

Computation of Energy, Intensity and Thermodynamic Parameters for the Interaction of Ln(III) with Nucleic Acid: Analysis of Structural Conformations, Chemical Kinetics and Thermodynamic Behaviour through $4f-4f$ Transition Spectra as Probe

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Abstract

Nucleosides and Nucleotides are polydentate ligands, offering potential binding sites for metal ions. Energy interaction parameters: Slater Condon F_k (cm^{-1}), Spin Orbit interaction ξ_{4f} (cm^{-1}), Nephelauxetic Ratio (β), Bonding ($b^{1/2}$) and Co-valency (δ) parameter for the interaction of Pr(III) with Nucleoside and Nucleotide are evaluated to study the mode of binding of the Nucleic Acid Components (Guanosine and Guanosine Triphosphate) with Pr(III). Further Intensity Parameters like Oscillation Strength and Judd Ofelt Parameter (T_2 , T_4 , T_6) have been evaluated to investigate degree of inner or outer sphere co-ordination of Pr(III) with Nucleic Acid ligands. Comparative Absorption Spectra in different solvents substantiate the informations, gathered from the evaluated values of both energy interaction and intensity parameters. Further evaluation of Thermodynamic parameters (ΔG , ΔH and ΔS) through Kinetic studies enable to provide the detailed information about the reaction pathways and thermodynamic behaviour of the complexation process of nucleosides and nucleotides with Pr(III) and Ca^{2+} .

Keywords

Nucleic Acid, $4f-4f$ Transition Spectra, Nephelauxetic Effect, Judd-Ofelt Parameters, Slater Condon, Reaction Rate, Thermodynamic

1. Introduction

Because of their remarkable and unmatched optical, spectroscopic, luminescent and magnetic properties, the lanthanides are under the limelight when it comes to high technology. The synthetic versatility, favorable optical and electronic properties are a wide spectrum for pharmacological, medicinal and biological activities of compounds. In view of the above applications and properties of lanthanide elements, it has become more important to understand the behaviors of lanthanide ion in biological system. Therefore the main idea behind this proposed work is to explore the potential of these fascinating lanthanides as spectral and structural probes in biochemical reactions which has immense importance in human metabolism. Solution spectral studies through kinetic and thermodynamic approach involving lanthanide complexes are very pertinent information about the mechanism, reaction pathways, and also about the chemical bonding and conformations.

The electronic transitions having high sensitivity of spectral intensities for ligand environment as a great phenomenon was first noticed by Moeller *et al.* [1] [2] 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 of some transitions even though they don't obey selection rule show sensitivities even minor changes of the coordinating environment. Such transitions have been called pseudoquadrupole in character [3] [4]. The hypersensitive transition have widely been used as probe in extracting information regarding the binding characteristics of the co-ordinating ligands, relative binding capability of different binding sites, degree of outer and inner sphere coordination and identification of immediate coordination environment in the complex species [5] [6] [7] [8].

Much of the interest in lanthanide biochemistry flows from the ability of Ln(III) ion to replace Ca(II) in a specific and often isomorphous manner. It is worth comparing the properties of Ln(III) and Ca(II) in greater detail. Good reviews of the biologically important chemical properties of Ca(II) have been provided by Levine and Williams [9] and Einspahr and Bug [10]. Martin [11] has reviewed the structural chemistry of calcium and the lanthanides.

Nucleosides and nucleotides are the structural subunit of nucleic acids, the heredity controlling components of all living cells. Nucleosides and nucleotides contain two nearly planar rings, that of the base and that of ribofuranose. The anti conformer has the smaller H-6 (pyrimidine) or H-8 (purine) atom above the sugar ring, while the syn conformer has the larger O-2 (pyrimidine) or N-3 (purine) in that position. Both nucleosides and nucleotides have UV absorption profiles rather similar to those of their constituent's bases and absorb strongly with λ_{max} values close to 260 nm and molar extinction coefficient of around 104. This property finds uses in the detection and quantitative analysis not only

of the free bases but also of nucleosides/nucleotides. They undergo marked changes when they are in close proximity to neighboring bases. Over the past 10 years there has been a resurgence of interest in the coordination chemistry of lanthanide complexes in solution. A renewed interest in this work may be connected with an enhanced appreciation of the rich functionality of lanthanide complexes [12] [13]. Much progress has been recently achieved in the coordination chemistry of lanthanides because of their medicinal and biochemical applications

Solution spectral studies through kinetic approach involving lanthanide complexes are very important because it can provide very pertinent information about the mechanism, reaction pathways, and also about the chemical bonding and conformations. Basing on the isomorphous characteristics of Ca^{2+} with Ln^{3+} , we have chosen Praseodymium ion among the lanthanides, since these ions have optimum ionic radii for the effective isomorphous substitution of Ca^{2+} in biomolecules consequently mimicking the interaction between Ca^{2+} and the metabolites occurring *in-vivo* intracellularly. Ca^{2+} being diamagnetic are spectroscopically silent towards optical and magnetic techniques. Therefore the isomorphous substitution of Ca^{2+} by Pr^{3+} can provide a very useful supplement to understand the interaction of Guanosine and Guanosine Triphosphate (GTP) with Ca^{2+} since Ln^{3+} are paramagnetic and spectroscopically active.

