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Research Article

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A Comparative Study on the Binding Interaction of Nd(III) with D-Proline and DL- Proline in Absence and Presence of Zn(II) using 4f-4f Transition Spectra as an Absorption Probe

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Abstract: The spectroscopic techniques involving comparative absorption, absorption difference and quantitative intensity analysis using 4f-4f transitions are used as a tool to understand the coordination of Nd(III) complexes with two forms of Proline (D-and DL-Proline) in absence and presence of Zn(II) in aqueous and aquated organic solvents. The changes in the oscillator strengths of different 4f-4f bands and Judd-Ofelt intensity (T_λ) parameters determined experimentally is being used to investigate the coordination changes in Nd(III) complexes caused by coordinating sites of ligands, denticity, the solvent nature, coordination number, the nature of bond and other parameters to mimic the interaction of Proline with Nd(III) in presence of Zn(II). The change in symmetry around Nd(III) and covalency in metal-ligand interaction is observed and found more sensitive in case of DL-Proline in coordination with Nd(III). The energy interaction parameters like Slator-Condon (F_k's), nephelauxetic effect (β), bonding ($b^{1/2}$) and percent covalency (δ) parameters are further computed to correlate with the binding interaction of metal and ligands.

Keywords: 4f-4f Transition Spectra; Nd(III); DL-Proline; Oscillator Strength; Judd-Ofelt Parameters

1. INTRODUCTION

The close resemblance between the lanthanides and calcium in terms of size and the coordination preference for higher coordination numbers have made the lanthanides to be used as probes in biochemical reactions and for structural studies of biomolecule compounds involving Ca(II) [1,2]. The paramagnetic nature and the presence of 4f electrons have given lanthanide ions properties which can be utilized as an absorption spectral probe. Absorption difference and comparative absorption spectroscopy involving 4f-4f transitions are one of the most effective techniques to reveal the interaction of biomolecules with lanthanide ions [3].

The lanthanide (III) ions are hard metal ions in Pearson's scheme and hence show strong preference for oxygen donor chelating ligands. Generally natural biological molecules contain centres of dissymmetry in molecular conformations; as a result, lanthanide complexes in these systems behave like chiral lanthanide complexes [4,5]. The studies of interaction between lanthanide(III) ions and amino acids are important for understanding the role of calcium ion in biological systems [6]. Their interactions have

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spurred considerable interest as a coordination phenomenon [7]. They are used as models in metal-protein reactions and biological systems where the properties of proteins are attached to them. Hence, it will be of great interest to study the interaction of Nd(III) with D-Proline and DL-Proline in absence and presence of Zn(II). Proline exits in three forms : L-proline, D-Proline and DL-Proline. L- and D-Proline are optically active and DL-Proline is an equimolar mixtures of L- and D-Proline. DL-Proline is synonymous of Proline. It is found in essentially most proteins and is a major constituent in collagens, the fibrous protein of connective tissue. Proline plays an important role to determine the protein structural shape when amino acids are incorporated into them. The absorption spectra of amino acid complexes of Pr(III) and Nd(III) have been analysed systematically by absorption difference and comparative absorption spectrophotometry by following the 4f-4f transitions in the visible and near-infrared region [8,9]. In our previous paper [10], we reported the absorption spectral studies of 4f-4f transitions for complexation of Pr(III) with L-proline in presence of Zn(II) in different aquated organic solvents and kinetics for the complexation of Pr(III):L-proline with Zn(II). The main aims of our present study is to examine the effect of spatial arrangement of donor sites of Proline on the immediate coordination of Nd(III) through the comparative study of various energy interaction and intensity parameters. We report the analysis of the sensitivity of hypersensitive transitions and utilize the magnitude and variation of energy interaction and intensity parameters to provide information on the mode of interaction of Nd(III) with Proline.

2. EXPERIMENTAL DETAILS

2.1. Materials

Neodymium nitrate hexahydrate of 99% purity is purchased from CDH, Mumbai and D- and DL-Proline are procured from the Acrose company, U.S.A. The solvents used are CH_3CN, CH_3OH, DMF and Dioxane of A.R. grade from E.Merk . The stoke solution of neodymiun(III) are standardized using the EDTA method reported elsewhere [11]. The D-Proline and DL-Proline solutions used for each experiment are freshly prepared.

