



Comparative absorption spectroscopy involving 4f–4f transitions to explore the kinetics of simultaneous coordination of uracil with Nd(III) and Zn(II) and its associated thermodynamics

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ABSTRACT

The interaction of uracil with Nd(III) has been explored in presence and absence of Zn(II) using the comparative absorption spectroscopy involving the 4f–4f transitions in different solvents. The complexation of uracil with Nd(III) is indicated by the change in intensity of 4f–4f bands expressing in terms of significant change in oscillator strength and Judd–Ofelt parameters. Intensification of this bands became more prominent in presence of Zn(II) suggesting the stimulative effect of Zn(II) towards the complexation of Nd(III) with uracil. Other spectral parameters namely Slator–Condon (F_k 's), nephelauxetic effect (β), bonding ($b^{1/2}$) and percent covalency (δ) parameters are computed to correlate their simultaneous binding of metal ions with uracil. The sensitivities of the observed 4f–4f transitions towards the minor coordination changes around Nd(III) has been used to monitor the simultaneous coordination of uracil with Nd(III) and Zn(II). The variation of intensities (oscillator strengths and Judd–Ofelt parameters) of 4f–4f bands during the complexation has helped in following the heterobimetallic complexation of uracil. Rate of complexation with respect to hypersensitive transition was evaluated. Energy of activation and thermodynamic parameters for the complexation reaction were also determined.

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1. Introduction

The unique similarity between the biologically important Ca(II) and paramagnetic lanthanides, Ln(III) in coordination characteristics, binding pattern, water exchange rate and even coordination number make the lanthanides to act as an “absorption probes” [1,2] in understanding the biochemical reactions and functions involving the isomorphous substitution of Ca(II) by Ln(III) [3–5]. Lanthanides are finding application in luminescent bio-sensing and bio-imaging [6–9] based on time-resolved detection and multiphoton excitation. Recently there has been renewed interest in the absorption of 4f–4f transitions and their intensity analysis to probe the finer details of structure in lanthanide complexes. Chemists have given particular attention to the intensity of hypersensitive transitions.

The majority of the observed optical transitions of lanthanides are induced electric dipole transitions. The intensities of such induced electric dipole transitions of lanthanide ions are almost independent of environment and the dipole strength of a particular (ED) transition of a lanthanide in different matrices varies by a factor less than two or three. However, a few transitions

are very sensitive to the environment and these are usually more intense in lanthanide complexes than for a uncomplexed lanthanide ions in aqueous solution. Jorsensen and Judd called these transitions “hypersensitive transitions” and they noted that all these hypersensitive transitions obey the same selection rule as electric quadrupole transitions [10]. Many experimental and/or theoretical studies have been devoted to hypersensitivity, and this work has been renewed recently by Goerller-Walrand and Binnemans [11]. And the practical interest have been given to the oscillator strength and band shapes of the hypersensitive transitions because of their ability to probe the complex formation, coordination geometry, ligand structure and complex–solvent interaction.

Birnbaum et al., for the first time studied the changes in the intensity of hypersensitive transition of Nd(III) in exploring the binding of Nd(III) with bovine serum albumin (BSA) [12]. In the later studies, the hypersensitive transitions of Ln(III) were used for the binding of Ln(III) with bovine trypsin [13]. Khan et al. [14] have used the intensity and band shapes for both hypersensitive and non-hypersensitive transitions in studying the effect of changes in the environment upon 4f–4f absorption spectra of Ho(III) and Er(III) complexes with thiocyanate and 2,2-bipyridine. Only a few references are available on lanthanide–organic metabolite interactions [15] and studies on lanthanide–nucleic acid interactions are still fewer [16,17]. Thus it was thought worthwhile to explore the

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interaction of Nd(III) with uracil in presence of Zn(II) by employing the electronic spectral studies. Zn(II), an endogenous metal occur intracellularly and is known to form very stable complex in vivo. So, Zn(II) may involve heterobimetallic simultaneous complexation with uracil. In addition, 4f–4f transition spectral intensity changes have very rarely been used for mechanistic and kinetic investigation [18–20]. Our study may be one of the few to report the kinetics of heterobimetallic complexation of uracil involving two chemically different metal ions Nd(III) and Zn(II) employing the 4f–4f transition intensity changes.

In the present paper, the sensitivities of 4f–4f transitions of Nd(III) towards the minor coordination changes are used to monitor the rate of complexation of uracil with Nd(III) and Zn(II). From the changes in the intensity of hypersensitive transition, we have determined the rate of reaction. Activation energy and thermodynamic parameters associated with simultaneous coordination are evaluated from the kinetic data.

2. Experimental

2.1. Materials

Nd(NO₃)₃·6H₂O (99.9% purity) from CDH, Mumbai, Zn(II) nitrate (Aldrich, USA) and ligand, uracil of G R grade from SRL India, were used without further purification. All the other chemicals used were of AR grade. All the solutions were prepared using the fresh double distilled water.