Though the solution spectral analysis may not give very distinctive quantitative data but it provides useful data for structural determination, mechanistic studies and for creating optimum experimental condition required for product formation of some desired pre-determined configurations with advanced technology adopting much better resolution of solution spectral $4f-4f$ bands. Quantitative Absorption Spectroscopy can prove as an improved tool on mechanistic, diagnostic and condensation studies too [14].

In this Paper we will use comparative absorption and absorption difference spectrophotometry involving $4f-4f$ transition spectra as probe in understanding the binding characteristics of Guanosine and GTP with lanthanides (Pr^{3+}) in the presence and absence of Ca^{2+} ; it will be further studied through kinetic and thermodynamic approach.

2. Methodology

The spectral analysis is made through Perkin Elmer Lambda-35 UV-V is Spectrophotometer at 298 K upgraded with computer attached.

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

$$E = \sum_k \int F_k + A_{\text{SO}} \xi_{4f} \quad (1.1)$$

where F_k and A_{SO} are the angular part of electrostatic and spin orbit interaction respectively and their values can be calculated by applying tensor operator technique; F_k and ξ_{4f} are radial integrals.

The energy E_j of the j^{th} energy level is given by:

$$E_j(F_k, \xi_{4f}) = E_{0j}(F_k^0, \xi_{4f}^0) + \sum_{k=2,4,6} \frac{\delta E_j}{\delta F_k} \Delta F_k + \frac{\delta E_j}{\delta \xi_{4f}} \Delta \xi_{4f} \quad (1.2)$$

where E_{0j} is the zero order energy of the j^{th} level.

Nephelauxetic effect, which measures the change in F_k with respect to free ion and expressed by a nephelauxetic ratio " β ", and is given as:

$$\beta_1 = \frac{F_k^0}{F_k^f}, \beta_2 = \frac{\xi_{4f}^0}{\xi_{4f}^f} \quad \text{and} \quad \beta = \left[\frac{\beta_1 + \beta_2}{2} \right] \quad (1.3)$$

where F_k^0 and F_k^f ($k = 2, 4, 6$) refers to parameters in complex and free ion respectively.

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.

$$\frac{P_{\text{obs}}}{\nu} = [(U^2)]^2 T_2 + [(U^4)]^2 T_4 + [(U^6)]^2 T_6 \quad (1.4)$$

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

For praseodymium complexes, four equations exist for the observed values of the four bands. Since $[(U^2)]^2$ and $[(U^6)]^2$ has zero value for the 3P_1 and 3P_0 levels, the ordinary simultaneous equation gave the values of T_2 , T_4 and T_6 by simple calculation.

3. Methods for Chemical Kinetic Studies

All the spectra were recorded on a different temperatures *i.e.* 298 K, 303 K, 308 K, 313 K, 318 K and at pH-4 and pH-2 for Guanosine and GTP ligands using water circulating HAAKE DC 10 Thermostat. The activation energy for the complexation of Pr(III): (Guanosine and GTP) with Ca(II) in DMF is calculated from the plot of $\log k$ (k = rate constant) against $1/T$ using Arrhenius rate equation.

4. Results and Discussions

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** and **Table 2**. 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 behavior and changes in the immediate co-ordination environment, and referred these transitions as ligand mediated pseudo-hypersensitive transitions [15]. Misra [16] [17] 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

Table 1. Computed values of energy interaction Slater Condon F_k (cm^{-1}), 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 298 K (pH4) are given below (L = Guanosine).

