4f-4f absorption spectral study for the interaction of Pr(III) and Nd(III) with uracil in presence and absence of Ca(II): A Model on the use of Ln(III) as probes at Ca(II) binding sites in biological systems.

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Abstract

A bioinorganic approach into the problem of the isomorphous substitution of calcium(II) by lanthanide(III) ions in biological system is explored through absorption difference and comparative absorption spectroscopy involving 4f-4f transitions. The interaction of Pr(III) and Nd(III) with uracil induced substantial changes in the intensities of 4f-4f bands and their perturbation was reflected through oscillator strength and Judd-Ofelt intensity (T_λ) parameters. Intensification of these bands became more prominent in presence of Ca(II) thereby suggesting that the changes in the oscillator strengths of different 4f-4f bands and Judd-Ofelt intensity (T_λ) parameters can be followed to predict in vivo intracellular complexation of uracil with Ca(II) in vitro as both Pr(III) and Nd(III) have unique similarity in their coordination with Ca(II).

1. Introduction

The unique spectroscopic and paramagnetic properties of lanthanide ions have made them a fascinating field of research in bioinorganic and coordination Chemistry [1,2]. Also their ability to substitute Ca(II) in isomorphous manner are gaining increasing importance for the perception of structural features of biomolecules so as to stimulate biological and biochemical research [3]. The Ca(II) has become involved in a vast array of intracellualar and extracellular biochemical processes and structures [4]. It is an essential component in the biominerilization of teeth, bones and shells, mainly in the forms of hydroxyapatite, calcite or aragonite. Within the cell, Ca(II) has a large number of diverse roles in metabolic regulation, nerve transmission, muscle contraction, cell motility, etc. This metal ion is also able to act as a "second messenger' activating various intracellular protein systems. Outside the cell, processes such as protein stability and enzyme catalysis may be Ca(II)-dependant. In biological processes, calcium ions commonly exert their effects by binding to proteins, normally via aspartate or glutamate residues and peptide oxygen [5]. The Ca(II) ion is almost spectroscopically silent, having no UV-Vis electronic spectrum and no EPR signal. Information regarding the structures of the binding sites in Ca(II)-binding protein is difficult to obtain using techniques other than X-ray protein crystallography. Lanthanide(III) ions occur in only trace amounts in organisms and do not seem to play any biological role. Moreover, Ln(III) ions are considered only slightly toxic. The trivalent lanthanides,

however, interact with biological materials in specific ways which along with their magnetic and spectroscopic properties make them very informative substitution probes for calcium-containing biological material [6]. Isomorphous substitution of metal ions in biological materials is indeed less sensitive to charge than to size. The lanthanide ions have several properties that facilitate Ca(II) substitution [6,8]. In many cases, the similarity in size and coordination geometries results in functional substitution. However, the difference in charge may eventually induce changes in the conformation of the biomolecules and/or in their activity. In some cases, it has been shown that Ca(II) substitution by Ln(III) probes is indeed perfectly isomorphous, for instance in thermolysin [7]. For other systems, for instances in calmodulin, Ln(III) probes do not seem to be the ideal models for study [7]. As the key point to the success of many biological investigations on Ca(II)-binding biomolecules is the assumption that Ln(III) ions replace Ca(II) isomorphously, it is important to establish what changes, if any, occur upon metal ion substitution. Despite size similarities, it is possible that Ln(III) ions may bind to Ca(II)-binding site in a significantly different manner than Ca(II) does. To contribute to this research area, we have recently initiated [9-12] a systematic comparative study of the coordination chemistry of trivalent lanthanides with ligands containing donor groups of biological relevance including DNA and amino acids. With these consideration in mind, we have explored the binding nature of uracil with Pr(III) in presence of Zn(II) in previous paper [13]. In the

present paper we herein report the interaction of Pr(III) and Nd(III) with uracil in presence of Ca(II) in different aquated organic solvents by following absorption difference and comparative absorption spectroscopy involving 4f-4f transitions to predict in vivo intracellular complexation of uracil with Ca(II) in vitro. The corresponding changes in the oscillator strengths of different 4f-4f bands and experimentally determined Judd-Ofelt intensity (T_λ) parameters are correlated with the binding of uracil. The values of other energy interaction parameters namely Slator-Condon (F_k), nephelauxetic (β), bonding $b^{1/2}$ and covalency (δ) parameters have been calculated to support the intensity data.

2. Experimental Methods and Materials
2.1. Materials
The solvents and chemicals used were of A.R./G.R. grade from Merck E. Neodymium nitrate hexahydrate and praseodymium nitrate hexahydrate of 99.999% purity were procured from CDH, Mumbai. Ca(II) nitrate (Aldrich USA) and uracil of A.R./G.R. grade was purchased from SRL India and used as such.
The absorption spectral data are recorded on Perkin Elmer Lambda -35 UV-Vis Spectrometer equipped with a device for kinetic and high resolution spectral analysis. The concentrations of Nd(III), Pr(III), uracil and Ca(II) were maintained at 0.01 mol L^{-1} and spectral analysis were carried out by using different solvents.

2.2. Method
The energy of 4f-4f transitions are composed of two main components : coulombic F_k and spin-orbit coupling 4f parameters, represented in the form of equation as follows

$$E_{obs} = f^k F_k + A_{so} \xi_{4f}$$

(1)

where f^k and A_{so} are the angular counterpart of coulombic and spin-orbit interaction, while F_k (Slator-Condon inter-electronic parameter) and ξ_{4f} are the radial integral known as Lande's parameter. The values of inter-electronic repulsion parameters i.e., Slator-Condon, F_k's and Spin-orbit coupling Lende's parameter, ξ_{4f} are determined by using the method outlined in our earlier papers [14,15].

