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Absorption Spectral Study of 4*f*-4*f* Transitions for the Interaction of Nd(III) with Different Amino Acids in Presence and Absence of Ca(II)/Zn(II)

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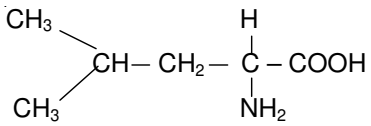
By employing comparative absorption and quantitative spectral analysis of hypersensitive and pseudohypersensitive transitions using 4*f*-4*f* transitions as probe, the interaction of Nd(III) with L-leucine, L(-)-hydroxyproline and L-(+)-arginine in presence and absence of Ca(II)/Zn(II) has been studied in four different aquated organic solvents, *i.e.*, methanol (CH_3OH), acetonitrile (CH_3CN), dimethylformamide (DMF), dioxane ($C_4H_8O_2$) and their equimolar mixtures. The various energy interaction parameters like Slator-Condon (F_K), Racah (E_K) and Lande (ξ_{4f}), nephelauxetic parameter (β), bonding parameter ($b^{1/2}$) and per cent covalency (∂) parameter are calculated using partial and multiple regression method. The values of oscillator strength (P) and computed values of Judd-Ofelt electric dipole intensity parameters (T_λ) ($\lambda = 2, 4, 6$) are also calculated for different 4*f*-4*f* transitions. The magnitude of changes in various energy interaction parameters as well as in the oscillator strength (P) and Judd-Ofelt intensity values (T_λ) were used to explore the degree of inner and outer sphere coordination, incidence of covalency and the extent of metal 4*f*-orbital involvement in binding with different ligands.

Key Words: Hypersensitive, Pseudohypersensitive, Oscillator strength, 4*f*-4*f* transitions.

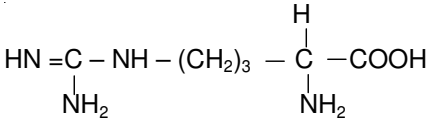
INTRODUCTION

Most of the trivalent lanthanides have internal 4*f* electron transition spectra in the accessible spectral region which are very much sensitive towards immediate coordination environment. This makes quantitative absorption spectral spectroscopy involving 4*f*-4*f* transitions a powerful tool in the investigation of lanthanide biochemistry. The justification for using paramagnetic lanthanide ions in biochemical investigations, relates to their ability to replace Ca(II) in a specific isomorphous manner. This is due to close similarities between lanthanide ions and Ca(II) in ionic size, donor atom preference, bonding and coordination characteristics[1]. Since lanthanide ions can substitute for Ca(II) in living systems, studies of the bonding modes and structures of lanthanide complexes with some amino acids are of interest. Studies on lanthanide complexes with some amino acids in solution have been carried out using NMR, luminescence and titration methods to determine the thermodynamic stability constants[2-4]. Shah and Shah[5] studied comparative 4*f*-4*f* transition spectra of Pr(III) with lysozyme by using the energy interaction parameters to explain the behaviour of binding between them. In our previous study[6], we have studied the interaction of Pr(III) with different amino acids in aqueous and aquated organic solvents. We has also studied the interaction of Nd(III) with DL-valine, DL-alanine and β-alanine in presence and absence of Ca(II)/Zn(II) in aqueous and different aquated organic solvents[6].

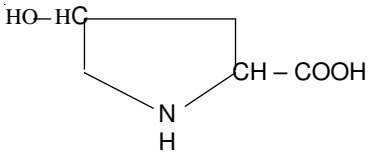
Amino acids are ligands which offer potential binding sites through carboxylate oxygen and amino nitrogen. The different amino acids chosen for study are L-leucine, L(-)-hydroxyproline and L-(+)-arginine. The first two amino acids are neutral amino acids and the last one is basic amino acid. Amino acids are very much necessary for maintaining good health in which some of them are essential and some are non-essential. Among them, L-leucine and L-(+)-arginine are essential amino acids while L(-)-hydroxyproline is non-essential amino acid. The structures of different amino acids are given in Fig. 1.