System	F_2	F_4	F_6	ξ_{4f}	β	$b^{1/2}$	δ
1. solvent: CH₃CN							
L = Guanosine							
Pr(III)	309.2775	42.6682	4.6671	721.3976	0.9459	0.1644	5.7170
Pr(III): L	309.1232	42.6645	4.6668	721.1872	0.9465	0.1645	5.7492
Pr(III): L: Ca(II)	309.1059	42.6621	4.6665	721.0225	0.9466	0.1647	5.7646
2. solvent: CH₃OH							
L = Guanosine							
Pr(III)	309.2092	42.6698	4.6672	721.6282	0.9461	0.1642	5.6974
Pr(III): L	309.1303	42.6613	4.6670	721.6277	0.9462	0.1644	5.6979
Pr(III): L: Ca(II)	309.1237	42.6545	4.6669	721.6127	0.9463	0.1648	5.6681
3. solvent: Dioxane							
L = Guanosine							
Pr(III)	309.2458	42.6638	4.6666	721.0352	0.9456	0.1649	5.7499
Pr(III): L	309.0907	42.6670	4.6663	721.0150	0.9462	0.1651	5.8906
Pr(III): L: Ca(II)	309.0703	42.6658	4.6660	721.0149	0.9469	0.1655	5.8909
4. solvent: DMF							
L = Guanosine							
Pr(III)	308.9664	42.6528	4.6654	720.3402	0.9450	0.1658	5.8161
Pr(III): L	308.9304	42.6478	4.6648	720.2060	0.9469	0.1660	5.8323
Pr(III): L: Ca(II)	308.9303	42.6467	4.6642	720.2059	0.9470	0.1668	5.8391
5. solvent: CH₃OH + CH₃CN							
L = Guanosine							
Pr(III)	309.2747	42.6733	4.6676	721.6556	0.9462	0.1641	5.6912
Pr(III): L	309.1764	42.6721	4.6675	721.4573	0.9465	0.1643	5.7077
Pr(III): L: Ca(II)	306.1620	42.3071	4.6276	721.2027	0.9467	0.1648	5.7256

Table 2. Computed value of energy interaction Slater Condon F_k (cm^{-1}), 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 298 K (pH₂) are given below (L = GTP).

system	F_2	F_4	F_6	ξ_{4f}	β	$b^{1/2}$	δ
1. solvent: CH₃CN							
L = GTP							
Pr(III)	309.2275	42.6672	4.6681	721.3676	0.9449	0.1634	5.7070
Pr(III): L	309.2242	42.6550	4.6669	721.3924	0.9501	0.1680	5.7521
Pr(III): L: Ca(II)	309.2191	42.6498	4.6660	721.3920	0.9575	0.1681	5.7440

Continued

2. solvent: CH ₃ OH							
= GTP							
Pr(III)	309.2192	42.6598	4.6572	721.6582	0.9460	0.1640	5.6972
Pr(III): L	309.1748	42.6368	4.6646	721.1405	0.9458	0.1645	5.6975
Pr(III): L: Ca(II)	309.1661	42.5812	4.6594	721.1210	0.9404	0.1646	5.6977
3. solvent: Dioxane							
L = GTP							
Pr(III)	309.2258	42.6838	4.6766	721.0332	0.9458	0.1648	5.7498
Pr(III): L	309.0960	42.6259	4.6534	721.0144	0.9469	0.1650	5.8082
Pr(III): L: Ca(II)	309.0631	42.6283	4.6436	721.0138	0.9471	0.1651	5.8888
4. solvent: DMF							
Pr(III)	308.9662	42.6526	4.6652	720.3401	0.9430	0.1654	5.8141
Pr(III): L	308.9385	42.6490	4.6650	718.3099	0.9436	0.1679	5.9766
Pr(III): L: Ca(II)	308.9245	42.6470	4.6648	718.0476	0.9437	0.1682	5.9990
L = GTP							
Pr(III)	308.9662	42.6526	4.6652	720.3401	0.9430	0.1654	5.8141
Pr(III): L	308.2099	42.6364	4.6631	720.2464	0.9453	0.1659	5.8234
Pr(III): L: Ca(II)	308.2057	42.6356	4.6623	720.2456	0.9456	0.1662	5.8247
5. solvent: CH ₃ OH + CH ₃ CN							
L = GTP							
Pr(III)	309.2743	42.6730	4.6677	721.6546	0.9450	0.1640	5.6913
Pr(III): L	309.2642	42.6353	4.6644	720.6934	0.9462	0.1641	5.6913
Pr(III): L: Ca(II)	309.2619	42.6226	4.6630	719.8930	0.9465	0.1651	5.7676

of the ligand and nature as well as the geometry of the complex species induced unusual sensitivity to this pseudo-hypersensitive transition. Karraker [18] studied the hypersensitive transition correlating with the co-ordination number of lanthanide ions. As such the interaction of ligands (Guanosine and GTP) with Pr(III) in different aquated organic solvents like Dimethylformamide (DMF), Methanol (CH₃OH), Acetonitrile (CH₃CN), Dioxane (DX) and solvent mixture have been investigated, which gives results of the shape, energy and oscillator strength of pseudo-hypersensitive transition that correlates with co-ordination number.