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), uracil and Zn(II) were maintained at 0.01 mol L⁻¹. And Nd(III):uracil was kept at 1:1 molar ratio and in multimetal interaction of Nd(III):uracil:Zn(II) was also kept in 1:1:1 molar ratio in concentration of 0.01 mol L⁻¹ for spectral analysis in different solvents. The temperature of all observations was maintained by using Perkin Elmer PTP1 Peltier-temperature system. For kinetic studies the electronic transition spectra of Nd(III):uracil:Zn(II) were recorded in DMF medium at different temperatures, i.e. 298, 303 and 308 K.

2.2. Theoretical

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

$$E_{\text{obs}} = f^k F_k + A_{\text{so}} \xi_{4f} \quad (1)$$

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 Lande's parameter, ξ_{4f} are determined by using the method outlined in our earlier papers [21,22].

If the f-orbital's are involved in covalent bond formation with the ligand, the metal wave function can be expressed [23] as

$$\langle \varphi_{4f} = (1 - b)^{1/2} < 4f | -b^{1/2} < \varphi_{\text{ligand}} | \quad (2)$$

where $b^{1/2}$ measures the amount of 4f-orbital mixing, i.e. covalency. Sinha [24] 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 (β , $b^{1/2}$, δ) of the complexes have been calculated using the relationship [23–25]:

$$\beta = \frac{F_k^c}{F_k^f} \quad \text{or} \quad \beta = \frac{E_c^k}{E_f^k} \quad (3)$$

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.

$$b^{1/2} = \left[\frac{1 - \beta}{2} \right]^{1/2} \quad (4)$$

$$\delta = \left(\frac{1 - \beta}{\beta} \right) \times 100 \quad (5)$$

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 [26] as

$$P = 4.6 \times 10^{-9} \times \varepsilon_{\text{max}} \times \Delta \nu_{1/2} \quad (6)$$

where ε_{max} is the molar extinction coefficient and $\Delta \nu_{1/2}$ 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 [27] and Ofelt [28] can be expressed as

$$P_{\text{cal}} = \sum_{k=2,4,6} T_{\lambda} \nu \langle f^n \psi_j | | U^{(\lambda)} | | f^n \psi_j \rangle^2 \quad (7)$$

which can be reduced to

$$\frac{P_{\text{cal}}}{\nu} = [U^{(2)}]^2 T_2 + [U^{(4)}]^2 T_4 + [U^{(6)}]^2 T_6 \quad (8)$$

where $U^{(\lambda)}$ is the matrix element of unit tensor operator connecting initial $\langle f^n \psi_j |$ and final $| f^n \psi_j \rangle$ through three phenomenological parameters T_{λ} ($\lambda=2,4,6$) 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 4fⁿ wavefunction of the perturbing configuration. The values of T_{λ} parameters have been computed by using the matrix elements given in our earlier paper [29].

3. Results and discussion

From Figs. 1 and 2, we can see that there is a red shift as uracil is added to Nd(III) and further shift towards longer wavelength is observed on addition of Zn(II). Table 1 shows 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:Zn(II) in different solvents. The binding of Nd(III)–uracil brings about changes in the energies of various 4f–4f bands which causes the degree of lowering in the energy interaction parameter, Slator–Condon which leads to nephelauxetic effect and intensities of 4f–4f electronic transitions. Lowering of these parameters become more significant when Zn(II) is added to binary mixture of Nd(III) and uracil.

Since lanthanides are hard metal ions in the Pearson classification scheme [30] they are preferentially attracted towards 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 [31]. The absolute values of oscillator strength (P) and Judd–Ofelt (T_{λ}) intensity parameters are determined under the different experimental conditions for the interaction of Nd(III) with uracil in presence of Zn(II) (Table 2). This clearly suggests significant changes, when