If the f-orbital's are involved in covalent bond formation with the ligand, the metal wave function can be expressed [16] as

$$<\varphi_{4f} = (1-b)^{1/2} < 4f \mid -b^{1/2} < \varphi_{ligand} \mid$$

(2)

where $b^{1/2}$ measures the amount of 4f-orbital mixing, i.e. covalency. Sinha [17] has proposed a δ scale to express the covalency. Both the parameters $b^{1/2}$ and δ are related to the nephelauxetic effect, i.e. β. The covalency parameter $(\beta, b^{1/2}, \delta)$ of the complexes have been calculated using the relationship [16-18] :

$$\beta = \frac{F_k{}^c}{F_k{}^f} \text{ or } \beta = \frac{E_c{}^k}{E_f{}^k}$$

(3)

where $F_k{}^c$ (k=2,4,6) and $E_c{}^k$ the Slator-Condon and Racah parameters for complex, and $F_k{}^f$ and $E_f{}^k$ for free ions respectively.

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

(4)

$$\delta = \left(1 - \beta \middle/ \beta \right) \times 100$$

(5)

The intensity of the absorption band is measured by experimentally determined oscillator strength (P_{obs}), which is directly proportional to the area under the absorption curve and is found out by Gaussian curve analysis [19] as

$$P = 4.6 \times 10^{-9} \times \varepsilon_{max} \times \Delta \upsilon_{1/2}$$

(6)

where ε_{max} is the molar extinction coefficient and $\Delta \upsilon_{1/2}$ is the half band width. The calculated oscillator strength of the induced dipole transition $\pi J \rightarrow \pi 'J'$ of the energy (cm^{-1}) in accordance with Judd [20] and Ofelt [21] can be expressed as

$$P_{cal} = \sum_{k=2,4,6} T_\lambda \upsilon \left\langle f^n \psi_j \middle\| U^{(\lambda)} \middle\| f^n \psi_{j'} \right\rangle^2$$

(7)

Which can be reduced to

$$P_{cal} \middle/ \upsilon = \left[U^{(2)} \right]^2 . T_2 + \left[U^{(4)} \right]^2 . T_4 + \left[U^{(6)} \right]^2 . T_6$$

(8)

where $U^{(\lambda)}$ is the matrix element of unit tensor operator connecting initial $< f^n \psi_j \mid$ and final $\mid f^n \psi_{j'} >$ through three phenomenological parameters T_λ (λ=2,4,6) called Judd-Ofelt parameters. These parameters are related to the radial wave function of the states and ligand field parameters that characterize the surrounding field. The three parameters T_2, T_4 and T_6 are related to the radial part of the 4f^n wavefunction of the perturbing configuration. The values of T_λ parameters have been computed by using the matrix elements given in our earlier paper [14].

3. RESULTS AND DISCUSSIONS
The absorption spectra of Nd(III) and Pr(III) has been carried out in aqueous and aquated organic solvents and their interaction with uracil in presence of Ca(II) is correlated with changes in the oscillator strengths and Judd-Ofelt (T_λ) parameters. The 4f-4f bands of Nd(III)and Pr(III) are used as a marker bands to investigate the interaction of Nd(III) and Pr(III) with uracil in solution.

3.1. Interaction of Nd(III)-uracil in presence of Ca(II)
We see that there is a red shift as uracil is added to Nd(III) and further shift towards longer wavelength on addition of Ca(II) (Fig. 1). The binding of Nd(III)-uracil brings about the changes in energies of various 4f-4f bands which causes the degree of lowering in the energy interaction parameters, Slator-Condon inter-electronic repulsion, which leads to the nephelauxetic effect and the intensifications of the f-f transitions. Nephelauxetic effect is taken as a measure of metal-ligand covalent bonding.

This effect may be visualized to be due to an expansion of the wave functions which results from interaction between the metal cations and neighbouring ligands.

Table-1 listing the variation of the magnitude of energy interaction parameters like Slator-Condon (F_k), nephelauxetic ratio (β), bonding ($b^{1/2}$) and percentage covalency (δ) for Nd(III), Nd(III):uracil and Nd(III):uracil:Ca(II) in different solvents reveals that the addition of uracil to Nd(III) brings about lowering of these parameters indicating the expansion of 4f orbitals on interaction. Since lanthanides are hard metal ions in the Pearson classification scheme [22] they prefer hard donor sites like oxygen atoms. This implies that interaction of Nd(III) with uracil is generally predominant with the carbonyl group of uracil. Hence the bonding between Nd(III) and uracil is basically electrostatic in nature as indicated by the absolute values of nephelauxetic effect (β), covalency (δ) and bonding parameters ($b^{1/2}$) thereby suggesting that the mode of binding of uracil to Nd(III) involves predominantly ionic mode [23]. The absolute values of the oscillator strength and Judd-Ofelt intensity (T_λ) parameters are determined under the different experimental conditions and are listed in Table-2. Table 2 has shown that the addition of uracil to Nd(III) brings about a noticeable enhancement in the oscillator strength of 4f-4f bands irrespective of solvent nature. Consequently, marked variation in the experimentally determined Judd-Ofelt (T_λ) intensity parameters was found. This intensification of 4f-4f bands can be interpreted in terms of interaction of 4f-orbital with ligand wavefunction. The intensification of bands and red shift were taken as an evident for the involvement of ligand in complexation. These suggest the binding of the uracil to Nd(III) in solution. Besides, the shape of 4f-4f bands and absorption spectra pattern as a whole has been found to be quite similar to that shown by Nd(III) aquo ion suggesting almost similar nonacoordinated environment around Nd(III) in Nd(III)-uracil complex in solution. Fig.1. also shows that the addition of Ca(II) to Nd(III)-uracil in 1:1:1 stoichiometry brought significant changes in the energies and intensity parameters. 4f-4f bands showed gradual increase in the intensity along with significant red shift, an indication that addition of Ca(II) to Nd(III):uracil (1:1:1) strengthened the binding of uracil to Nd(III). This means that the increased probability of interaction of 4f-orbital with ligand wavefunction .