The comparative absorption spectra of Pr(III), Pr(III): Ligands, Pr(III): Ligands: Ca(II) (*Ligands-Guanosine and GTP*) are shown in **Figure 1** and **Figure 2**, as sample among the various figures, which shows that the addition of ligands to Pr(III) ions enhances the intensities of the different $4f4f$ transitions *i.e.* there is a red shift in all the energy bands. Also the intensities of the different $4f4f$ transitions increases when Ca(II) ion is added to the solution. As a consequence,

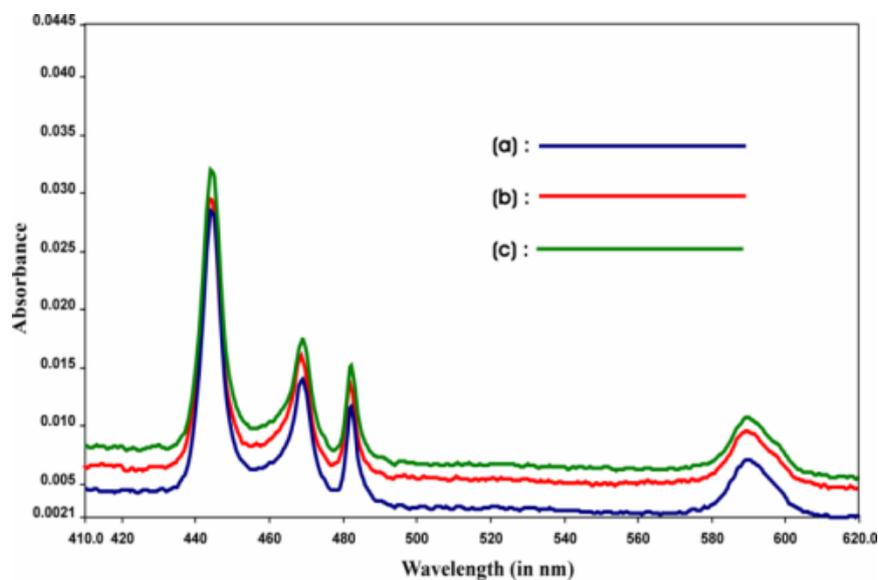


Figure 1. Comparative absorption spectra of (a) Pr(III), (b) Pr(III): Guanosine, Pr(III): Guanosine: Ca(II) in acetonitrile.

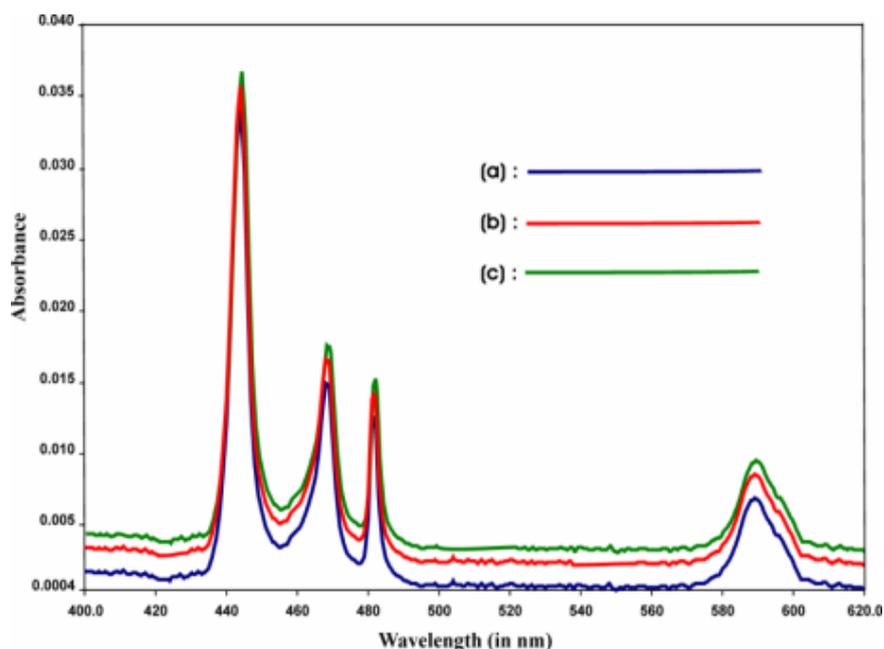


Figure 2. Comparative absorption spectra of (a) Pr(III), (b) Pr(III): GTP (c) Pr(III): GTP: Ca(II) in acetonitrile.

we have observed noticeable increase in the magnitude of Judd-Ofelt intensity parameters (T_{λ}). These suggest the binding of Ligands 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.

As a result, the nephelauxetic effect increases when the co-ordination number

decreases. Misra *et al.* [19] 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 1** and **Table 2** show the variations of the magnitude of energy interaction parameters like Slater-Condon (F_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 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 value of F_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.

Table 3 and **Table 4** give the absolute values of Oscillator strength and Judd-Ofelt intensity parameter T_λ ($\lambda = 2, 4, 6$) which have suggested three phenomenological parameters (T_2, T_4, 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 and also 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 showing 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 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. 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 in the inner sphere co-ordination of Pr(III).

