957	0.168	5.744
(II)	91	98	0	20	40	46	28	5	1	0
2.solvent: CH₃OH, L= Guanosine										
Pr(III)	309.20	42.66	4.667	721.62	3509.59	23.75	614.48	0.946	0.164	5.697
	92	98	2	82	95	01	99	1	2	4
Pr(III):L	309.13	42.66	4.667	721.62	3509.52	23.75	614.46	0.946	0.164	5.697
	03	13	0	77	60	19	2	2	4	9
Pr(III):L:Ca	309.12	42.65	4.666	721.61	3509.49	23.75	614.45	0.946	0.164	5.668
(II)	37	45	9	27	11	17	85	3	8	1
L= GTP										
Pr(III)	309.20	42.66	4.667	721.62	3509.59	23.75	614.48	0.946	0.164	5.697
	92	98	2	82	95	01	99	1	2	4
Pr(III):L	309.17	42.63	4.664	721.14	3509.16	23.74	614.45	0.945	0.164	5.697
	48	68	6	05	33	74	53	8	5	5
Pr(III):L:Ca	309.16	42.58	4.659	721.12	3509.16	23.74	614.09	0.940	0.164	5.697
(II)	61	12	4	10	14	21	4	4	6	7
3.solvent: Dioxane, L= Guanosine										
Pr(III)	309.24	42.66	4.666	721.03	3509.22	23.74	614.40	0.945	0.164	5.749
	58	38	6	52	70	67	37	6	9	9
Pr(III):L	309.09	42.66	4.666	721.01	3509.22	23.74	614.39	0.946	0.165	5.890

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	07	70	3	50	67	62	29	2	1	6
Pr(III):L:Ca	309.07	42.66	4.666	721.01	3509.22	23.74	614.35	0.946	0.165	5.890
(II)	03	58	0	49	52	60	24	9	5	9
L= GTP										
Pr(III)	309.24	42.66	4.666	721.03	3509.22	23.74	614.40	0.945	0.164	5.749
	58	38	6	52	70	67	37	6	9	9
Pr(III):L	309.09	42.62	4.653	721.01	3509.21	23.74	614.29	0.946	0.165	5.808
	60	59	4	44	86	13	86	9	0	2
Pr(III):L:Ca	309.06	42.62	4.643	721.01	3509.21	23.73	614.29	0.947	0.165	5.888
(II)	31	83	6	38	30	26	27	1	1	8
4.solvent: DMF, L= Guanosine										
Pr(III)	308.96	42.65	4.665	720.34	3508.20	23.74	614.24	0.945	0.165	5.816
	64	28	4	02	58	06	59	0	8	1
Pr(III):L	308.93	42.64	4.664	720.20	3507.79	23.73	614.17	0.946	0.166	5.832
	04	78	8	60	71	79	43	9	0	3
Pr(III):L:Ca	308.93	42.64	4.664	720.20	3507.76	23.73	614.16	0.947	0.166	5.839
(II)	03	67	2	59	44	73	61	0	8	1
L= GTP										
Pr(III)	308.96	42.65	4.665	720.34	3508.20	23.74	614.24	0.945	0.165	5.816
	64	28	4	02	58	06	59	0	8	1
Pr(III):L	309.20	42.63	4.663	720.24	3508.17	23.74	614.23	0.945	0.165	5.823
	99	64	1	64	06	93	30	3	9	4
Pr(III):L:Ca	309.20	42.63	4.662	720.24	3508.15	23.74	614.23	0.945	0.166	5.824
(II)	57	56	3	56	00	06	14	6	2	7
5.solvent: CH₃OH+CH₃CN, L= Guanosine										
Pr(III)	309.27	42.67	4.667	721.65	3509.88	23.75	614.54	0.946	0.164	5.691
	47	33	6	56	93	20	06	2	1	2
Pr(III):L	309.17	42.67	4.667	721.45	3509.79	23.75	614.52	0.946	0.164	5.707
	64	21	5	73	46	14	41	5	3	7
Pr(III):L:Ca	306.16	42.30	4.627	721.20	3509.76	23.54	614.26	0.946	0.164	5.725
(II)	20	71	6	27	90	82	69	7	8	6
L= GTP										
Pr(III)	309.27	42.67	4.667	721.65	3509.88	23.75	614.54	0.946	0.164	5.691
	47	33	6	56	93	20	06	2	1	2
Pr(III):L	309.26	42.63	4.664	720.69	3509.79	23.74	614.43	0.946	0.164	5.691
	42	53	4	34	30	66	42	2	1	3
Pr(III):L:Ca	309.26	42.62	4.663	719.89	3509.74	23.73	614.25	0.946	0.165	5.767
(II)	19	26	0	30	47	95	07	5	1	6