The $^4I_{9/2} \rightarrow {}^4G_{5/2}$ transition of Nd(III) is considered as hypersensitive transition as it obeys selection rules for quadrupole transitions and undergoes very high intensification on complexation [24,25]. Small changes in the immediate coordination environment around Nd(III) brings about wide variation of oscillator strength. The other transitions of Nd(III) are reported to very sensitive even on minor changes in the coordination environment [10,11]. Iftikar [26] has reported a marginal increase (15%) in the oscillator strength of the non-hypersensitive transitions, contrary to the several fold increase shown by hypersensitive $^4I_{9/2} \rightarrow {}^4G_{5/2}$ transition. Table 2 clearly shows the variation of the oscillator strength of $^4I_{9/2} \rightarrow {}^4G_{7/2}$, $^4I_{9/2} \rightarrow {}^4F_{3/2}$, $_{/2} \rightarrow {}^4F_{5/2}$, and $^4I_{9/2} \rightarrow {}^4F_{7/2}$ which do not obey the

selection rule, yet these show significant sensitivity evidenced by large variation of oscillator strength which is almost same as shown by hypersensitive $^4I_{9/2} \rightarrow {}^4G_{5/2}$ transition. We are reporting the high sensitivity of these non-hypersensitive transitions. It appears that the nature of ligand and lability and geometry of complex species induce the unusual sensitivity to these non-hypersensitive transitions.

Solvents have been found to play a significant role in the interaction of Nd(III) with uracil. Comparative absorption spectra of Nd(III):uracil in different aquated organic solvents (Fig. 2) clearly shows the affinity of solvents towards the Nd(III) coordination environment. DMF appears to have strongest influence on Nd(III):uracil followed by dioxane and least in acetonitrile. This means that DMF has larger impact in promoting 4f-4f electric dipole intensity, which is in accordance with our previous studies [10]. This large increase in oscillator strength in DMF might be due to ligand polarization effect. The difference in oscillator strength in different solvents may be associated to ligand (solvent) structure and their coordination behaviours. The DMF has two coordination sites but it generally binds via oxygen when it coordinates to hard acids like lanthanides.

The red shift observed in the energies of all the 4f-4f bands are considered as marker for quantitative analysis in Nd(III) ion. Although we have found red shift in energies of all transitions, the effect is more pronounced in DMF. The red shift is due to the expansion of the metal orbital radius which leads to nephelauxetic effect. At the same time, the nephelauxetic effect brings about a shortening of the metal-ligand bond length thereby increasing the probability of interaction between metal and ligand orbital. This clearly shows the involvement of uracil in the inner sphere coordination around the metal ion. Though the ligand environment has only weak influence on the electronic cloud of the Nd(III), the 4f shell is efficiently shielded by the close 5s and 5p shells. This clearly shows without doubt that the interaction of Nd(III)-uracil is effected significantly by the nature of solvents. All results obtained clearly suggest that minor coordination changes around the Nd(III) are caused by different coordinating sites of uracil, solvent nature, coordination number, nature of Nd(III):uracil band which do induce significant variation in the intensity of 4f-4f transitions.

3.2. Interaction of Pr(III)-uracil with Ca(II)

The interaction of Pr(III) with uracil indicates noticeable changes in the energy interaction parameters as observed in the Nd(III) ion which became more prominent in presence of Ca(II). However, the changes in the nephelauxetic parameter, β is varied significantly and found to be less than unity thereby suggesting that the Pr(III)-uracil bond is a more covalent type than the Nd(III)-uracil bond in similar experimental conditions (Table-3). The different solvents and their different compositions have a momentous effect on the biological activities of uracil (Fig.3).

Table 1:
Computed values of Slator-Condon(F_k), spin-orbit coupling constant (ξ_{4f}), nephelauxetic ratio (β), bonding ($b^{1/2}$) and covalency parameters (δ) for the complexation of Nd(III) with uracil in presence and absence of Ca(II) in aqueous and aquated organic solvents at 25^0C.