The observation made from the Tables is further supported by the comparative absorption spectra shown in **Figure 1** and **Figure 2** (among the various spectra), where there is significant change in the intensity of the peak of the spectra when Pr(III) interacts with different ligands in solution, (*Viz-Guanosine and GTP*) resulting significant enhancement in the Oscillator strength of different $4f-4f$ transitions. 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):

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(1:1) and Pr(III): L: Ca(II) (1:1:1), (L = Guanosine) in different Aqueated Organic Solvents at 298 K (pH4).

System	$^3H_4 \rightarrow ^1D_2$	$^3H_4 \rightarrow ^3P_0$	$^3H_4 \rightarrow ^3P_1$	$^3H_4 \rightarrow ^3P_2$	T_2	T_3	T_4
	P_{obs} (P_{cal})	P_{obs} (P_{cal})	P_{obs} (P_{cal})	P_{obs} (P_{cal})			
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
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
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 (3.343981)	0.8609 (0.6872)	0.4963 (0.6774)	0.9885 (0.9885)	-49.61	1.8783	10.566
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
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	10.968

Table 4. 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(1:1) and Pr(III): L: Ca(II) (1:1:1), (L = GTP) in different Aqueated Organic Solvents at 298 K (pH2).

System	$^3H_4 \rightarrow ^1D_2$	$^3H_4 \rightarrow ^3P_0$	$^3H_4 \rightarrow ^3P_1$	$^3H_4 \rightarrow ^3P_2$	T_2	T_3	T_4
	P_{obs} (P_{cal})	P_{obs} (P_{cal})	P_{obs} (P_{cal})	P_{obs} (P_{cal})			
1. Solvent: CH₃CN							
L = GTP							
Pr(III)	2.441861 (2.441861)	0.8824 (0.6527)	0.4164 (0.6426)	0.7152 (0.7152)	-2.339	1.8407	6.5293
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 = GTP							
Pr(III)	2.649057 (2.649057)	0.7866 (0.5953)	0.3978 (0.5761)	0.7668 (0.7668)	1.4253	1.623	8.2898
Pr(III): L	2.933212 (2.933212)	0.7998 (0.6109)	0.4139 (0.6073)	0.7881 (0.7881)	-53.78	1.799	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	1.912	9.642
3. Solvent: Dioxane							
L = GTP							
Pr(III)	2.629602 (2.629602)	0.7323 (0.5826)	0.4166 (0.5737)	0.7649 (0.7649)	2.1298	1.5906	8.3253
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 = GTP							
Pr(III)	3.046379 (3.046379)	0.8665 (0.6606)	0.4574 (0.6704)	0.8226 (0.8226)	-7.583	1.8484	9.5285
Pr(III): L	3.111372 (3.111372)	1.0156 (0.7235)	0.5161 (0.7187)	0.8627 (0.8627)	-98.86	2.0885	9.9804
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	10.8392
5. Solvent: CH₃OH + CH₃CN							
L = GTP							
Pr(III)	2.80359 (2.80359)	0.6412 (0.5186)	0.3699 (0.5004)	0.6799 (0.6799)	-28.15	1.4295	8.8345
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

Ligand. This is due to the involvement of Ca(II) to the other ligating site of the Ligands.

We have used comparative absorption and absorption difference spectroscopy, along with the variation of different spectral intensity parameters (P and T_λ) involving intra $4f-4f$ transitions as probe in following the simultaneous coordination of selected ligands with Pr(III) and Ca(II) and to investigate their rate of reaction, activation energy and consequently thermodynamic behavior, evaluating their thermodynamic parameters like ΔH° , ΔS° and ΔG° .

The time scan absorption spectra of the formation of the Pr(III): Guanosine complexes with Ca(II) respectively at 298 K, 308 K, 310 K and 318 K are recorded. Several sets of kinetic experiments were conducted for the selected ligands but for brevity only ten sets of kinetic run showing changes in absorbance with time at different temperatures. From the selected **Figure 3** it can be observed that there is an increase of absorbance and intensity with time. Both hypersensitive and pseudohypersensitive transitions of Pr(III) display significant changes during complexation, which can be seen from the spectral changes with time (**Figure 3**) The top most curve in all the cases represent the stage of apparent completion of the complexation and no further changes were noted over the next few days.

Only one **Table 5** is selected from various tables which show the observed (P_{obs}) and calculated (P_{cal}) values of oscillator strengths and Judd-Ofelt intensity parameter, T_λ ($\lambda = 2.4.6$) for complexation of Pr(III): Nucloeside/Nucleotide with Ca(II) in DMF at different temperatures, viz; 298 K, 303 K, 308 K, 313 K and 318 K respectively. The rate of complexation for both Pr(III): (Nucloeside/Nucleotide): Ca(II) at different temperatures were evaluated by plotting the oscillator strength against time.