Equation (13) represents the nephelauxetic effect as a functions of two variables, S^*R and N which vary with changes in metal-ligand bond distance in opposite directions. However, any variations in the value of R leads to a larger change in $(S^*R)^2$ compared to that in N . As a result, the nephelauxetic affect increases when the co-ordination number decreases. The variations in the value of E^k ($k=2, 4, 6$) corresponds to that in the value of (F_k) , since they are interrelated. Misra *et al.*, (Abdi SHR *et al.*, 1992) observed a general decrease in the values of F_k , E^k and ξ_{4f} as compared to corresponding parameters of the free ion. Table.2 shows the variations of the magnitude of energy interaction parameters like Slater-Condon (F_k), Racah (E^k), Lande spin orbit coupling parameter (ξ_{4f}), Nephelauxetic ratio (β), bonding parameter ($b^{1/2}$), Percentage covalency (δ) for Pr(III), Pr(III):L (L- Guanosine/GTP) and Pr(III):L:Ca(II) in different aquated organic solvents. From these values it has been observed that, there is a steady decrease in the

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value of F_k , E^k , ξ_{4f} which indicates the lowering of both coulombic (F_k) and spin-orbit interaction (ξ_{4f}) parameters thus results in the expansion of the central metal ion orbital on complexation. Further it has also been observed that the value of nephelauxetic ratio (β) in this system is also less than unity (0.9404-0.9575) and the values of bonding parameters ($b^{1/2}$) are positive which indicates co-valent character in metal-ligand bond. The changes in the energy interaction parameters and nephelauxetic effect are not apparently significant. More emphasis has been given to quantitative 4f-4f transition intensity analysis because changes in intensities are more significant as compared to energy parameters. Table.3, gives the absolute values of Oscillator strength and Judd-Ofelt intensity parameter T_λ ($\lambda=2, 4, 6$) which have been determined under different experimental conditions for the interaction of Pr(III) and Guanosine/GTP.

Table 3: Observed and Computed values of Oscillator Strengths ($P \times 10^6$) and Judd- Ofelt ($T_\lambda \times 10^{10}$) parameters for Pr(III), Pr(III):L and Pr(III):L:Ca(II), (1:1:1) in different aquated organic solvents 298K(pH4), (L= Guanosine,GTP)