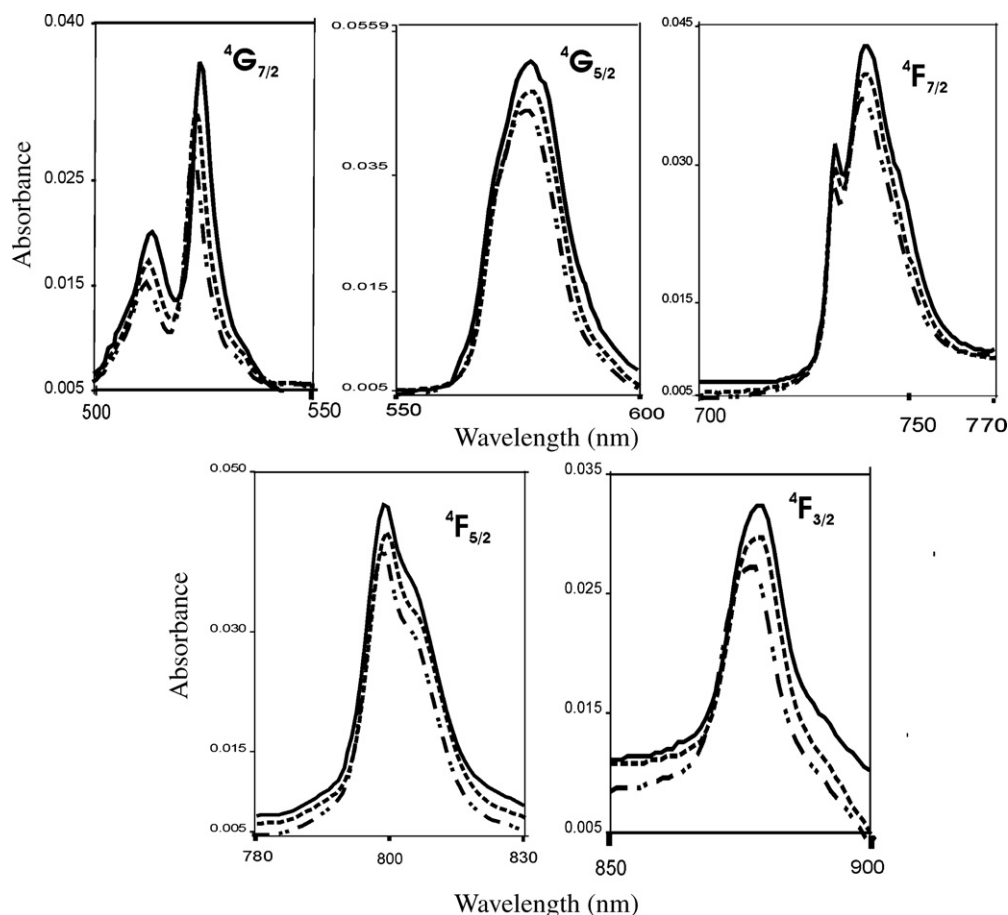


Fig. 1. Comparative absorption spectra of —Nd(III):uracil:Zn(II) ---- Nd(III):uracil - - - - Nd(III) in DMF.

Nd(III) interacts with uracil in the solution. Comparative absorption spectra of Nd(III), Nd(III):uracil and Nd(III):uracil:Zn(II) in DMF clearly shows that the addition of uracil to Nd(III) results in significant enhancement in the oscillator strengths of different 4f–4f transitions (Fig. 1). As a consequence, we have observed noticeable increase in the magnitude of Judd–Ofelt (T_{λ}) intensity parameters. This suggests the binding of uracil to Nd(III) in solution. This intensification of 4f–4f bands became more prominent when Zn(II) was added to the binary mixture of Nd(III) and uracil. This clearly suggested that heterobimetallic interaction of uracil was much stronger than binary complexation of uracil. Therefore, we can say that different metal bindings are stimulative to each other.

The $^4I_{9/2} \rightarrow ^4G_{5/2}$ transition of Nd(III) is universally accepted as hypersensitive transition as it obeys selection rules for quadrupole transitions and undergoes very high intensification on complexation [32,33]. Small changes in the immediate coordination environment around Nd(III) brings about wide variation of oscillator strength. Contrary to this, the intensities of non-hypersensitive transitions are reported either very slightly or not changes at all or sometimes decrease [34,35]. Iftikar [32] 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 that the percentage variation of the oscillator strength of $^4I_{9/2} \rightarrow ^4G_{7/2}$, $^4I_{9/2} \rightarrow ^4F_{3/2}$, $^4I_{9/2} \rightarrow ^4F_{5/2}$, 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.

The spectra of Nd(III):uracil:Zn(II) in all different solvents have been found to shift towards the longer wavelength (red shift) as compared to the position in the respective aqua-ion. This red shift has long been regarded as a measure of covalency [36]. The nephelauxetic effect requires that the orbital should expand on complex formation. The introduction of the ligand and electron into the outer orbital of the lanthanide ion will reduce the effective nuclear charge, thus allowing the required expansion. The nephelauxetic parameter β , bonding parameter $b^{1/2}$ and covalency parameter δ , for the complex have been calculated from the spectra and are presented in Table 2. The nephelauxetic parameter is less than one and bonding and covalency parameters are positive for these complexes showing the incident of some covalent nature in the bonding between the metal and the ligand. The values of $b^{1/2}$ and δ are highest for DMF followed by MeCN, MeOH and Dioxane. It is reasonable to associate this increase with ligand polarization effect brought about by DMF which is highly polarizable. It means that DMF is the strongest ligand in a nephelauxetic sense and follows that DMF is effective in promoting 4f–4f electric dipole intensity thereby showing largest covalency in this solvent. The same trend was found in our earlier works of different systems [4].