From **Table 5**, we can clearly see that the rates of complexation of Pr(III): (Nucloesides/Nucleotides) with Ca(II) linearly increases with the increase in time and temperature. Since the intensity of $4f-4f$ transitions show substantial

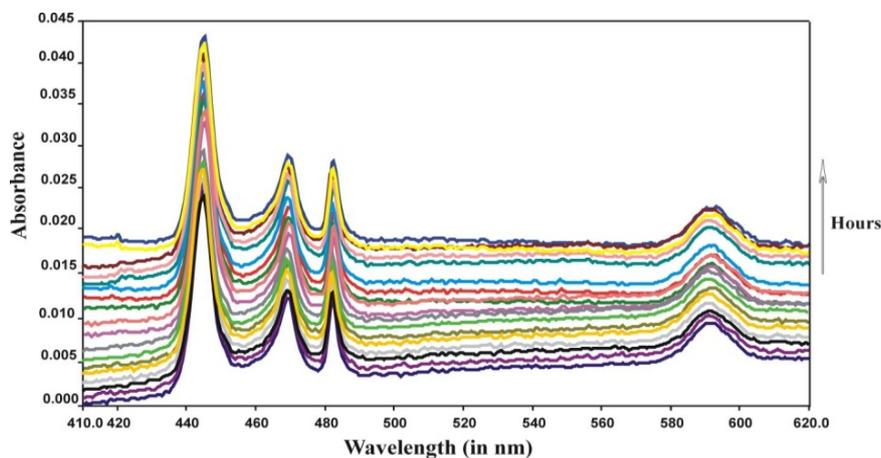


Figure 3. Comparative absorption spectra of Pr(III): Guanosine complexation with Ca(II) in DMF at 289 K (25°C) and at different times (hour).

Table 5. Observed and calculated Oscillator strengths ($P \times 10^6$) and Judd Ofelt parameter (T_λ , $\lambda = 2, 4, 6 \times 10^{10} \text{ cm}^{-1}$) parameters for Pr(III): Guanosine: Ca(II) complex at 298 K (25°C) at different time (hrs).

Time (hr)	$^3\text{H}_4 \rightarrow ^3\text{P}_2$		$^3\text{H}_4 \rightarrow ^3\text{P}_1$		$^3\text{H}_4 \rightarrow ^3\text{P}_0$		$^3\text{H}_4 \rightarrow ^1\text{D}_2$		T_2	T_4	T_6
	Pobs	Pcal	Pobs	Pcal	Pobs	Pcal	Pobs	Pcal			
0	0.6627	0.6627	0.1762	0.1526	0.127	0.1502	0.3103	0.3103	26.59	0.4193	2.0628
2	0.6783	0.6783	0.1766	0.1527	0.1288	0.1513	0.3235	0.3235	28.584	0.4198	2.1145
4	0.6959	0.6959	0.1848	0.1602	0.1335	0.1527	0.3309	0.3309	29.073	0.4202	2.166
6	0.6986	0.6986	0.1873	0.1628	0.1361	0.1602	0.3382	0.3382	30.567	0.4472	2.1729
8	0.7177	0.7177	0.1904	0.1652	0.1377	0.1626	0.3389	0.3389	31.358	0.4537	2.2343
10	0.7251	0.7251	0.1915	0.1672	0.1407	0.1685	0.3394	0.3394	31.768	0.4705	2.2442
12	0.7388	0.7388	0.1934	0.1689	0.1463	0.1695	0.3425	0.3425	32.349	0.4745	2.2535
14	0.7537	0.7537	0.1968	0.1692	0.1474	0.1727	0.3437	0.3437	32.606	0.4762	2.2723
16	0.7593	0.7593	0.1973	0.1694	0.1486	0.1735	0.3449	0.3449	33.108	0.4867	2.2993
18	0.7653	0.7653	0.1993	0.1699	0.1496	0.1759	0.3464	0.3464	33.805	0.4888	2.3131
20	0.7674	0.7674	0.2085	0.1743	0.1519	0.1767	0.3488	0.3488	35.598	0.4914	2.3287
22	0.7752	0.7752	0.2129	0.1752	0.1568	0.1774	0.3493	0.3493	35.683	0.4945	2.3456
24	0.7754	0.7754	0.2176	0.1767	0.1596	0.1781	0.3544	0.3544	36.391	0.4965	2.3598
26	0.7878	0.7878	0.2192	0.1774	0.1599	0.1791	0.3547	0.3547	36.417	0.4998	2.3694
28	0.7947	0.7947	0.2197	0.1779	0.1626	0.1831	0.3558	0.3558	37.294	0.5198	2.3786
30	0.8092	0.8092	0.2291	0.1784	0.1641	0.1848	0.3575	0.3575	37.886	0.5299	2.3888
32	0.8167	0.8167	0.2391	0.1786	0.1651	0.1865	0.3584	0.3584	38.621	0.5305	2.3976
34	0.8221	0.8221	0.2398	0.1792	0.1693	0.1896	0.3593	0.3593	39.393	0.5334	2.3997