System	${}^3H_4 \rightarrow {}^1D_2$ P _{obs} , (P _{cal})	${}^3H_4 \rightarrow {}^3P_0$ P _{obs} , (P _{cal})	${}^3H_4 \rightarrow {}^3P_1$ P _{obs} , (P _{cal})	${}^3H_4 \rightarrow {}^3P_2$ P _{obs} , (P _{cal})	T ₂	T ₃	T ₄
1.Solvent:CH₃CN, L= Guanosine							
Pr(III)	2.443861 (2.443861)	0.8924 (0.6627)	0.4264 (0.6526)	0.7052 (0.7052)	-2.439	1.8207	7.5293
Pr(III):L	2.884613 (2.884613)	0.8955 (0.6725)	0.4329 (0.653)	0.831 (0.831)	-2.833	1.8823	9.0123
Pr(III):L:Ca(II)	2.900472 (2.900472)	0.9035 (0.6839)	0.4473 (0.6644)	0.8849 (0.8849)	-14.32	1.914	9.0552
L= GTP							
Pr(III)	2.443861 (2.443861)	0.8924 (0.6627)	0.4264 (0.6526)	0.7052 (0.7052)	-2.439	1.8207	7.5293
Pr(III):L	2.654619 (2.654619)	0.8997 (0.6713)	0.4304 (0.6598)	0.7078 (0.7078)	-61.08	0.2501	8.0601
Pr(III):L:Ca(II)	2.728307 (2.728307)	0.9066 (0.6739)	0.4393 (0.6625)	0.7601 (0.7601)	-47.55	0.2576	8.9726
2. Solvent: CH₃OH, L= Guanosine							
Pr(III)	2.669057 (2.669057)	0.7966 (0.6053)	0.4078 (0.5961)	0.7868 (0.7868)	1.4653	1.663	8.3098
Pr(III):L	2.991033 (2.991033)	0.8058 (0.6254)	0.4382 (0.6159)	0.7966 (0.7966)	-17.57	1.7181	9.3518
Pr(III):L:Ca(II)	2.997821 (2.997821)	0.8469 (0.6329)	0.4396 (0.4854)	0.8058 (0.8058)	-23.69	1.7541	9.4903
L= GTP							
Pr(III)	2.669057 (2.669057)	0.7966 (0.6053)	0.4078 (0.5961)	0.7868 (0.7868)	1.4653	1.663	8.3098
Pr(III):L	2.933212 (2.933212)	0.7998 (0.6109)	0.4139 (0.6073)	0.7881 (0.7881)	-53.78	1.699	9.1772
Pr(III):L:Ca(II)	2.945997 (2.945997)	0.8312 (0.6232)	0.4237 (0.6122)	0.8035 (0.8035)	-35.2	1.732	9.642
3. Solvent: Dioxane, L= Guanosine							
Pr(III)	2.689602 (2.689602)	0.7523 (0.5826)	0.4066 (0.5737)	0.7949 (0.7949)	2.1498	1.6006	8.3953
Pr(III):L	3.330865 (3.330865)	0.8596 (0.677)	0.4869 (0.6667)	0.9848 (0.9848)	2.6164	1.86	10.43
Pr(III):L:Ca(II)	3.343981	0.8609	0.4963	0.9885	-49.61	1.8783	10.566

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	(3.343981)	(0.6872)	(0.6774)	(0.9885)			
L= GTP							
Pr(III)	2.689602 (2.689602)	0.7523 (0.5826)	0.4066 (0.5737)	0.7949 (0.7949)	2.1498	1.6006	8.3953
Pr(III):L	2.692734 (2.692734)	0.7676 (0.5987)	0.4445 (0.5833)	0.8422 (0.8422)	-101.1	1.9843	9.4772
Pr(III):L:Ca(II)	3.809138 (3.809138)	0.8227 (0.6472)	0.4677 (0.6436)	0.9218 (0.9218)	-91.77	1.9986	9.7447
4. Solvent: DMF, L= Guanosine							
Pr(III)	3.066379 (3.066379)	0.8865 (0.6906)	0.4874 (0.6804)	0.8626 (0.8626)	-7.603	1.8984	9.5585
Pr(III):L	3.125784 (3.125784)	1.0515 (0.795)	0.5306 (0.7834)	0.866 (0.866)	-17.88	2.1858	10.6778
Pr(III):L:Ca(II)	3.673293 (3.673293)	1.6665 (0.8077)	0.5312 (0.789)	0.8729 (0.8729)	16.251	2.6434	11.7374
L= GTP							
Pr(III)	3.066379 (3.066379)	0.8865 (0.6906)	0.4874 (0.6804)	0.8626 (0.8626)	-7.603	1.8984	9.5585
Pr(III):L	3.111372 (3.111372)	1.0156 (0.7235)	0.5161 (0.7187)	0.8627 (0.8627)	-98.86	2.0885	9.5804
Pr(III):L:Ca(II)	3.263881 (3.263881)	1.2437 (0.7788)	0.5295 (0.7748)	0.8695 (0.8695)	-98.16	2.3661	9.6392
5. Solvent: CH₃OH+ CH₃CN, L= Guanosine							
Pr(III)	2.82359 (2.89359)	0.6812 (0.5386)	0.3899 (0.5304)	0.6999 (0.6999)	-28.18	1.4795	8.8645
Pr(III):L	3.180095 (3.180095)	1.0815 (0.77)	0.4516 (0.7583)	0.8795 (0.8795)	-11.54	2.1153	9.8644
Pr(III):L:Ca(II)	3.195112 (3.195112)	1.086 (0.7834)	0.4525 (0.779)	0.8885 (0.8885)	-15.02	2.173	9.968
L= GTP							
Pr(III)	2.82359 (2.82359)	0.6812 (0.5386)	0.3899 (0.5304)	0.6999 (0.6999)	-28.18	1.4795	8.8645
Pr(III):L	2.846376 (2.846376)	0.9439 (0.6909)	0.4358 (0.6895)	0.7733 (0.7733)	-39.08	2.2492	9.7052
Pr(III):L:Ca(II)	3.033962 (3.033962)	1.0425 (0.7529)	0.4411 (0.714)	0.7975 (0.7975)	-10.03	2.2546	9.7632