For the spectral studies on the structures of co-ordination compounds of lanthanides in solution, any evidence of the structure is of special interest. Jorgensen and Ryan [35] noticed the depen-

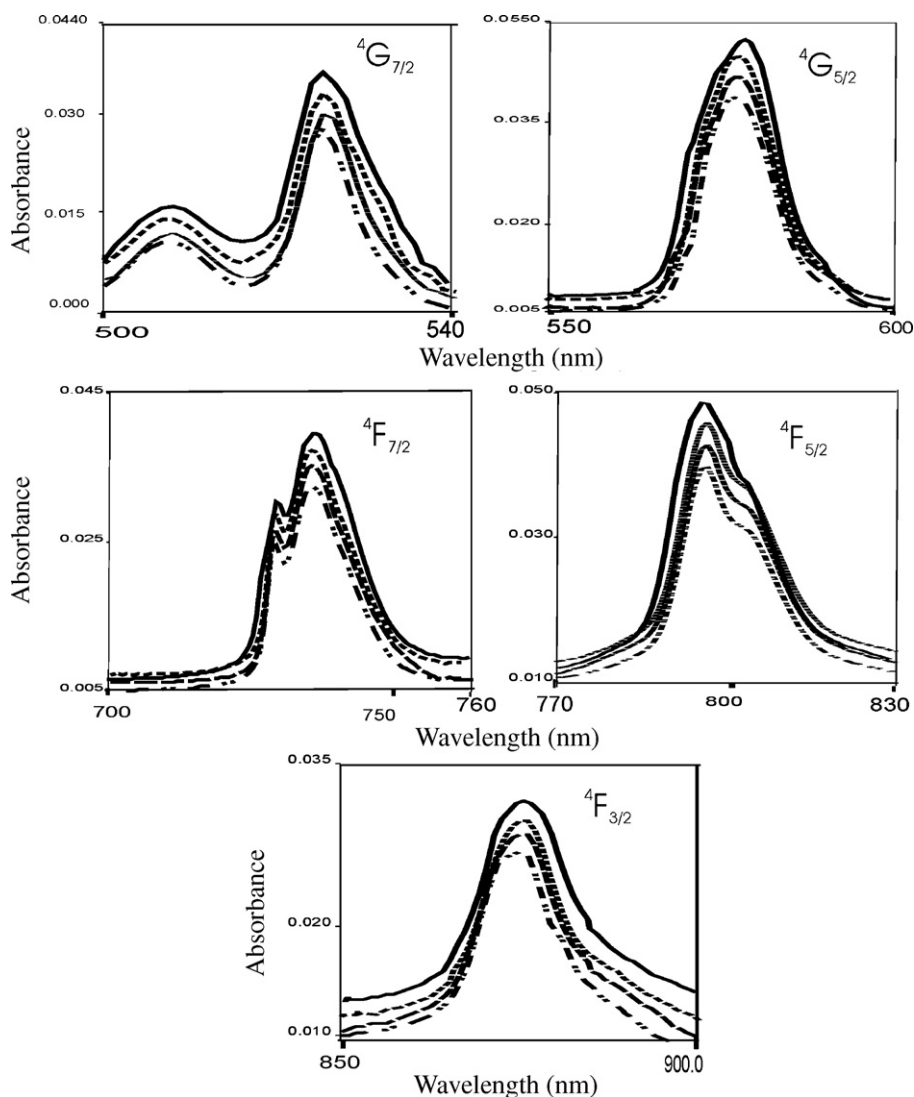


Fig. 2. Comparative absorption spectra of Nd(III):uracil:Zn(II) (1:1:1) in different solvents. — DMF MeCN ---- Dioxane - - - - MeOH.

dence of nephelauxetic effect on the coordination number. Frey and Dew Horrocks [37] confined this study on Eu^{+3} and suggested that the nephelauxetic effect is related with the covalency in the metal–ligand bond and with the coordination number (lower the coordination number higher is the magnitude of nephelauxetic effect). The analysis of the oscillator strengths and Judd–Ofelt (T_λ) intensity parameters are used in the investigation of formation and nature of Nd(III):uracil complexes. The high values of the T_2 parameter are remarkable indicating very intense hypersensitive transitions compared with the same transitions in aqueous solution. The intensity enhancement can be attributed to the high polarisability of uracil and to the anisotropy of this polarisability. According to the ligand polarisation model [11,38,39], the radiation field of the light dynamically polarises the ligand charge distributions and the instantaneous dipoles couple to the induced electric dipoles of the lanthanide ion. The low site symmetry of the complex promotes intense f–f transitions, because in an asymmetric environment it is more unlikely that some of the odd crystal field parameter (necessary for mixing states of opposite parity in to the 4f states) will have a very small value or will vanish [11]. Additionally part of the intensity enhancement of the hypersensitive transition can be attributed to the replacement of water by DMF as solvent [40]. The values of T_4 and T_6 parameters of the complexes

are not significantly larger than the corresponding values in aqueous solution. The insensitivity of T_4 and T_6 in comparison with T_2 can be explained by the small ligand polarisation distribution to these parameters.

Table 2 clearly reflects, that T_4 and T_6 are effected significantly in the presence of different solvents, which suggest that not only immediate coordination environment of Nd(III) but symmetry of the complex species is also changed dramatically. These changes are considered to be good evidence for the involvement of uracil in the inner sphere coordination of Nd(III) 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 coordination of uracil with Nd(III) and Zn(II) is effected significantly by the nature of solvents inducing significant variation in the intensity of 4f–4f transitions.