System	F_2	F_4	F_6	ξ_{4f}	β	$b^{1/2}$	δ
H₂O							
Nd(III)	331.07	48.77	5.18	917.72	1.00	0.053	0.566
Nd(III):uracil	331.25	48.64	5.17	917.73	1.00	0.058	0.522
Nd(III):uracil:Ca(II)	330.90	48.60	5.21	917.68	1.01	0.074	1.011
MeOH							
Nd(III)	331.08	48.59	5.18	921.88	1.007	0.061	0.746
Nd(III):uracil	331.05	48.60	5.19	921.28	1.007	0.062	0.779
Nd(III):uracil:Ca(II)	331.03	48.63	5.18	921.84	1.007	0.062	0.762
Dioxane							
Nd(III)	330.92	48.64	5.21	926.25	1.010	0.070	1.063
Nd(III):uracil	331.77	49.11	5.23	915.22	1.007	0.071	0.745
Nd(III):uracil:Ca(II)	330.90	48.60	5.21	927.19	1.011	1.011	1.100
MeCN							
Nd(III)	330.87	48.61	5.20	926.89	1.010	0.073	1.079
Nd(III):uracil	330.87	48.60	5.20	927.29	1.011	0.074	1.102
Nd(III):uracil:Ca(II)	330.87	48.60	5.20	927.21	1.011	0.074	1.097
DMF							
Nd(III)	331.27	48.63	5.17	917.35	1.004	0.069	0.482
Nd(III):uracil	331.25	48.64	5.17	917.83	1.005	0.076	0.522
Nd(III):uracil:Ca(II)	331.51	48.61	5.15	911.61	1.001	0.022	0.101
MeCN : Dioxane							
Nd(III)	330.78	48.63	5.21	928.98	1.012	0.078	1.227
Nd(III):uracil	330.79	48.62	5.21	928.99	1.012	0.080	1.220
Nd(III):uracil:Ca(II)	330.61	48.62	5.22	932.59	1.014	0.085	1.439
DMF:MeCN							
Nd(III)	330.90	48.62	5.20	926.02	1.010	0.072	1.032
Nd(III):uracil	330.90	48.61	5.20	926.42	1.010	0.079	1.010
Nd(III):uracil:Ca(II)	330.88	48.60	5.21	927.39	1.011	0.075	1.111
MeOH : Dioxane							
Nd(III)	330.85	48.62	5.21	928.09	1.011	0.077	1.170
Nd(III):uracil	330.86	48.62	5.21	927.83	1.011	0.068	1.150
Nd(III):uracil:Ca(II)	330.75	48.64	5.22	929.61	1.012	0.080	1.267
MeOH : DMF							
Nd(III)	330.83	48.61	5.21	928.78	1.012	0.078	1.205
Nd(III):uracil	330.83	48.61	5.21	928.53	1.012	0.072	1.186
Nd(III):uracil:Ca(II)	330.71	48.61	5.21	930.13	1.013	0.080	1.281
DMF : Dioxane							
Nd(III)	330.77	48.62	5.21	929.02	1.012	0.068	1.217
Nd(III):uracil	330.77	48.62	5.21	928.98	1.012	0.069	1.214
Nd(III):uracil:Ca(II)	330.64	48.60	5.22	931.72	1.014	0.083	1.376
MeOH : MeCN							
Nd(III)	331.03	48.65	5.19	921.92	1.007	0.062	0.783
Nd(III):uracil	331.03	48.64	5.19	922.54	1.008	0.070	0.817
Nd(III):uracil:Ca(II)	331.07	48.66	5.19	921.13	1.007	0.060	0.736

Table 2:

Experimental values of oscillator strength ($P_{exp} \times 10^{-6}$) and Judd-Ofelt (T_λ) parameters for the complexation of Nd(III) with uracil in different aquated organic solvents at 25 °C.

System	$^4G_{7/2}$	$^4G_{5/2}$	$^4F_{7/2}$	$^4F_{5/2}$	$^4F_{3/2}$	T_2	T_4	T_6
H₂O								
Nd(III)	1.317	4.781	2.601	2.517	0.463	26.06	6.55	46.94
Nd(III):uracil	1.181	4.783	2.603	2.453	0.467	24.91	3.17	50.47
Nd(III):uracil:Ca(II)	0.981	4.401	3.023	2.495	0.470	28.33	5.61	59.08
MeOH								
Nd(III)	1.050	5.141	2.622	2.319	0.549	29.13	4.80	47.46
Nd(III):uracil	1.051	5.203	2.716	2.291	0.540	32.86	2.95	66.48
Nd(III):uracil:Ca(II)	1.100	5.286	4.313	2.646	0.763	32.12	3.46	69.03
Dioxane								
Nd(III)	1.097	5.473	3.076	2.427	0.6107	32.28	6.29	51.13
Nd(III):uracil	1.134	5.751	3.229	2.560	0.6121	34.82	5.35	54.33
Nd(III):uracil:Ca(II)	1.221	6.092	3.296	2.704	0.579	35.16	5.42	54.02
MeCN								
Nd(III)	1.067	5.987	3.167	2.420	0.644	31.24	5.03	50.68
Nd(III):uracil	1.130	6.005	3.287	2.542	0.684	32.05	6.02	52.6
Nd(III):uracil:Ca(II)	1.448	5.784	3.379	2.666	0.555	32.87	5.37	54.91
DMF								
Nd(III)	1.223	6.193	3.209	2.524	0.547	32.28	3.52	53.30
Nd(III):uracil	1.261	6.151	3.393	2.509	0.502	41.08	3.36	56.87
Nd(III):uracil:Ca(II)	1.321	6.922	3.452	2.742	0.541	41.21	0.90	58.29
MeCN : Dioxane								
Nd(III)	1.029	6.344	3.519	2.401	0.628	29.77	6.70	50.22
Nd(III):uracil	1.015	6.492	3.603	2.504	0.668	70.59	8.73	59.56
Nd(III):uracil:Ca(II)	1.081	5.854	3.625	2.637	0.616	28.07	14.79	47.07
DMF : MeCN								
Nd(III)	1.223	6.254	3.159	2.559	0.681	35.86	5.13	54.10
Nd(III):uracil	1.274	6.581	3.549	2.607	0.617	34.31	8.00	65.40
Nd(III):uracil:Ca(II)	1.427	6.582	3.698	2.941	0.586	37.75	6.18	56.05
MeOH:Dioxane								
Nd(III)	1.218	5.724	3.030	2.492	0.606	33.58	2.02	51.26
Nd(III):uracil	1.139	5.647	3.206	2.372	0.532	33.73	7.20	51.26
Nd(III):uracil:Ca(II)	1.306	5.567	3.122	2.609	0.569	32.04	5.43	52.27
MeOH : DMF								
Nd(III)	1.075	6.044	3.266	2.565	0.610	32.97	7.54	49.00
Nd(III):uracil	1.171	5.928	3.171	2.425	0.678	35.91	25.72	49.10
Nd(III):uracil:Ca(II)	1.185	6.288	3.218	2.588	0.601	37.63	5.40	54.24
DMF : Dioxane								
Nd(III)	0.925	5.503	2.833	2.187	0.539	48.82	4.60	98.96
Nd(III):uracil	0.999	5.684	2.842	2.166	0.525	49.32	3.56	99.16
Nd(III):uracil:Ca(II)	1.075	5.685	2.859	2.307	0.473	43.85	2.90	99.58
MeOH : MeCN								
Nd(III)	1.140	5.592	3.152	2.615	0.644	32.10	6.39	52.45
Nd(III):uracil	1.219	5.743	3.210	2.622	0.605	33.89	6.06	53.75
Nd(III):uracil:Ca(II)	1.127	5.547	3.239	2.729	0.591	31.29	7.30	56.35