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), Zn(II), D- Proline and DL-Proline are maintained at 0.01 mol L^{-1} and spectral analysis are carried out by using different solvents. The temperature of all observations is maintained by using Perkin Elmer PTP1 Peltier -temperature system.

2.2 Methods

The energy level structures of Nd(III) ion to a first approximation may be considered to arise from the electrostatic and magnetic interaction between the 4f electrons. The electrostatic term, E_o is expressed in terms of product of Slator radial integral, also known as Slator-Condon [12,13] parameter F_k, and angular coefficient f_k as

$$E_o = \sum_{k=0}^{k=6} K^k F^k = \sum_{k=0}^{k=6} f_k F^k \qquad (1)$$

The energy, E_{so} arising from the most important magnetic interaction which is spin- orbit interaction may be written as

$$E_{so} = A_{so}\xi_{4f} \qquad (2)$$

where A_{so} is the angular part of spin orbit interaction and ξ_{4f} is 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].

The energy levels of various transitions are obtained experimentally as well as computed by using the following relationship:

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$$E_j\left(F_k,\xi_{4f}\right)=E_{oj}\left(F_k^{\,0},\xi_{4f}^{\,0}\right)+\sum_{k=2,4,6}\left(\frac{dE_j}{dF_k}\right)\Delta F_k+\left(\frac{dE_j}{d\xi_{4f}}\right)\Delta\xi_{4f} \quad (3)$$

where E_{oj} is the zero order energy of the jth level.

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

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

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 (β, $b^{1/2}$, δ) of the complexes have been calculated using the relationship [16-18] :

$$\beta=\frac{F_K{}^c}{F_K{}^f} \quad \text{or} \quad \beta_2=\xi_{4f}{}^c\Big/\xi_{4f}{}^f \quad (5)$$

where F_k^c (k=2,4,6) and F_k^f refers to the parameters for complex and free ions respectively.

$$b^{1/2}=\left[\frac{1-\beta}{2}\right]^{1/2}$$
$$\delta=\frac{1-\beta}{\beta}\times 100 \quad (6)$$

The intensity of the absorption band is measured by experimentally determined oscillator strength (P), which is directly proportional to the area under the curve and can be expressed by the relationship :

$$P=4.31\times10^{-9}\left[\frac{9\eta}{\left(\eta^2+2\right)^2}\right]\int\varepsilon(\upsilon)d\upsilon \quad (7)$$

where υ is the energy of transition, ε molar extinction coefficient and η the refractive index of the medium, which are calculated using the procedures outlined in the previous papers [19,20]. Theoretically, the oscillator strength, P_{cal} of the induced-dipole transition of energy (cm^{-1}) in accordance with Judd-Ofelt relation [21,22] can be expressed as

$$P_{cal}=\sum_{k=2,4,6}T_\lambda\upsilon\left\langle f^n\psi_j\left\|U^{(\lambda)}\right\|f^n\psi_{j'}\right\rangle^2 \quad (8)$$

where $U^{(\lambda)}$ is the matrix element of unit tensor operator connecting initial $< f^n\psi_j\,|$ and final $|\, f^n\psi_{j'} >$ 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 from the Judd-Ofelt expression by using the partial multiple regression method where the values of reduced matrix elements have been taken from Carnall et al. [23]. For Nd(III) complexes, the Judd-Ofelt relation is applicable in the present form:

$$\frac{P_{cal}}{\upsilon}=\left[U^{(2)}\right]^2.T_2+\left[U^{(4)}\right]^2.T_4+\left[U^{(6)}\right]^2.T_6 \quad (9)$$

The transition levels and the matrix elements used for the intensity analysis of Nd(III) complexes are given in Table S1.