increase with Time, hence absorption spectral analysis of $4f4f$ transitions can be used to explore the kinetics of the formation of the complexes. The observed values of rate (k) have been evaluated in terms of the complex formed during the progress of the reaction and the same has been evaluated from the plots of oscillator strength of $^3\text{H}_1 \rightarrow ^3\text{P}_2$ transitions of Pr(III) complex formation versus time (in hour) [Figure 4]. The values of activation energy (E_a) and thermodynamic parameters is evaluated from the Vant Hoff plot of $\ln k$ against $1/T$ [Figure 5] This technique can provide a means to determine indirectly the thermodynamic parameters of the complexation of Pr(III): ligands and Ca(II) ions in DMF medium.

From the above mentioned tables it was clearly seen that rate of complexation increases with increase in temperature and from which the rate of reaction and activation energy E_a of the complexation is evaluated as shown in Table 6. From the values of the thermodynamic parameters in Table 7, we observe that the values of ΔH° and ΔS° are positive which indicates that the complexation reaction is endothermic and entropy increasing process. Further, since $T\Delta S^\circ > \Delta H^\circ$ the coordination reaction is entropy driven process. Negative values of standard

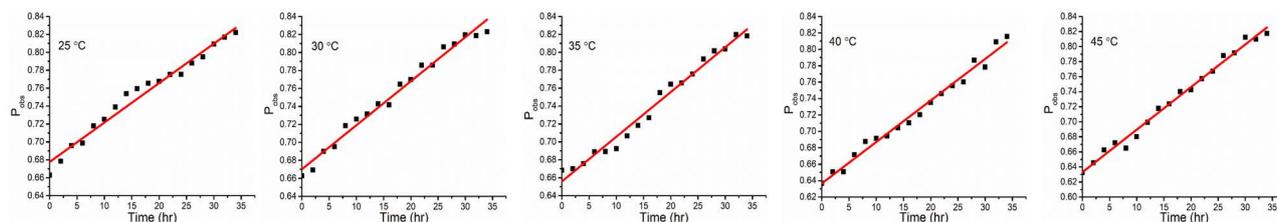


Figure 4. Plot of P_{obs} and time (Hr) for the ${}^3\text{H}_4 \rightarrow {}^3\text{P}_2$ transition of Pr(III): Guanosine and Ca(II) at different temperatures.

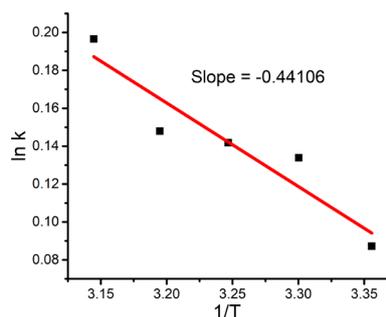


Figure 5. Plot of $\ln k$ versus $(1/T) \times 10^{-3}$ for the complexation of Pr(III): Guanosine: Ca(II) in DMF medium.

Table 6. Rate at different temperatures; *i.e.* 298 K, 303 K, 308 K, 313 K and 318 K and activation energy E_a .

Temp (K)	$1/T \times 10^3$	Rate $\text{mol}\cdot\text{L}^{-1}\cdot\text{hr}^{-1}$	Rate (K) $\text{mol}\cdot\text{L}^{-1}\cdot\text{s}^{-1} \times 10^{-6}$	Log K	Activation Energy E_a (KJ)
298	3.3557	0.0044	1.2222	0.087142	
303	3.3003	0.0049	1.3611	0.133890	
308	3.2468	0.00499	1.3861	0.141795	0.008445
313	3.1949	0.00506	1.4056	0.147862	
318	3.1447	0.00566	1.5722	0.196508	

Table 7. Rate and thermodynamic parameters for the complexation of Pr(III): Guanosine: Ca(II) at different temperatures.