Table 3:
Computed values of energy interaction parameters Slator-Condon (F_k), Spin-orbit coupling constants (ξ_{4f}), nephelauxetic ratio(β), bonding ($b^{1/2}$) and covalency (δ) parameters for Pr(III); Pr(III):uracil; Pr(III):uracil:Ca(II) in different solvents.

System	F_2	F_4	F_6	ξ_{4f}	β	$b^{1/2}$	δ
H₂O							
Pr(III)	309.06	42.66	4.66	722.17	0.9464	0.1637	5.6599
Pr(III):uracil	309.09	42.66	4.66	722.16	0.9468	0.1631	5.6200
Pr(III):uracil:Ca(II)	309.13	42.67	4.66	722.16	0.9467	0.1633	5.6344
MeOH							
Pr(III)	308.95	42.65	4.66	722.16	0.9463	0.1639	5.6779
Pr(III):uracil	308.95	42.65	4.66	722.15	0.9463	0.1638	5.6734
Pr(III):uracil:Ca(II)	308.95	42.65	4.66	722.14	0.9463	0.1639	5.6742
DMF							
Pr(III)	308.83	42.63	4.66	722.87	0.9460	0.1643	5.7053
Pr(III):uracil	308.81	42.63	4.66	721.84	0.9458	0.1646	5.7261
Pr(III):uracil:Ca(II)	308.72	42.61	4.66	722.31	0.9460	0.1643	5.7041
MeCN							
Pr(III)	308.93	42.64	4.66	722.23	0.9462	0.1640	5.6838
Pr(III):uracil	308.92	42.64	4.66	722.13	0.9462	0.1640	5.6838
Pr(III):uracil:Ca(II)	308.91	42.63	4.66	722.13	0.9463	0.1639	5.6755
Dioxane							
Pr(III)	308.93	42.65	4.66	722.28	0.9463	0.1638	5.6721
Pr(III):uracil	308.92	42.64	4.66	722.25	0.9466	0.1634	5.6442
Pr(III):uracil:Ca(II)	308.92	42.64	4.66	722.21	0.9465	0.1636	5.6554
DMF:Dioxane							
Pr(III)	308.84	42.63	4.66	722.33	0.9462	0.1640	5.6826
Pr(III):uracil	308.83	42.63	4.66	722.14	0.9461	0.1642	5.6991
Pr(III):uracil:Ca(II)	308.73	42.62	4.66	722.16	0.9460	0.1644	5.7137
DMF:MeCN							
Pr(III)	308.87	42.64	4.66	722.83	0.9461	0.1642	5.6970
Pr(III):uracil	308.84	42.63	4.66	722.82	0.9466	0.1635	5.6455
Pr(III):uracil:Ca(II)	308.92	42.64	4.66	722.69	0.9466	0.1634	5.6436
MeOH:MeCN							
Pr(III)	308.95	42.65	4.66	722.02	0.9462	0.1640	5.6884
Pr(III):uracil	308.95	42.65	4.66	721.98	0.9461	0.1641	5.6923
Pr(III):uracil:Ca(II)	308.90	42.65	4.66	722.11	0.9463	0.1638	5.6736
MeOH:Dioxane							
Pr(III)	308.94	42.65	4.66	722.33	0.9464	0.1637	5.6663
Pr(III):uracil	308.93	42.64	4.66	722.28	0.9465	0.1635	5.6495
Pr(III):uracil:Ca(II)	308.92	42.64	4.66	722.26	0.9466	0.1639	5.6752
MeOH:DMF							
Pr(III)	308.88	42.64	4.66	722.65	0.9465	0.1635	5.6515
Pr(III):uracil	308.85	42.62	4.66	722.51	0.9466	0.1638	5.6684
Pr(III):uracil:Ca(II)	308.78	42.62	4.66	722.45	0.9465	0.1640	5.6840
MeCN:Dioxane							
Pr(III)	308.93	42.64	4.66	722.11	0.9462	0.1640	5.6853
Pr(III):uracil	308.92	42.63	4.66	722.10	0.9463	0.1640	5.6856
Pr(III):uracil:Ca(II)	308.91	42.64	4.66	722.10	0.9463	0.1640	5.6855

Table 4:

Experimental values of oscillator strength (Px10^{-6}) and Judd-Ofelt (T$_\lambda$) parameters for Pr(III); Pr(III):uracil; Pr(III):uracil:Ca(II) in different solvents.