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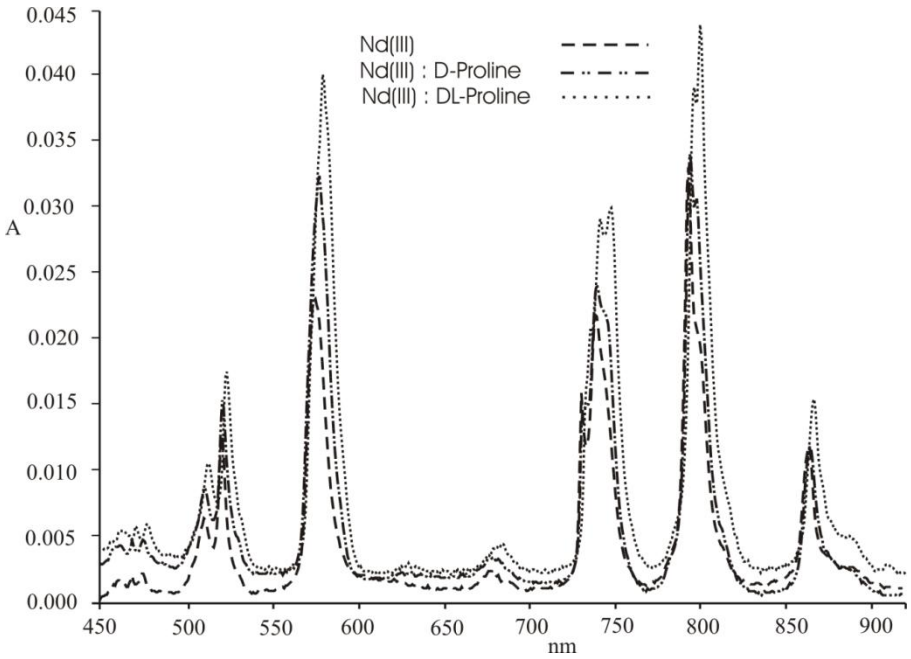

Figure 1. Comparative absorption spectra of Nd(III), Nd(III):D-proline and Nd(III):DL-proline in DMF.

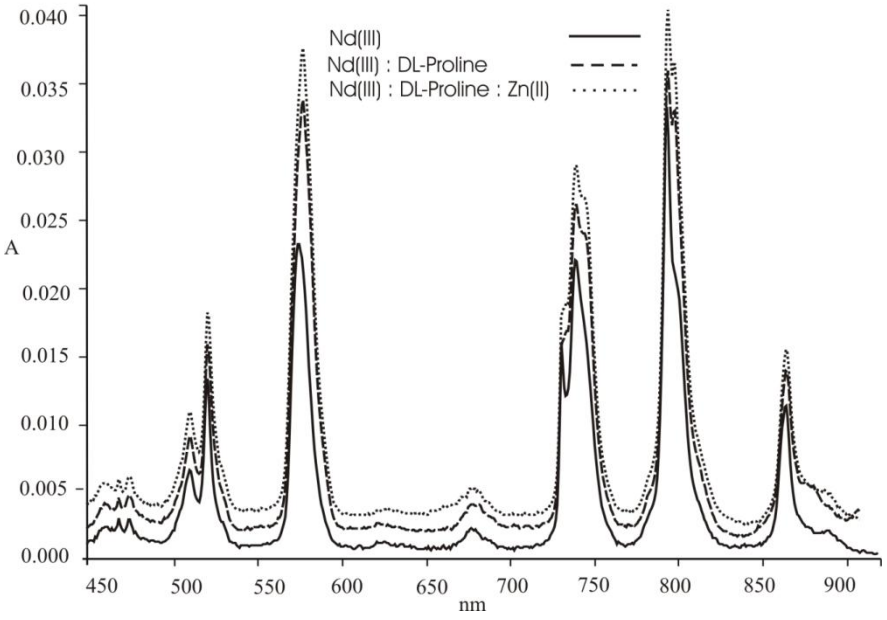

Figure 2. Comparative absorption spectra of Nd(III), Nd(III):DL-proline and Nd(III):DL-proline:Zn(II) in CH_3OH.

3. RESULTS AND DISCUSSION

The intensities of induced electric dipole transitions of lanthanide ions are almost independent of the environment and dipole strength of a particular electric dipole transition of a lanthanide in different matrices. However, few transitions are very sensitive to the environment and these are usually more intense in lanthanide complexes than for uncomplexed ions in aqueous solution. Jorgensen called these

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transitions as hypersensitive transitions obeying the selection rules for quadrupole transition [24]

$\Delta J \leq 2$, $\Delta L \leq 2$ and $\Delta S = 0$

With Nd(III), Peacock [25] observed hypersensitivity in the $^4I_{9/2} \rightarrow {}^4G_{5/2}$ transition.