3.1. Kinetic study

While investigating the interaction of uracil with Nd(III) and Zn(II) in different solvents, the intensities of 4f–4f transitions and consequently the evaluated spectral intensity parameters viz, oscillator strength P of the observed five 4f–4f bands and experimentally

Table 1
Computed values of energy interaction parameters, Slater–Condon (F_k), nephelauxetic ratio (β), bonding parameters ($b^{1/2}$) and covalency parameters (δ) for the complexation of Nd(III) with uracil in presence and absence of Zn(II) in aquated organic solvents at 25 °C.

System	F_2	F_4	F_6	β	$b^{1/2}$	δ
MeOH						
Nd(III)	331.08	48.59	5.18	1.007	0.061	0.746
Nd(III):Uracil	331.05	48.60	5.19	1.007	0.062	0.779
Nd(III):Uracil:Zn(II)	331.02	48.64	5.18	1.008	0.060	0.736
Dioxane						
Nd(III)	330.92	48.64	5.21	1.000	0.070	1.063
Nd(III):Uracil	331.77	49.11	5.23	1.007	0.071	0.745
Nd(III):Uracil:Zn(II)	330.90	48.60	5.21	1.011	0.074	1.107
MeCN						
Nd(III)	330.87	48.61	5.20	1.010	0.073	1.079
Nd(III):Uracil	330.87	48.60	5.20	1.011	0.074	1.102
Nd(III):Uracil:Zn(II)	330.92	48.62	5.20	1.012	0.072	1.041
DMF						
Nd(III)	331.27	48.63	5.17	1.011	0.069	0.482
Nd(III):Uracil	331.25	48.64	5.17	1.012	0.076	0.522
Nd(III):Uracil:Zn(II)	331.23	48.60	5.14	1.014	0.078	0.538
MeCN:Dioxane (1:1)						
Nd(III)	330.78	48.63	5.21	1.012	0.078	1.227
Nd(III):Uracil	330.79	48.62	5.21	1.012	0.080	1.220
Nd(III):Uracil:Zn(II)	330.66	48.60	5.22	1.014	0.084	1.397
DMF:MeCN (1:1)						
Nd(III)	330.90	48.62	5.20	1.010	0.072	1.032
Nd(III):Uracil	330.90	48.61	5.20	1.010	0.079	1.010
Nd(III):Uracil:Zn(II)	330.90	48.61	5.21	1.011	0.074	1.099
MeOH:Dioxane (1:1)						
Nd(III)	330.85	48.62	5.21	1.011	0.077	1.170
Nd(III):Uracil	330.86	48.62	5.21	1.011	0.068	1.150
Nd(III):Uracil:Zn(II)	330.74	48.65	5.22	1.012	0.080	1.266
MeOH:DMF (1:1)						
Nd(III)	330.83	48.61	5.21	1.012	0.078	1.205
Nd(III):Uracil	330.83	48.61	5.21	1.012	0.072	1.186
Nd(III):Uracil:Zn(II)	330.72	48.60	5.22	1.013	0.081	1.312
DMF:Dioxane (1:1)						
Nd(III)	330.77	48.62	5.21	1.012	0.068	1.217
Nd(III):Uracil	330.77	48.62	5.21	1.012	0.069	1.214
Nd(III):Uracil:Zn(II)	330.68	48.59	5.20	1.013	0.082	1.336
MeOH:MeCN (1:1)						
Nd(III)	331.03	48.65	5.19	1.007	0.062	0.783
Nd(III):Uracil	331.03	48.64	5.19	1.008	0.070	0.817
Nd(III):Uracil:Zn(II)	331.02	48.63	5.19	1.007	0.060	0.731

determined Judd–Ofelt (T_λ ($\lambda = 2,4,6$)) parameters have been found to exhibit significant sensitivity towards minor changes occurring around the Nd(III); hence 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 uracil with Nd(III) and Zn(II).

The comparative absorption spectra, showing an increase in absorbance with time, during the complexation of uracil with Nd(III) and Zn(II) is given in Fig. 3. The data showing an increase in oscillator strengths with time during complexation reaction are given in Table 3. Data given in Table 3 shows that T_2 , T_4 and T_6 parameters shows progressive increase with oscillator strengths of observed 4f–4f transition bands. The addition of Zn(II) to Nd(III):uracil leads to sharp changes in the oscillator strengths of 4f–4f bands, as well as substantial variation in the magnitude of T_λ parameters. Several sets of kinetic experiments were conducted and for brevity only one sets of kinetic run showing changes in absorbance with time at 298 K is given in Fig. 3.