| System	$^3P_2$	$^3P_1$	$^3P_0$	$^1D_2$	T_2	T_4	T_6
H$_2$O							
Pr(III)	2.976	0.752	0.396	0.873	-10.93	1.58	09.33
Pr(III):uracil	1.467	0.736	0.379	0.868	-28.77	1.54	04.40
PrIII):uracil:Ca(II)	2.903	0.719	0.401	0.890	-23.55	1.54	09.10
MeOH							
Pr(III)	3.297	0.786	0.441	0.9272	-28.03	1.69	10.36
Pr(III):uracil	3.249	0.782	0.161	1.1801	-52.97	1.30	10.31
PrIII):uracil:Ca(II)	3.436	0.807	0.457	0.9637	-48.93	1.74	10.80
DMF							
Pr(III)	3.415	1.017	0.515	1.129	-29.73	2.11	10.64
Pr(III):uracil	3.545	0.878	0.494	1.156	-27.69	1.89	11.12
PrIII):uracil:Ca(II)	3.769	1.030	6.366	1.174	-26.85	10.30	12.61
MeCN							
Pr(III)	3.174	0.772	0.417	0.924	-10.49	1.64	09.97
Pr(III):uracil	3.517	0.821	0.435	0.946	-18.10	1.73	11.07
PrIII):uracil:Ca(II)	3.521	0.825	0.442	0.956	-10.12	1.82	11.05
Dioxane							
Pr(III)	3.541	0.764	0.445	0.995	-08.45	1.67	11.17
Pr(III):uracil	3.558	0.910	0.473	1.067	-08.16	1.91	11.06
PrIII):uracil:Ca(II)	4.025	0.754	0.462	0.980	-43.85	1.68	12.75
DMF:Dioxane							
Pr(III)	3.091	0.836	0.435	0.945	-09.49	1.75	09.67
Pr(III):uracil	3.117	0.830	0.431	0.947	-08.34	1.74	09.76
Pr(III):uracil:Ca(II)	3.314	0.836	0.451	1.236	-16.03	1.78	10.40
DMF:MeCN							
Pr(III)	3.108	0.875	0.435	0.985	-17.44	1.81	09.71
Pr(III):uracil	3.267	0.842	0.453	0.983	-16.19	1.79	10.24
PrIII):uracil:Ca(II)	3.311	0.846	0.435	0.955	-12.77	1.77	10.39
MeOH:MeCN							
Pr(III)	2.786	0.863	0.423	0.872	-13.01	1.77	08.66
Pr(III):uracil	2.915	0.936	0.449	0.852	-10.11	1.91	09.05
PrIII):uracil:Ca(II)	3.123	0.968	0.474	0.816	-22.08	1.99	09.71
MeOH:Dioxane							
Pr(III)	3.367	0.637	0.388	0.932	-11.01	1.41	10.66
Pr(III):uracil	3.378	0.694	0.406	0.936	-24.62	1.52	10.34
PrIII):uracil:Ca(II)	3.383	0.657	0.389	0.822	-37.10	1.44	10.71
MeOH:DMF							
Pr(III)	3.751	0.845	0.467	0.977	-26.71	1.81	11.82
Pr(III):uracil	3.891	0.908	0.472	0.754	-84.06	1.90	13.72
PrIII):uracil:Ca(II)	3.899	0.821	0.439	0.942	-21.05	1.74	10.06
MeCN:Dioxane							
Pr(III)	3.084	0.838	0.433	0.975	-16.91	1.75	09.65
Pr(III):uracil	3.084	0.840	0.434	0.894	-10.53	1.76	09.64
PrIII):uracil:Ca(II)	3.235	0.820	0.453	0.925	-14.31	1.76	10.14
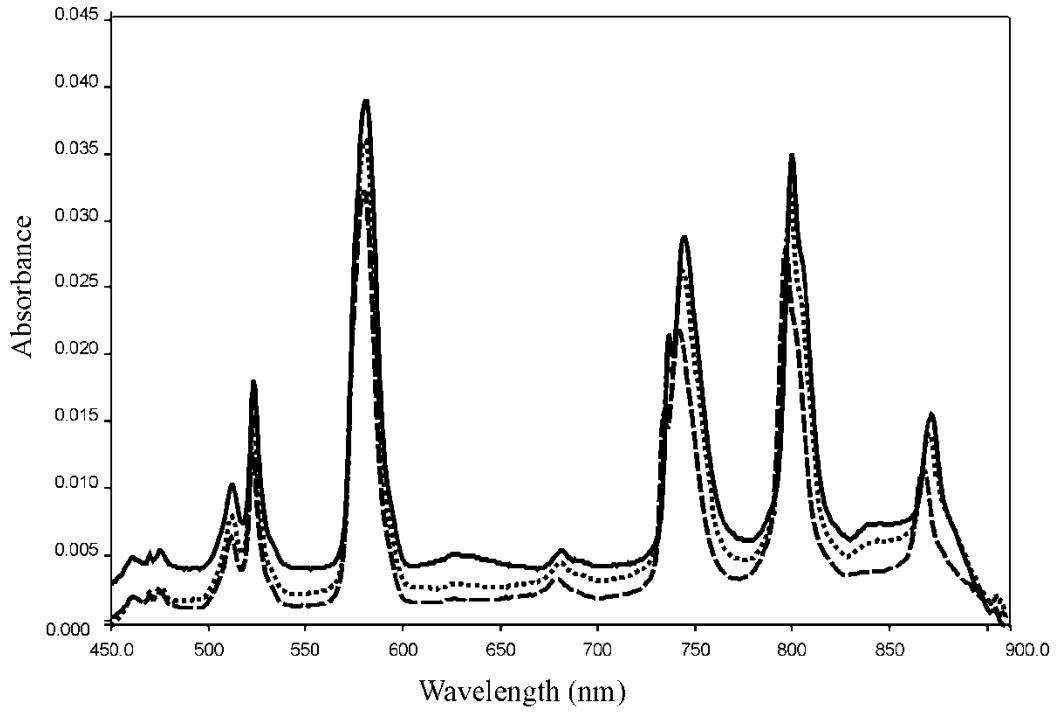
Fig. 1. Comparative absorption spectra of
Nd(III) ――― Nd(III) : uracil ········ Nd(III) : uracil ; Ca(II) ――― in DMF.
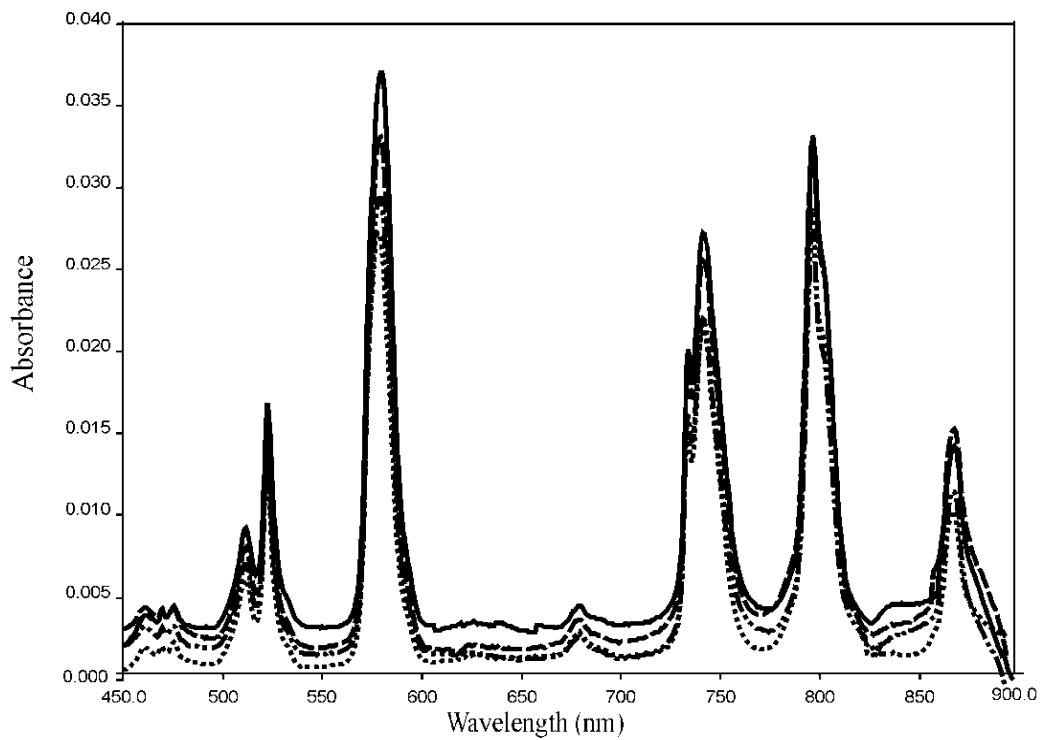
Fig. 2. Comparative absorption spectra of Nd(III):uracil in
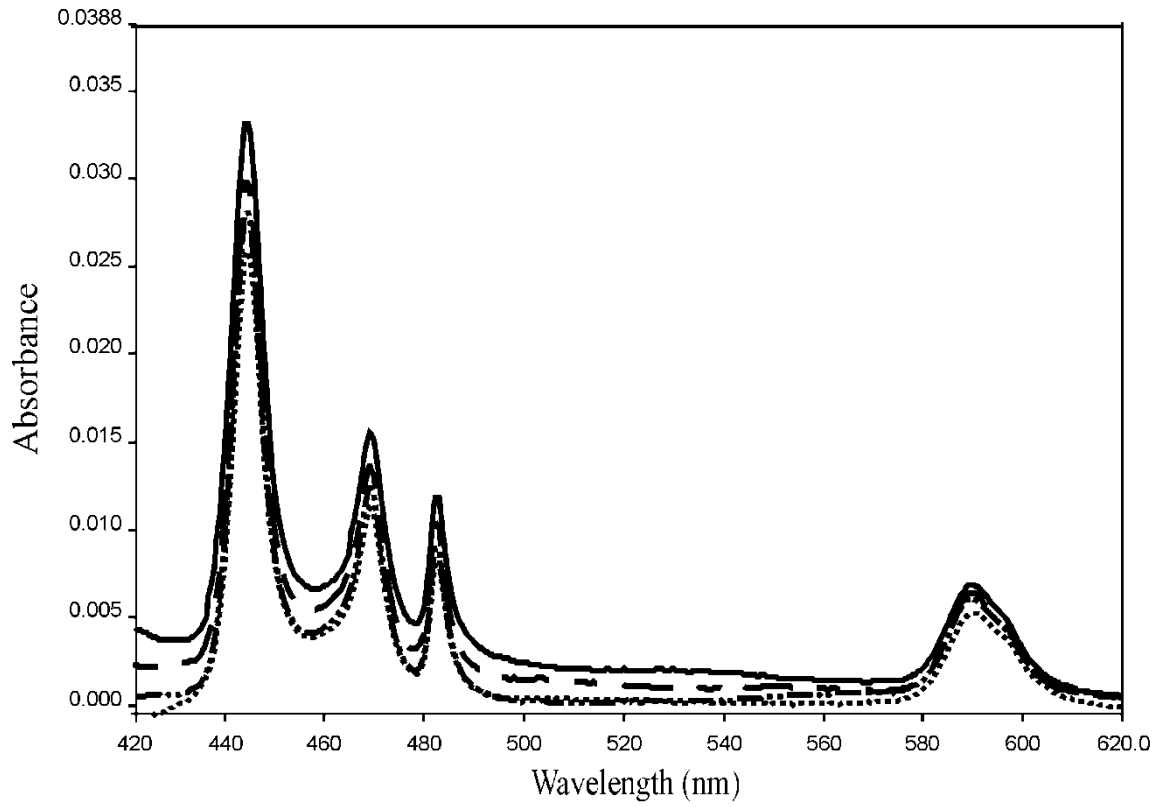DMF ――― Dioxane ――― MeCN ―··―· MeOH ········