Table 1

Computed values of energy interaction paramters Slator-Condon, $F_k(cm^{-1})$, nephelauxetic effect(β), bonding($b^{1/2}$) and covalency(δ) parameters for Nd(III); Nd(III):D-Proline (1:1); Nd(III):D-Proline:Zn(II) (1:1:1) and Nd(III):DL-Proline (1:1); Nd(III):DL-Proline:Zn(II) (1:1:1) in absence and presence of Zn(II) in different solvents at 298 K

System	F_2	F_4	F_6	ξ_{4f}	β	1-β	$b^{1/2}$	δ	F_4/F_2	F_6/F_2
1.H_2O										
Nd(III)	331.96	48.63	5.10	898.56	0.9925	0.0075	0.0612	0.7553	0.146494	0.015363
Nd(III):D-Proline	331.95	48.63	5.10	898.71	0.9926	0.0074	0.0608	0.7442	0.146498	0.015364
Nd(III):D-Proline:Zn(II)	331.92	48.63	5.10	898.90	0.9927	0.0073	0.0605	0.7377	0.146511	0.015365
Nd(III):DL-Proline	331.94	48.63	5.10	898.68	0.9926	0.0074	0.0610	0.7502	0.146502	0.015364
Nd(III):DL-Proline:Zn(II)	331.91	48.63	5.10	898.99	0.9927	0.0073	0.0602	0.7312	0.146516	0.015366
2.CH_3CN										
Nd(III)	332.14	48.73	5.10	896.16	0.9918	0.0082	0.0641	0.8275	0.146715	0.015355
Nd(III):D-Proline	332.09	48.72	5.10	896.97	0.9922	0.0078	0.0626	0.7888	0.146707	0.015357
Nd(III):D-Proline:Zn(II)	332.05	48.71	5.10	897.62	0.9925	0.0075	0.0612	0.7549	0.146695	0.015359
Nd(III):DL-Proline	332.09	48.71	5.10	897.00	0.9922	0.0078	0.0625	0.7879	0.146677	0.015357
Nd(III):DL-Proline:Zn(II)	332.08	48.71	5.11	897.38	0.9924	0.0076	0.0616	0.7650	0.146682	0.015388
3.CH_3OH										
Nd(III)	331.81	48.64	5.11	901.50	0.9944	0.0056	0.0529	0.5621	0.146590	0.015400
Nd(III):D-Proline	331.81	48.64	5.11	901.43	0.9943	0.0057	0.0532	0.5690	0.146590	0.015402
Nd(III):D-Proline:Zn(II)	331.77	48.64	5.11	902.28	0.9949	0.0051	0.5060	0.5145	0.146608	0.015402
Nd(III):DL-Proline	331.84	48.64	5.11	900.65	0.9939	0.0061	0.0554	0.6175	0.146577	0.015399
Nd(III):DL-Proline:Zn(II)	331.78	48.63	5.11	902.17	0.9948	0.0052	0.0510	0.5234	0.146573	0.015402
4.Dioxane										
Nd(III)	331.74	48.62	5.12	904.33	0.9962	0.0038	0.0436	0.3815	0.146561	0.015434
Nd(III):D-Proline	331.72	48.61	5.12	905.37	0.9969	0.0031	0.0395	0.3133	0.146539	0.015435
Nd(III):D-Proline:Zn(II)	331.69	48.63	5.12	905.35	0.9969	0.0031	0.0391	0.0374	0.146613	0.015436
Nd(III):DL-Proline	331.72	48.62	5.12	905.19	0.9968	0.0032	0.0402	0.3243	0.146569	0.015435
Nd(III):DL-Proline:Zn(II)	331.69	48.62	5.13	906.17	0.9974	0.0026	0.0357	0.2559	0.146583	0.015466
5.DMF										
Nd(III)	329.35	50.07	5.28	926.16	1.0174	0.0174	0.0925	1.6828	0.152027	0.016032
Nd(III):D-Proline	329.37	50.04	5.28	926.31	1.0171	-0.0171	0.0924	1.6799	0.151926	0.016031
Nd(III):D-Proline:Zn(II)	329.36	50.07	5.28	926.03	1.0171	-0.0171	0.0924	1.6795	0.152022	0.016031
Nd(III):DL-Proline	329.35	50.05	5.28	926.37	1.0172	-0.0172	0.0927	1.6881	0.151966	0.016032
Nd(III):DL-Proline:Zn(II)	329.39	50.05	5.28	925.97	1.0169	-0.0169	0.0919	1.6622	0.151948	0.016030