The kinetic experiments were conducted by monitoring the increasing changes in the absorbance with time corresponding to five bands and their spectral changes are given in Fig. 3. It is clear from Fig. 3 that all the five bands of Nd(III) are almost identically sensitive. The rate of the complexation corresponding to only universally accepted hypersensitive transition was calculated by spectrophotometrically determining the maximum absorbance

reached for complexation. Rate of complexation was calculated by plotting the oscillator strength against time (Fig. 4) and listed in parentheses in Table 4. Rates calculated by absorbance and oscillator strength measurement methods were found to be almost identical. And the rate of reaction increases with temperatures. This observation of the rate of complexation supported the relevance of the use of absorption spectral intensity analysis involving the heterobimetallic complexation of uracil.

3.2. Determination of Activation energy and thermodynamic parameters

Considering the dependence of rate constant on temperature, activation energy determination and a thermodynamic process were considered to be responsible for characterizing the complexation reaction. Therefore, The energy of activation and the thermodynamic parameters dependent on temperature were analyzed in order to further characterize the simultaneous coordination of uracil with Nd(III) and Zn(II).

The energy of activation is determined from well known Arrhenius equation

$$\ln k = \ln A - \frac{E_a}{RT} \quad (9)$$

where A is the pre-exponential factor called frequency factor, E_a the energy of activation, R is the gas constant and T is the temperature

Table 2

Experimental values of oscillator strength and Judd–Ofelt parameters for the interaction of Nd(III) with uracil in absence and presence of Zn(II) 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
MeOH								
Nd(III)	1.0502	5.1412	2.6226	2.3195	0.5493	29.1375	4.8023	47.4634
Nd(III):Uracil	1.0512	5.2030	2.7168	2.2917	0.5405	32.8662	2.9574	66.481
Nd(III):Uracil:Zn(II)	1.1836	5.8782	4.3924	2.8134	0.6182	30.8944	5.5747	65.6895
Dioxane								
Nd(III)	1.0970	5.473	3.0764	2.4275	0.6107	32.2897	6.2955	51.1372
Nd(III):Uracil	1.1348	5.751	3.2296	2.5605	0.6121	34.8259	5.3554	54.3399
Nd(III):Uracil:Zn(II)	1.1896	6.1501	3.2840	2.6863	0.5939	25.8417	6.9438	55.377
MeCN								
Nd(III)	1.0677	5.9870	3.1679	2.4202	0.6449	31.2448	5.0393	50.6846
Nd(III):Uracil	1.1300	6.0053	3.2873	2.5425	0.6845	32.0572	6.023	52.6167
Nd(III):Uracil:Zn(II)	1.0847	6.4289	3.2133	2.4403	0.5408	31.9455	2.4324	53.1477
DMF								
Nd(III)	1.2235	6.1939	3.2096	2.5247	0.5476	32.2801	3.5202	53.3006
Nd(III):Uracil	1.2612	6.1518	3.3933	2.5093	0.5026	41.0804	3.3607	56.8795
Nd(III):Uracil:Zn(II)	1.3297	6.7763	3.5565	2.6969	0.4983	31.8843	5.8231	57.7862
MeCN:Dioxane (1:1)								
Nd(III)	1.0295	6.3448	3.5191	2.4012	0.6282	29.7799	6.7097	50.2253
Nd(III):Uracil	1.0158	6.4929	3.6035	2.5040	0.6680	70.5924	8.7356	50.5637
Nd(III):Uracil:Zn(II)	1.0184	5.6900	3.1845	2.3490	1.1171	72.4652	8.8892	50.8754
DMF:MeCN (1:1)								
Nd(III)	1.2234	6.2540	3.1599	2.5598	0.6819	35.8641	5.131	54.1081
Nd(III):Uracil	1.2741	6.5816	3.5491	2.6075	0.6177	34.310	8.0058	55.4022
Nd(III):Uracil:Zn(II)	1.2557	6.6142	3.3924	2.8219	0.6188	31.728	7.3599	59.2574
MeOH:Dioxane (1:1)								
Nd(III)	1.2189	5.7249	3.0302	2.4927	0.6062	33.5821	2.028	51.2659
Nd(III):Uracil	1.1396	5.6472	3.2069	2.3728	0.5325	30.7365	7.204	51.2659
Nd(III):Uracil:Zn(II)	1.1638	5.6648	3.1797	2.6019	0.5723	35.0915	4.1441	53.191
MeOH:DMF (1:1)								
Nd(III)	1.0751	6.0446	3.2667	2.5658	0.6101	32.9777	7.5431	49.002
Nd(III):Uracil	1.1714	5.9283	3.1712	2.4259	0.6787	27.9135	7.725	46.002
Nd(III):Uracil:Zn(II)	1.2531	6.5273	3.3382	2.6474	0.6218	32.2513	8.3088	45.8867
DMF:Dioxane (1:1)								
Nd(III)	0.9250	5.5031	2.8330	2.1874	0.5392	48.8276	4.6047	48.9681
Nd(III):Uracil	0.9998	5.6849	2.8423	2.1663	0.5255	33.322	3.5608	47.1689
Nd(III):Uracil:Zn(II)	1.1334	5.7271	2.9421	2.3515	0.4511	30.6817	7.3899	51.4907
MeOH:MeCN (1:1)								
Nd(III)	1.1407	5.5925	3.1529	2.6153	0.6444	32.1078	6.3985	52.4591
Nd(III):Uracil	1.2194	5.7434	3.2106	2.6229	0.6052	30.8979	6.068	53.7502
Nd(III):Uracil:Zn(II)	1.2320	5.7115	3.3330	2.9661	0.5717	33.7325	6.4006	57.3015