Fig. 3. Comparative absorption spectra of Pr(III):uracil in
DMF ———— Dioxane ━ ━ MeCN ━ ·· ━ · MeOH ·········
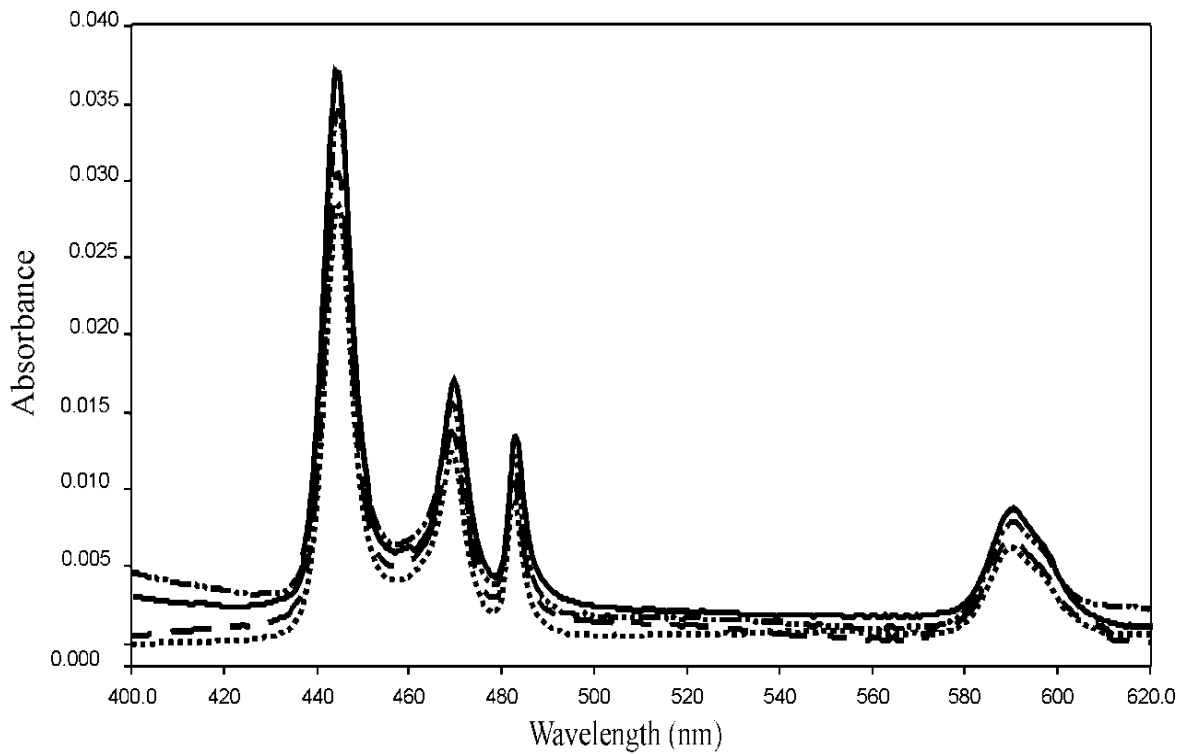
Fig. 4. Comparative absorption spectra of Pr(III) : uracil : Ca(II) in
DMF ———— Dioxane ━·━·━· MeCN ━ ━ MeOH ·········