Judd and Ofelt have suggested three phenomenological parameters (T_2 , T_4 and T_6) which are sensitive towards the changes in the immediate co-ordination environment. It has been observed that there is a significant change in the Oscillator strength of 4f-4f bands, when Pr(III) interacts with the ligands (Guanosine/GTP). We also observed noticeable increase in the magnitude of Judd-Ofelt parameters suggesting the binding of ligands in solution. The intensification became more when Ca(II) ion is added to the binary mixture of Pr(III) and ligands (Guanosine/GTP). This shows the stimulated effect of Ca(II) towards the complexation. It has been observed that among the three T_λ parameters, T_6 is the best defined while T_2 is the least defined parameter for Pr(III) complex since by definition, $T_\lambda \geq 0$ and their order is $T_6 > T_4 > T_2$. In practice both the Oscillator strength of the transitions and the T_λ parameters have provided significant structural information about lanthanide co-ordination especially in solution state. The values of T_2 for most of the complexes appear to be negative which is meaningless. This is because ${}^3F_2 \rightarrow {}^3H_4$ transition has a significant $U^{(2)}$ matrix and it is not included in the data set of any of the complex as it is

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beyond the range of UV region. However, T_4 and T_6 are affected significantly. Both parameters are related to changes in symmetry properties of the complex species. At the same time, the extent of mixing of 4f and 4d orbital also influences T_6 parameter predominantly, while some influence of T_4 can also be extended.

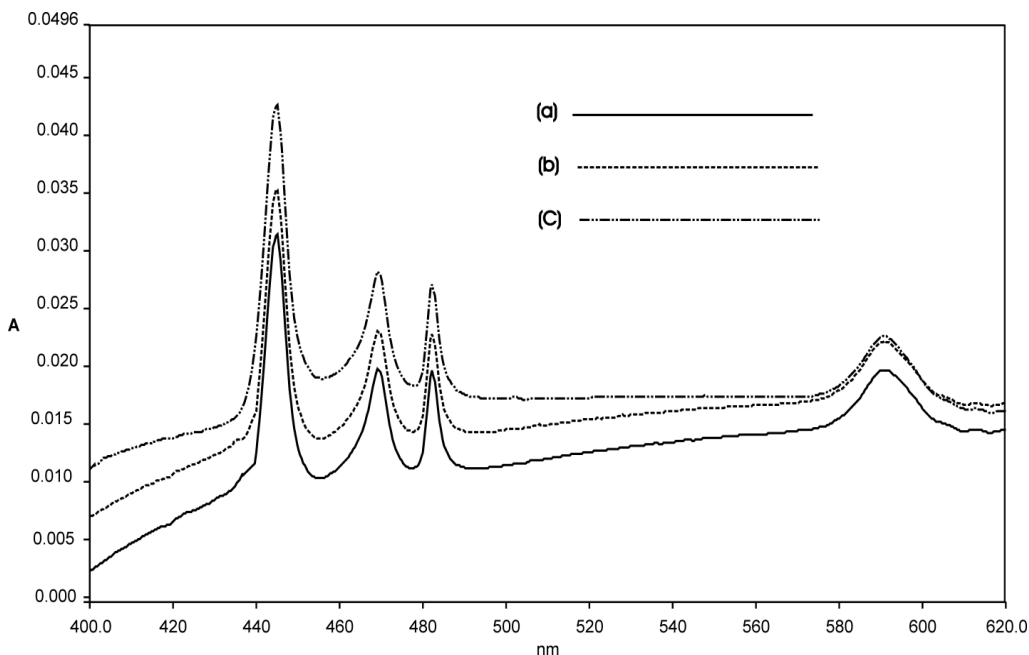


Figure 1: Comparative absorption spectra of (a) Pr(III) (b) Pr(III): Guanosine (c) Pr(III): Guanosine: Ca(II) (1:1:1) in DMF solvent.