The binding of Nd(III)–Proline brings about changes in energies of various 4f-4f bands which causes the degree of lowering in the energy interaction parameters like Slator-Condon and inter-electronic repulsion parameters, which lead to nephelauxetic effect. The data in Table 1 shows that significant lowering of these parameters takes place in complexes as compared to the values for aquo ions indicating the expansion of the central metal ion orbital on complexation and is in accordance with the theory for the origin and intensity of f-f transitions reported earlier [26,27]. The average value of F_4/F_2 for Nd(III) complexes (=0.14695) is nearer to the values for the free ion. The same trend has been observed for the ratio F_6/F_2. A comparison of the observed and calculated values of the energy levels (Supplementary Table S2.) shows that the r.m.s. deviation lies between 25.32 to 67.50. This indicates good results even though the radial eigenfunctions have been assumed to be hydrogenic and also best fit

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for the partial regression method. The positive values of $b^{1/2}$ indicate some covalent character in metal-ligand bond. The small value and small variation of it suggests that the 4f-orbitals are very slightly involved in the bonding of the lanthanide complexes.

Table 2
Observed and computed values of oscillator strength ($Px10^6$) and Judd-Ofelt intensity parameters T_λ (λ= 2, 4,6)($T_\lambda x10^{10}$) $cm^{-1}$of the five bands observed for Nd(III) complexes with D-Proline and DL-Proline in absence and presence of Zn(II) in different aquated organic solvents at 298 K

System	$^4I_{9/2} \rightarrow {}^4G_{7/2}$		$^4I_{9/2} \rightarrow {}^4G_{5/2}$		$^4I_{9/2} \rightarrow {}^4F_{7/2}$		$^4I_{9/2} \rightarrow {}^4F_{5/2}$		$^4I_{9/2} \rightarrow {}^4F_{3/2}$		T_2	T_4	T_6	T_4/T_6
	P_{exp}	P_{cal}	P_{exp}	P_{cal}	P_{exp}	P_{cal}	P_{exp}	P_{cal}	P_{exp}	P_{cal}				
1.H_2O														
Nd(III)	0.944	0.828	2.882	2.888	3.669	3.506	2.883	3.074	0.519	0.405	15.76	0.75	60.96	0.0123
Nd(III):D-Proline	0.746	0.797	3.015	3.012	4.165	4.040	3.266	3.404	0.451	0.322	18.67	4.74	70.82	0.0669
Nd(III):D-Proline:Zn(II)	0.607	0.704	2.626	2.620	3.627	3.544	2.901	2.992	0.395	0.289	16.12	3.90	62.09	0.0628
Nd(III):DL-Proline	0.752	0.943	2.729	2.719	3.586	3.369	2.872	3.109	0.806	0.551	11.98	6.92	58.00	0.1193
Nd(III):DL-Proline:Zn(II)	0.851	0.807	3.038	3.040	3.842	3.687	2.991	3.167	0.485	0.358	17.79	1.86	64.39	0.0288
2.CH_3CN														
Nd(III)	1.655	0.923	2.858	2.899	3.332	3.186	2.753	2.948	0.437	0.529	13.27	6.90	54.80	0.1259
Nd(III):D-Proline	0.896	0.819	3.056	3.060	3.354	3.263	2.778	2.884	0.462	0.402	16.62	1.66	56.64	0.0293
Nd(III):D-Proline:Zn(II)	0.968	0.844	3.191	3.197	3.452	3.339	2.822	2.954	0.477	0.413	17.41	1.75	57.97	0.0301
Nd(III):DL-Proline	0.873	0.777	2.951	2.956	3.301	3.189	2.668	2.797	0.442	0.369	16.43	0.72	55.46	0.0129
Nd(III):DL-Proline:Zn(II)	1.900	1.035	3.317	3.365	3.550	3.382	2.939	3.165	0.489	0.601	15.26	8.82	58.01	0.1520
3.CH_3OH														
Nd(III)	0.616	0.728	2.940	2.935	3.579	3.513	2.902	2.973	0.389	0.294	18.01	3.56	61.52	0.0578
Nd(III):D-Proline	0.636	0.752	3.034	3.028	3.474	3.447	2.919	2.945	0.378	0.318	18.11	2.35	60.25	0.0390
Nd(III):D-Proline:Zn(II)	0.961	1.022	3.773	3.770	3.461	3.298	2.883	3.066	0.732	0.565	18.39	7.78	56.65	0.1373
Nd(III):DL-Proline	1.002	0.896	3.245	3.251	3.335	3.188	2.726	2.897	0.578	0.476	16.47	4.82	55.03	0.0875
Nd(III):DL-Proline:Zn(II)	1.056	0.971	3.524	3.529	3.561	3.474	3.052	3.153	0.566	0.514	17.94	5.09	59.99	0.0848
4.Dioxane														
Nd(III)	0.931	0.799	3.604	3.612	3.366	3.160	2.515	2.754	0.496	0.349	20.99	0.05	55.01	0.0009
Nd(III):D-Proline	0.945	0.821	3.599	3.606	3.263	3.101	2.548	2.736	0.486	0.377	20.39	1.40	53.85	0.0259
Nd(III):D-Proline:Zn(II)	0.850	0.761	3.424	3.429	3.058	2.904	2.370	2.549	0.454	0.341	19.66	0.81	50.48	0.0160
Nd(III):DL-Proline	1.072	0.817	4.050	4.064	3.556	3.454	2.818	2.945	0.328	0.313	24.89	2.58	60.38	0.0427
Nd(III):DL-Proline:Zn(II)	0.981	0.915	4.056	4.059	3.515	3.367	2.815	2.984	0.538	0.424	22.83	2.06	58.42	0.0352
5.DMF														
Nd(III)	1.392	1.333	5.942	5.944	3.712	3.777	3.638	3.565	0.618	0.697	30.89	10.74	65.34	0.0164
Nd(III):D-Proline	1.332	1.159	5.959	5.969	3.827	3.662	3.113	3.307	0.617	0.519	34.02	4.35	63.93	0.0680
Nd(III):D-Proline:Zn(II)	1.306	1.197	6.131	6.137	3.921	3.768	3.231	3.408	0.646	0.539	34.88	4.68	65.77	0.0712
Nd(III):DL-Proline	1.256	1.225	6.087	6.089	3.859	3.783	3.367	3.450	0.634	0.572	34.02	5.88	65.90	0.0892
Nd(III):DL-Proline:Zn(II)	1.334	1.155	6.289	6.299	4.020	3.851	3.212	3.412	0.578	0.477	37.12	1.92	67.47	0.0284