Temp (K)	Rate (k) $\text{mol}\cdot\text{L}^{-1}\cdot\text{s}^{-1} \times 10^{-6}$	ΔH° (kJ $\cdot\text{mol}^{-1}$)	ΔS° (J $\cdot\text{K}^{-1}\cdot\text{mol}^{-1}$)	ΔG° (kJ $\cdot\text{mol}^{-1}$)
298	1.2222		0.0017	-0.49722
303	1.3611		0.0026	-0.77677
308	1.3861	0.008445	0.0027	-0.83621
313	1.4056		0.0028	-0.88614
318	1.5722		0.0038	-1.19649

Gibbs energy (ΔG°) indicates that the simultaneous coordination is a spontaneous processes and the process is favored in solution. We can further justify that the simultaneous complexation reaction between Pr(III) ions with (Nucleoside/Nucleotide) and metal ions, Ca(II) occurs but at a spontaneous pace, fol-

lowing the randomness of the system when it approaches higher temperatures (increasing ΔS° values). Further, we have also observed that the activation energies (E_a) for Guanosine was the lowest *i.e.*, 0.008445 in Pr(III); the same trend was observed for GTP with 0.0047 in Pr(III), which supports our earlier report that the most sensitive ligand for nucleoside in binding with Pr(III) was Guanosine. The lower values of E_a gives further evidence that the reaction involved are fast reactions.

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Conflicts of Interest

The authors declare no conflicts of interest regarding the publication of this paper.

References

- [1] Moeller, T. and Brantley, J.C. (1958) *J. Am. Chem. Soc.*, **72**, 5447. <https://doi.org/10.1021/ja01168a022>
- [2] Moeller, T. and Jackson, D.E. (1950) *Anal. Chem.*, **22**, 1393.
- [3] Gorller-Wairand, C. and Billemans, K. (1996) Spectral Intensities of f-f Transition, In: Gschneidner, K.A. and Eyring, L., Eds., *Handbook on Physics and Chemistry of Rare Earth*, North Holland Amsterdam, Ch. 23, Vol. 155, 121.
- [4] Evers, A. and Chrysochoos (1973) *Chem. Phys. Lett.*, **18**, 115. [https://doi.org/10.1016/0009-2614\(73\)80353-7](https://doi.org/10.1016/0009-2614(73)80353-7)
- [5] Sinha, S.P. (1976) *Struct. and Bonding.*, **25**, 69. https://doi.org/10.1007/3-540-07508-9_3
- [6] Misra, S.N. (1985) *J. Scient. Ind. Res.*, **44**, 366.
- [7] Mason, S.F., Peacock, R.D. and Stewart, B. (1975) *Molec. Phys.*, **30**, 1829.
- [8] Mason, S.F. (1986) *J. Indian Chem. Soc.*, **63**, 73.
- [9] Levine, B.A. and William, R.J.P. (1982) The Chemistry of Calcium Ion and Its Biological Relevance, in the Role of Calcium in Biological System. In: Anghileri, L.J. and Tuffet-Anghileri, A.M., Eds., Vol. 1, CRC Press, Boca Raton, FL, 3-26.
- [10] Einspahr, H. and Bugg, C.E. Crystal Structure Studies of Calcium Complexes and Implications for Biological System. In: Sigel, H., Ed., *Metal Ions in Biological System*, Marcel Dekker, New York, 51-97.
- [11] Martin, R.B. (1983) Structural Chemistry of Calcium: Lanthanides as Probes. In: Spiro, T.G., Ed., *Calcium Biology*, Wiley, New York, 237-270.
- [12] Godin, B., Sakamoto, J.H., Serda, R.E., Grattoni, A., Boumarini, A. and Ferrari, M. (2010) *Trends Pharmacol. Sci. [TiPS]*, **31**, 199-205. <https://doi.org/10.1016/j.tips.2010.01.003>
- [13] Babailov, S.P. (2012) *Inorg. Chem.*, **51**, 1427-1433. <https://doi.org/10.1021/ic201662q>
- [14] Misra, S.N., Ramchandriah, G., Gagnani, M.A., Shukla, R.S. and Devi, M.I. (2006) *Appl. Spectrosc. Rev.*, **38**, 433-493. <https://doi.org/10.1081/ASR-120026330>
- [15] Devlin, M.T., Stephens, E.M. and Richardson, F.S. (1988) *Inorg. Chem.*, **27**, 1517.

- <https://doi.org/10.1021/ic00282a003>
- [16] Peacock, R.D. (1970) *Chem. Phys. Lett*, **7**, 187.
[https://doi.org/10.1016/0009-2614\(70\)80282-2](https://doi.org/10.1016/0009-2614(70)80282-2)
- [17] Devi, M.I. and Misra, S.N. (1997) *Spectrochim. Acta*, **53**, 1941.
[https://doi.org/10.1016/S1386-1425\(97\)00064-4](https://doi.org/10.1016/S1386-1425(97)00064-4)
- [18] Karkaker, D.G. (1969) *J. Inorg. Nucl. Chem*, **31**, 2815-2832.
[https://doi.org/10.1016/0022-1902\(69\)80198-3](https://doi.org/10.1016/0022-1902(69)80198-3)
- [19] Abdi, S.H.R., Anjaiah, K., Joseph, G.K. and Misra, S.N. (1992) "B". *Indian J. Biochem. Biophys*, **27**, 285-290.