(A)



(B)



(C)

Fig. 1. Structures of (A) L-leucine, (B) L-(+)-arginine, (C) L (-)-hydroxyproline

Cacium(II) and zinc(II) are endogenous metal ions which have different coordinating behaviour towards biological molecules *i.e*., Ca(II) which is a hard metal ion prefers hard donor sites like carboxylic and carbonyl groups and Zn(II) which is a soft metal ion prefers soft donor sites like amino group in amino acids. Since Pr(III)/Nd(III) resembles to Ca(II) and Zn(II), its complexation can provide information about the coordination characteristics of diamagnetic molecules, *i.e*., Ca(II) and Zn(II) with biomolecules during biochemical reactions. This is the reason that the paramagnetic lanthanides are good spectral probes for exploring the biological roles of Ca(II) by its isomorphous substitute[1]. The present work is mainly concentrated to the quantitative spectral energy interaction parameters and intensity parameters of Nd(III) complexation with L-leucine, L(-)-hydroxyproline and L-(+)-arginine in presence and absence of Ca(II) and Zn(II) in aqueous and different aquated organic solvents. The present work reports the ligand mediated pseudohypersensitive transitions $^4I_{9/2} \rightarrow {}^4F_{3/2}$, $^4I_{9/2} \rightarrow {}^4F_{5/2}$, $^4I_{9/2} \rightarrow {}^4F_{7/2}$ and $^4I_{9/2} \rightarrow {}^4G_{7/2}$ of Nd(III) and uses the magnitude and variation of the various energy interaction parameters in support of the intensity parameters like oscillator strength (P) and Judd-Ofelt electric dipole intensity parameters, (T_λ) (λ = 2, 4, 6) to reveal the mode of binding with different ligands.

EXPERIMENTAL

Neodymium(III) nitrate of 99.9 % purity was purchased from CDH analytical reagent and amino acids, *i.e*., L-leucine, L(-)-hydroxyproline and L-(+)-arginine from Loba Chemie Indo-Australian Co were used for spectral analysis. The solvents used are methanol (CH_3OH), acetonitrile (CH_3CN), dimethylformamide (DMF), dioxane ($C_4H_8O_2$). They are of AR grade from Qualigens.

The solutions of Nd(III) nitrate, corresponding amino acid, Ca(II) and Zn(II) salts of 10^{-2} M were prepared in different solvents. The solution spectrum of each solution at pH 4 and at temperature 298 K were recorded on a Perkin-Elmer Lambda-35 UV-VIS spectrophotometer upgraded with high resolution and expansion of scale having water jacket cell holder in the range 350-900 nm.

The energy of 4*f*-4*f* transitions, E_{so}, arising from the most important magnetic interactions which are spin-orbit interactions may be written as

$$E_{so} = A_{so}\xi_{4f} \quad (1)$$

where, A_{so} is the angular part of spin-orbit interaction and ξ_{4f} is the radial integral and is known as Lande's parameter.

By first order approximation the energy E_j of the jth level is given by Wong[7] as

$$F_j(F_K, \xi_{4f}) = E_{oj}(F_k^0, \xi_{4f}^0) + \sum_{k=2,4,6} \frac{\partial E_j}{\partial F_K}\Delta F + \frac{\partial E_j}{\partial \xi_{4f}}\Delta\xi_{4f} \quad (2)$$

where, E_{0j} is the zero order energy of the jth level. The values of F_K and ξ_{4f} are given by

$$F_K = F_K^0 + \Delta F_K \quad (3)$$

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

when $\Delta F_K << F_K^0$ and $\Delta\xi_{4f} << \xi_{4f}^0$.

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

$$\Delta E_j = \sum_{K=2,4,6} \frac{\delta E_j}{\delta F_K} + \frac{\delta E_j}{\delta \xi_{4f}}\Delta\xi_{4f} \quad (5)$$

By using the zero order energy and partial derivatives of Nd(III) ion given by Wong[7,8], the above equation can be solved by least square technique and the value of ΔF_2 and $\Delta\xi_{4f}$ can be found out. From these the values of F_2 and ξ_{4f} are obtained by relations (3) and (4). The estimated values of F_4 and F_6 are calculated by the relations,

$$\frac{F_4}{F_2} = 0.1380 \text{ and } \frac{F_6}{F_2} = 0.0150 \quad (6)$$

Nephelauxetic ratio has long been regarded as a measure of covalency[8-10]. The nephelauxetic effect has been interpreted in terms of Slater-Condon and Racah parameters (inter-electronic repulsion parameters) as well as by the ratio of the free ion and complex ion[11-15].