Since the interaction of Nd(III) with Proline is generally predominant with carboxylic group of Proline, the bonding between Nd(III) and Proline is basically electrostatic in nature although some covalent character is also being associated in metal-ligand bond. Since lanthanides are hard metal ions, their preference will be for hard donor site like oxygen atom. The absolute values of oscillator strengths and Judd-Ofelt intensity (T_λ) parameters are determined under different experimental conditions for Nd(III) complexes with Proline (Table 2). This clearly shows a significant change in the oscillator strengths of 4f-4f bands of the Nd(III) ion, i.e. for hypersensitive transition ($^4I_{9/2} \rightarrow {}^4G_{5/2}$). Substantial changes are also observed in the non-hypersensitive transitions called Pseudohypersensitive transitions like, $^4I_{9/2} \rightarrow {}^4G_{7/2}$, $^4I_{9/2} \rightarrow {}^4F_{3/2}$, $^4I_{9/2} \rightarrow {}^4F_{5/2}$, and $^4I_{9/2} \rightarrow {}^4F_{7/2}$ when Nd(III) interact with Proline in solution.

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Comparative absorption spectra of Nd(III); Nd(III):D-Proline and Nd(III):DL-Proline in DMF (Figure 1) clearly show that the addition of Proline to Nd(III) results in significant enhancement in the oscillator strengths of different 4f-4f transitions. We also observe noticeable increase in the magnitude of Judd-Ofelt parameters. This suggests the binding of the Proline to Nd(III) in solution. Comparative absorption spectra of Nd(III); Nd(III):DL-Proline and Nd(III):DL-Proline:Zn(II) in methanol (Figure 2) shows without doubt, that the introduction of Zn(II) to binary system of Nd(III):DL-Proline yields noticeable changes in the oscillator strengths and in the magnitude of Judd-Ofelt (T_λ) intensity parameters. This result obviously shows further enhancement in interaction of Nd(III)-Proline in solution.