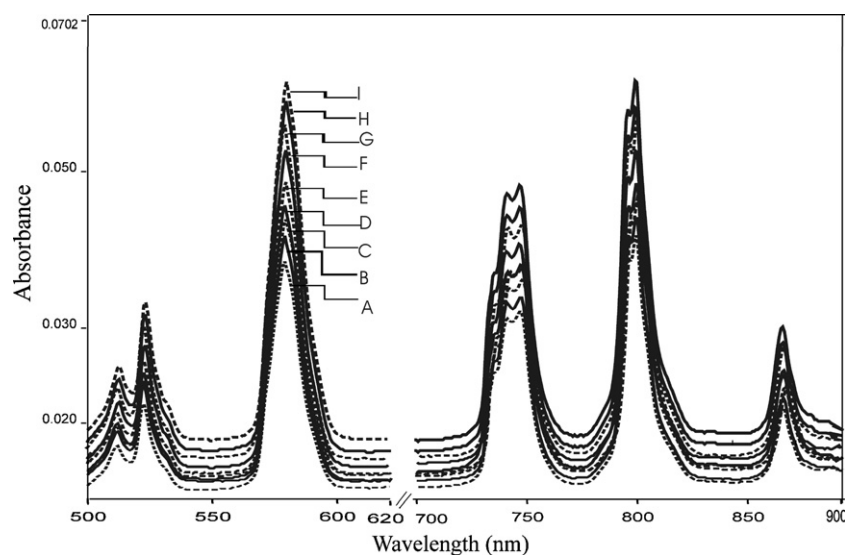


Fig. 3. Time-dependant absorption spectra for Nd(III):uracil:Zn(II) at 25 °C at (A) 0, (B) 0.5, (C) 1, (D) 2, (E) 4, (F) 6, (G) 8, (H) 12 and (I) 14 h in DMF.

Table 3
Oscillator strength ($P_{\text{obs}} \times 10^6$) and computed values of Judd–Ofelt intensity T_λ parameters for the complexation of uracil with Nd(III) and Zn(II) in DMF at different time intervals (25 °C).

Time (h)	${}^4I_{9/2} \rightarrow {}^4G_{7/2}$	${}^4I_{9/2} \rightarrow {}^4G_{5/2}$	${}^4I_{9/2} \rightarrow {}^4F_{7/2}$	${}^4I_{9/2} \rightarrow {}^4F_{5/2}$	${}^4I_{9/2} \rightarrow {}^4F_{3/2}$	T_2	T_4	T_6
0	1.33	6.40	3.58	2.69	0.48	31.88	5.54	48.69
0.5	1.37	6.58	3.60	2.89	0.59	32.37	6.87	49.26
1	1.40	6.60	3.95	3.19	0.61	32.85	7.20	50.48
2	1.45	7.39	4.02	3.26	0.65	33.36	8.41	51.49
4	1.49	7.70	4.08	3.32	0.67	34.36	9.25	51.99
6	2.30	8.14	4.41	3.58	0.70	34.81	10.40	52.61
8	2.50	8.69	4.69	3.89	0.73	35.32	11.67	53.34
12	2.80	9.48	5.03	4.05	0.78	35.87	12.45	54.49
14	3.50	10.50	5.89	4.89	0.80	36.01	14.39	56.51

Table 4
Rate constant and thermodynamic parameters for the complexation of Nd(III):uracil with Zn(II) at different temperatures and activation energy for the complexation reaction.

Temperature (K)	Rate constant (k) ($\text{mol L}^{-1} \text{h}^{-1}$)	Rate constant (k) ($\text{mol L}^{-1} \text{s}^{-1}$)	Activation energy (kJ mol^{-1})	ΔH (kJ mol^{-1})	ΔS ($\text{JK}^{-1} \text{mol}^{-1}$)	ΔG (kJ mol^{-1})
298	0.271(0.265)	4.52 (4.41)	13.14 ± 0.06	13.14 ± 0.06	56.70 ± 0.06	-3.75 ± 0.06
303	0.297(0.290)	4.95 (4.83)				-4.04 ± 0.06
308	0.323(0.319)	5.38 (5.31)				-4.32 ± 0.06