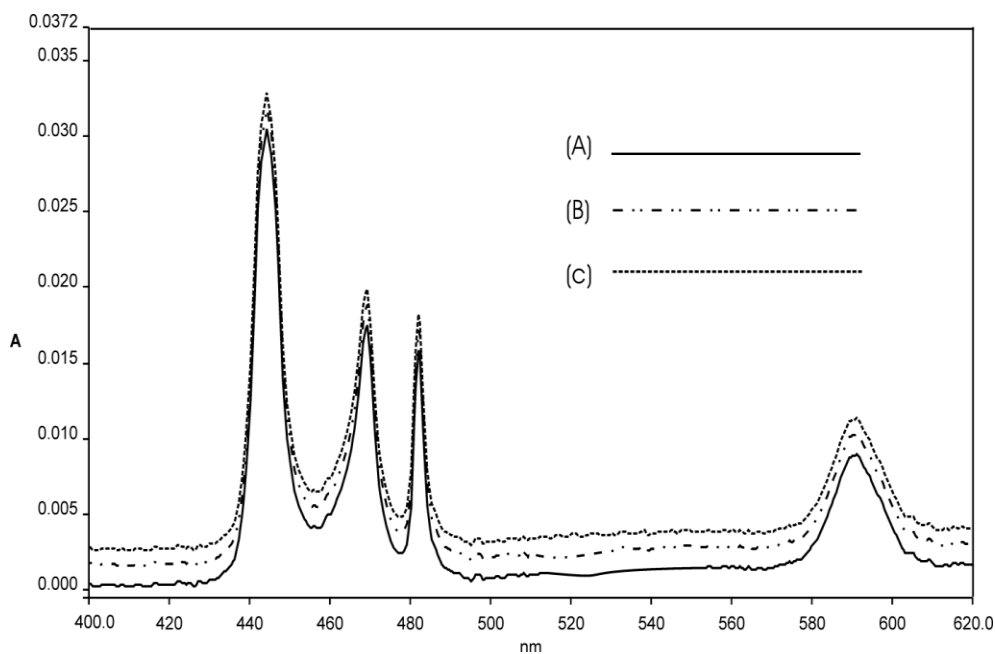


Figure 2: Comparative absorption spectra of (A) Pr(III), (B) Pr(III): GTP, (C) Pr(III): GTP: Ca(II) (1:1:1) in DMF solvent.

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It is also noted that T_4 and T_6 are greatly affected in the presence of different solvents. These suggest that the symmetry of the complex species changed significantly and not only the immediate co-ordination of environment of Pr(III), these changes are considered to be a good evidence for the involvement of ligands (Guanosine/GTP) in the inner sphere co-ordination of Pr(III). The observation made from the Tables is supported by the comparative absorption spectra shown in Figure 1 and 2, where there is significant change in the intensity of the peak of the spectra when Pr(III) interacts with Guanosine/GTP in solution. Comparative absorption spectra of Pr(III), Pr(III):L (L=Guanosine/GTP) and Pr(III):L:Ca(II) in DMF clearly show that the addition of the ligands (Guanosine/GTP) results in significant enhancement in the Oscillator strength of different 4f-4f transitions (Figure 1 and 2).