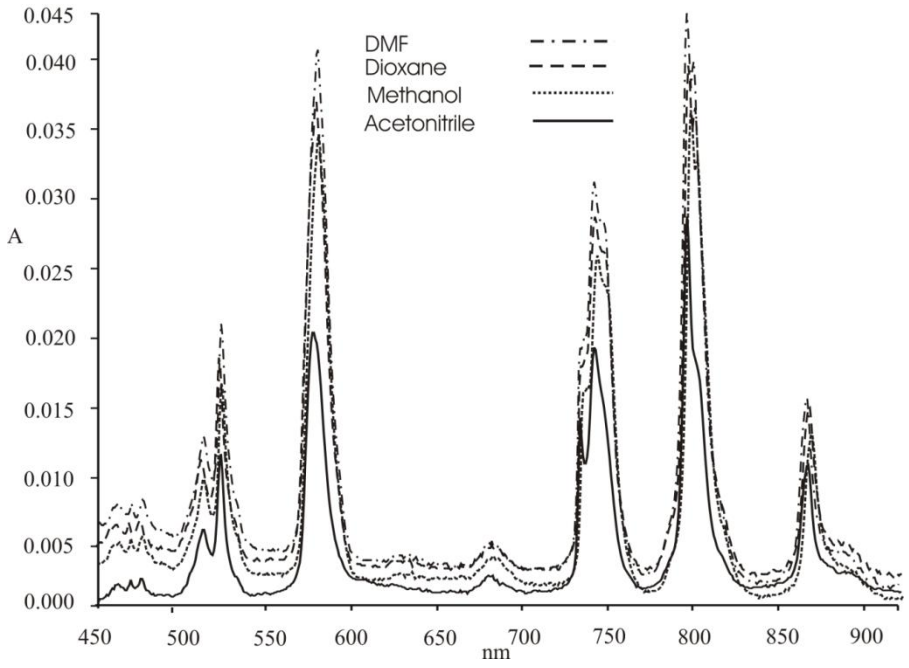

Figure 3. Comparative absorption spectra of Nd(III):D-proline in different solvents.

Choppin *et al.* [28,29] have suggested the strong inner sphere complexation in glycinate complexes. According to them, during the formation of these complexes the hydration sphere around lanthanides is disrupted completely by the amino acid moiety. Henrie *et al.* [30] at the same time believed that increase in the degree of inner sphere complexation contributes towards the enhancement of intensity of intra f↔f transitions. Contrary to this, the observed intensities of these complexes are very low (P = 0.288×10^{-6} - 6.2992×10^{-6}) (Table 2). No doubt amino acids are expected to form inner sphere complexes by forming an ionic linkage with carboxylic oxygen and additional linkage due to the amino group. The proton from the carboxylic group migrates towards the amino group and the oxygen of the carboxylic group links to the metal ion while the remaining amino acid molecule hangs in space. The classical zwitterions resonance form of the acid is promoted by the highly charged lanthanide ion. This in fact contributes a significant amount of electron density to the lanthanide ion. This might be one of the reasons why low intensities of these bands are observed in these complexes. The r.m.s. deviation with respect to oscillator strength are also in the acceptable range.

Comparative absorption spectra of Nd(III)-D-Proline and Nd(III)-DL-Proline in different aquated organic solvents (Figures 3 and S1) clearly suggest the significant role of solvents on complexation. DMF appears to induce the strongest complexation influence on Nd(III)-Proline (D- and DL-Proline)

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complexes. The red shift is observed in the energies of all five bands (including combined bands), which