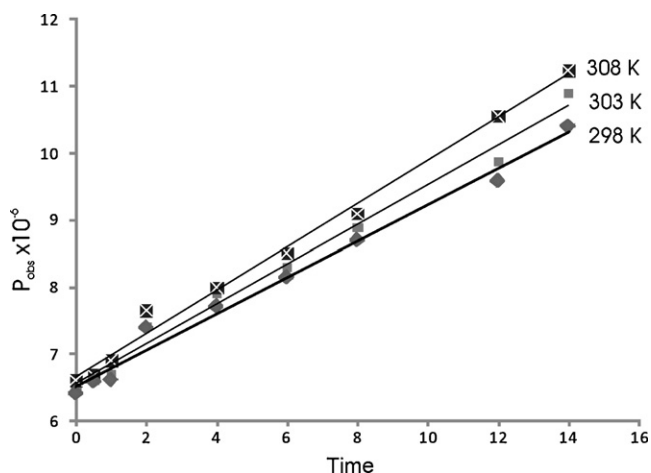


Fig. 4. Plot of oscillator strength versus time for ${}^4I_{9/2} \rightarrow {}^4G_{5/2}$ transitions of Nd(III):uracil:Zn(II) in DMF at (a) 298, (b) 303 and (c) 308 K.

in Kelvin. Kinetic studies were carried out at 298, 303 and 308 K and rate constants corresponding to these temperatures were listed in Table 4. The energy of activation E_a was obtained from slope of the plot based on $\ln k$ versus $1/T$.

The thermodynamic parameters can be evaluated using the following equation [41].

$$\ln k = -\frac{\Delta G}{RT} = -\frac{\Delta H^\circ}{R} \left(\frac{1}{T} \right) + \frac{\Delta S^\circ}{R} \quad (10)$$

Table 4 shows that k increases with increasing temperature. This approach provides a good means to determine indirectly the thermodynamic parameters of simultaneous coordination of uracil to Nd(III) and Zn(II) by using the plots of $1/T$ versus $\ln k$ in the temperature ranges. The enthalpy change (ΔH°) and entropy change (ΔS°) were obtained from the slope and intercept of the linear Van't Hoff plot based on $\ln k$ versus $1/T$ (Fig. 5) by assuming that H is independent of temperature over the range of employed temperatures [36]. The free energy change (ΔG°) is estimated from the following relationship:

$$\Delta G^\circ = \Delta H^\circ - T\Delta S^\circ \quad (11)$$

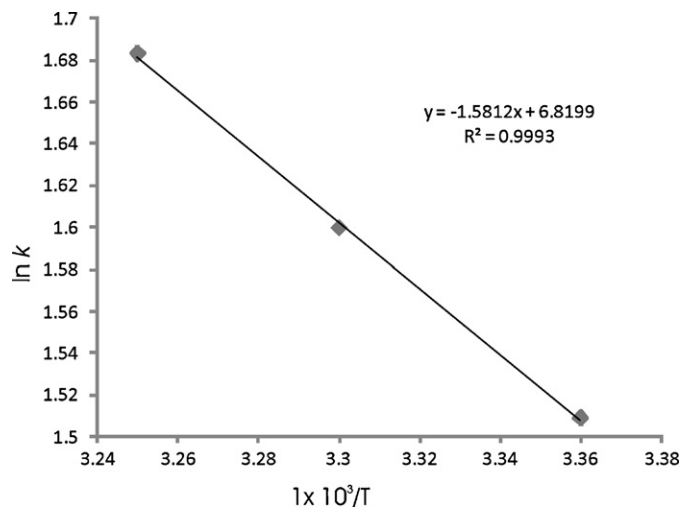


Fig. 5. Plot of $\ln k$ versus $1 \times 10^3/T$ for the complexation of Nd(III):uracil and Zn(II) in DMF medium.

The values of ΔH° , ΔS° and ΔG° are listed in Table 4. The positive enthalpy and entropy values indicates that the complexation reaction is an endothermic and entropy increasing process. Because of $T\Delta S^\circ > \Delta H^\circ$ and the entropy increasing effect result in $\Delta G^\circ < 0$, the reaction is an entropy driven process. Overall speaking, the negatively changes of standard Gibbs energy indicates that the simultaneous coordination is a spontaneous processes and the process is favored in solution.

4. Conclusion

From the above discussions through the variation in energy interaction parameters and intensity parameters, it can be revealed that heterobimetallic complexation of uracil is stronger than binary complexation of Nd(III)–uracil showing the stimulated effect of Zn(II) towards the complexation of Nd(III) with uracil. Basically, our study is meant to illustrate the versatility of comparative absorption spectral studies involving 4f–4f transitions, even understanding the complexation reaction occurring during the simultaneous coordination of uracil with Nd(III) and Zn(II). The study clearly shows that monitoring the variation of the oscillator strengths of different 4f–4f transitions with time could help

in understanding the kinetic nature of simultaneous complexation of uracil with Nd(III) and Zn(II) in solution medium. The rate of the complexation reaction increases with temperature and activation energy for the reaction is found to be $13.14 \text{ kJ mol}^{-1}$. This speaks to the relevance of absorption spectral intensity analysis in complexation reaction involving the heterobimetallic complexation of uracil. Thermodynamic functions of the complex formed show that simultaneous coordination is an endothermic process (positive values of ΔH) and proceeds spontaneously (negative values of ΔG). The entropy changes have positive values, showing that heterobimetallic complexation of uracil is a favorable process.

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