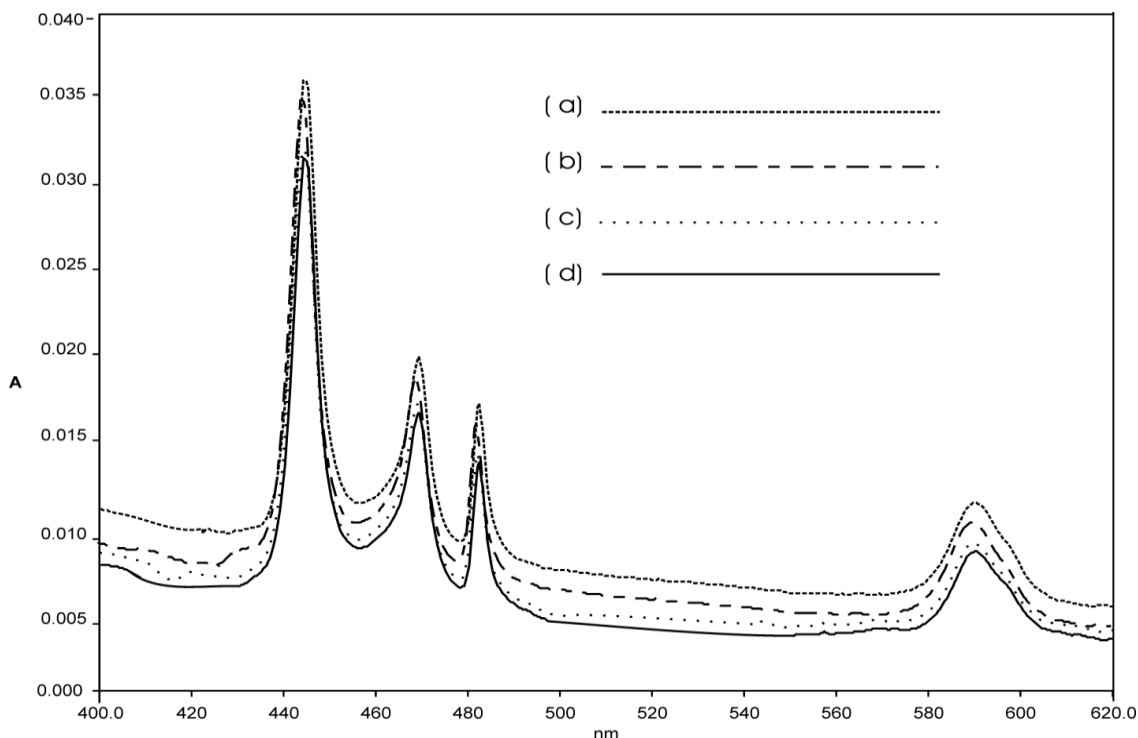


Figure 3: Comparative absorption spectra of Pr(III):Guanosine in (a) DMF (b) CH₃CN (c) Dioxane (d) CH₃OH

As a result we have observed noticeable increase in the magnitude of Judd-Ofelt T_λ parameters. Such increase in the value of Oscillator strength and T_λ is more when Ca(II) is added to the solution of Pr(III):L (L=Guanosine/GTP). This is due to the involvement of Ca(II) to the other legating site of Guanosine/GTP. The effect of the solvent on complexation is quite interesting. The occurrence of different intensification of the bands of the four transitions reveals the sensitivities of the solvents in the formation of the complex of Pr(III):L (L=Guanosine/GTP) as shown in Figure 3, where the order of sensitivities are DMF>CH₃CN>Dioxane>CH₃OH. That is DMF appears to induced the strongest influence on Pr(III):L complex and least in the case of methanol. This is because of the participation of nitrogen donor site of DMF in the complexation and nitrogen has stronger bonding capacity than the oxygen of methanol.

Conclusion

From the present systematic investigation, it has been concluded that the interaction of Pr(III) with Guanosine and GTP has been determined by absorption spectroscopy and can be used to study the nature of binding of some biologically important ligands. The results show that the increase in the value of nephelauxetic (β), bonding parameter ($b^{1/2}$) and percent covalency (δ) leads to stronger binding of metal ions with Guanosine/GTP and Ca(II). The decrease in the values of inter-electronic repulsion parameters,

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Slater-Condon (F_k), Racah (E^k) and spin-orbit coupling constant (ξ_{4f}) indicates the expansion of the central metal ion orbital when ligands are added to Pr(III) and also on further addition of Ca(II) ion, leading to lowering of co-ordination number and shortening of M-L bond, when metal ion is co-ordinated with the ligands in the presence and absence of Ca(II). And also increase in the observed values of Oscillator strength and Judd-Ofelt when ligands are added to the metal ion further supported the mentioned information. From the comparative absorption spectra of complexation of Pr(III) with Guanosine/GTP, it is found that among all the solvents used, DMF is the most favoured solvent whereas methanol is the least. This is due to the presence of N-donor ligand, which is more electronegative than the O-donor ligand of methanol.

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