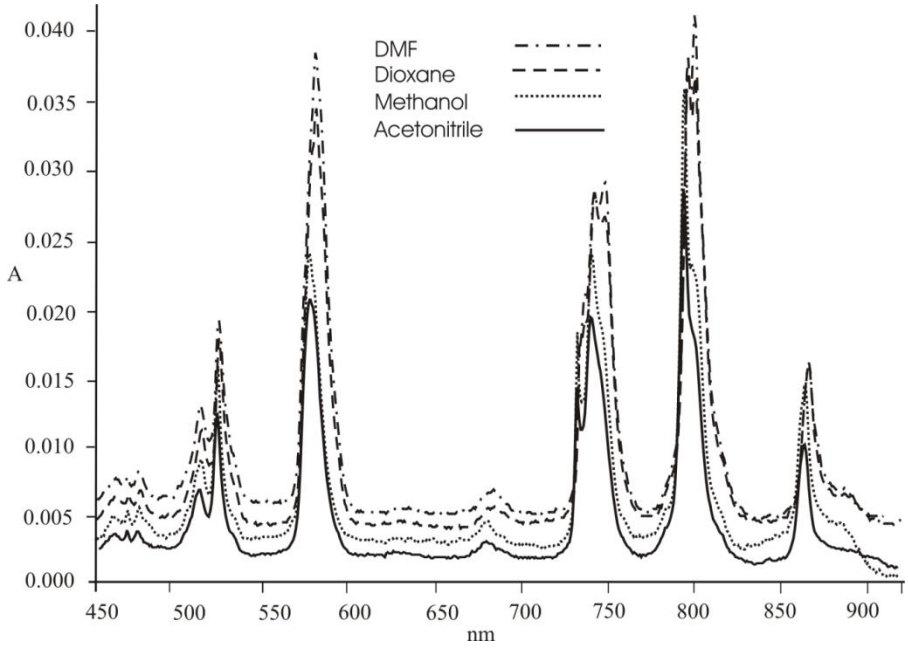

Figure 4. Comparative absorption spectra of Nd(III):DL-proline in different solvents.

are considered as marker for quantitative analysis of Nd(III) ion i.e. $^4I_{9/2} \rightarrow {}^4G_{5/2,}$ the hypersensitive transition and other transitions, $^4I_{9/2} \rightarrow {}^4G_{7/2}$, $^4I_{9/2} \rightarrow {}^4F_{3/2}$, $^4I_{9/2} \rightarrow {}^4F_{5/2}$, and $^4I_{9/2} \rightarrow {}^4F_{7/2}$. The influence of solvents like methanol and acetonitrile are less on complexation of Nd(III)-Proline. 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 resulting in the decrease of inter-electronic repulsion which leads to the phenomenon of nephelauxetic effect and thus can lead to lowering of coordination number [31, 32]. 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)-Proline complexes. T_2 parameter changes significantly as a function of ligand concentration. The values of T_2 parameter which increase in presence of organic solvents suggest that organic solvents have a better coordinating power in comparison with water. T_4 and T_6 are slightly affected in comparison with T_2 parameter. Both parameters are related to changes in symmetry properties of the complex species [33] being shown by ratio T_4/T_6 which varies from 0.0008 to 0.1373. This indicates a very slight change in symmetry around Nd(III) in the present system under study. At the same time, the extend of mixing of 4f and 5d orbital might also have influence on T_4. Table 2 clearly reflects that T_4 and T_6 are affected significantly in the presence of different solvents suggesting that not only immediate coordination environment of Nd(III) but symmetry of the complex species are also changed accordingly. These changes are also considered to be good evidence for the involvement of Proline(D- and DL-Proline) in the inner sphere coordination of Nd(III) ion. The ligand environment has only weak influence on the electronic cloud of the Nd(III) and at the same time the 4f shell is efficiently shielded by the closed 5s and 5p shells. This clearly shows without doubt that the complexation of Nd(III)-Proline in absence and presence of Zn(II) is affected significantly by changes in the nature of solvent. All the results obtained clearly suggest that minor coordination changes in the Nd(III) complexes are caused by spatial arrangement of coordinating sites of Proline, denticity, solvent nature, coordination number, nature of Nd(III)-Proline bond, which do induce significant variation in the intensity of f-f transitions.

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4 CONCLUSION

From the above discussion through variation in the magnitude of energy interaction and intensity parameters we can suggest that 4f-4f transitions of Nd(III) with DL-Proline is more sensitive than its coordination with D-Proline. This clearly suggest that although both show similar affinity towards Nd(III), their binding to Nd(III) is rather different.. It is also clearly revealed by the comparative absorption spectra of Nd(III) with D-Proline and DL-Proline in different solvents and DMF induce most significant changes in coordination towards the Nd(III) as compared to other solvents.

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SUPPORTING INFORMATION

Tables S1 & S2 are included in the supporting information

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The authors declare no conflict of interest

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