All the four transitions of Pr(III) ($^3H_4\rightarrow^3P_2$, $^3H_4\rightarrow^3P_1$, $^3H_4\rightarrow^3P_0$ and $^3H_4\rightarrow^1D_2$) show a significant changes in the spectral pattern with the changes in the values of oscillator strengths (Fig. 4 & Table 4). This means that the all the four band of Pr(III) are found to sensitive even on minor coordination changes around Pr(III). This enhancement of oscillator strength and band shape demonstrated change in symmetry of complexes due to the possibility of solvent coordination, which enhances the coordination number of the metal ion.

4. CONCLUSIONS

Electronic spectral studies of the Nd(III) and Pr(III) complexes in different solvents, which differ with respect to donor atoms, reveal that the chemical environment around the lanthanide ion has a great impact on f-f transitions and any change in the environment in terms of solvent results in modifications of the spectra. However, the variation in energy interaction and intensity parameters hereby suggest that 4f-4f transitions of Pr(III) are more sensitive than that of Nd(III) in similar experimental conditions. Besides, the presence of Ca(II) strengthen the binding of Nd(III) to uracil than Pr(III) does. Our results in this study seem to confirm that Ln(III) ions have a preferences for higher coordination number when bound to calcium-selective ligand. This effect should be taken in to account when employing Ln(III) ions to probe the structure at and about calcium binding sites in biomolecules.

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