$$\beta = \frac{F_K^c}{F_K^f} \text{ or } \beta = \frac{E_c^K}{E_f^K} \quad (7)$$

where, F_K (K = 2, 4, 6) is the Slater-Condon parameter and E^K is the Racah parameters for complex and free ions, respectively. The bonding parameter and percent covalency are inter-related to nephelauxetic effect and calculated as

$$\beta^{1/2} = \left[\frac{1-\beta}{2}\right]^{1/2} \quad (8)$$

$$\delta = \left[\frac{1-\beta}{\beta}\right] \times 100 \quad (9)$$

Judd and Ofelt[16,17] observed that the oscillator strength of an induced electric dipole transition relating to the energy of transition ($\bar{\nu}$), square of the matrix element of unit tensor operator, $U^{(\lambda)}$ connecting initial $\langle f^n \Psi J|$ and final $|f^n \Psi' J'\rangle$ through 3 phenomenological parameters, T_λ (λ = 2, 4, 6) can be expressed as

$$P = \sum_{\lambda=2,4,6} T_\lambda \bar{\nu} \langle f^n \Psi J \| U^\lambda \| f^n \Psi J' \rangle \quad (10)$$

where, $U^{(\lambda)}$ is the matrix element of rank λ. The three quantities T_2, T_4 and T_6 are related to the radial parts of the $4f^N$ wave functions, the wave functions of perturbing configurations of which the nearest is $4f^{N-1}5d$.

The intensity of the absorption band is measured by the experimentally determined Oscillator strength P_{obs} which is directly proportional to the area under the absorption curve given by the expression

TABLE-1
COMPUTED VALUES OF ENERGY INTERATION PARAMETERS OF Nd(III), Nd(III) : AMINO ACID (1:1), Nd(III): AMINO ACID: Ca(II) (1 :1 :1) AND Nd(III): AMINO ACID: Zn(II) (1:1:1) IN AQUEOUS AND DIFFERENT AQUATED ORGANIC SOLVENTS (50:50) AT pH 4

System	F_2	F_4	F_6	ξ_{4f}	β	$b^{1/2}$	δ
1. Solvent-water							
L-Leucine							
Nd(III)	328.10	48.72	5.26	957.87	1.0286	0.1196	2.7790
Nd(III): Leu	328.08	48.72	5.26	957.85	1.0287	0.1198	2.7920
Nd(III): Leu : Ca(II)	327.88	48.70	5.26	957.83	1.0300	0.1225	2.9142
Nd(III): Leu : Zn(II)	327.82	48.69	5.26	957.80	1.0305	0.1234	2.9566
L(-)Hydroxyproline							
Nd(III)	328.25	48.62	5.25	956.21	1.0270	0.1162	2.6292
Nd(III): Hyp	328.21	48.62	5.25	956.19	1.0274	0.1170	2.6667
Nd(III): Hyp : Ca(II)	327.91	48.61	5.25	956.10	1.0295	0.1214	2.8616
Nd(III): Hyp : Zn(II)	327.86	48.60	5.26	956.07	1.0300	0.1225	2.9137
L(+)-Arginine							
Nd(III)	328.05	48.66	5.25	957.87	1.0281	0.1186	2.7349
Nd(III) : Arg	328.01	48.66	5.25	957.82	1.0287	0.1198	2.7905
Nd(III) : Arg : Ca(II)	327.91	48.65	5.25	957.80	1.0295	0.1216	2.8704
Nd(III) : Arg: Zn(II)	327.88	48.65	5.24	957.75	1.0300	0.1224	2.9088
2. Solvent -Methanol							
L-Leucine							
Nd(III)	330.05	48.20	5.13	927.69	1.0070	0.0591	0.6946
Nd(III): Leu	329.99	48.20	5.12	927.65	1.0078	0.0624	0.7719
Nd(III): Leu : Ca(II)	329.97	48.20	5.10	927.63	1.0079	0.0631	0.7905
Nd(III): Leu : Zn(II)	329.96	48.24	5.08	927.60	1.0080	0.0635	0.7992
L(-)Hydroxyproline							
Nd(III)	330.11	48.09	5.13	928.78	1.0072	0.0599	0.7126
Nd(III): Hyp	330.09	48.09	5.13	928.76	1.0076	0.0617	0.7552
Nd(III): Hyp : Ca(II)	330.02	48.05	5.12	928.74	1.0114	0.0754	1.1248
Nd(III): Hyp : Zn(II)	329.99	48.05	5.10	928.73	1.0116	0.0761	1.1451
Nd(III): Ala : Zn(II)	329.98	48.08	5.10	928.49	1.0119	0.0772	1.1786
L(+)-Arginine							
Nd(III)	330.08	48.12	5.13	928.80	1.0074	0.0607	0.7321
Nd(III) : Arg	329.95	48.12	5.12	928.78	1.0116	0.0764	1.1526
Nd(III) : Arg : Ca(II)	329.84	48.11	5.10	928.75	1.0128	0.0801	1.2658
Nd(III) : Arg: Zn(II)	329.82	48.10	5.09	928.73	1.0132	0.0811	1.2980
3. Solvent - MeCN							
L-Leucine							
Nd(III)	330.00	48.20	5.13	928.95	1.0078	0.0625	0.7760
Nd(III): Leu	329.99	48.20	5.12	928.90	1.0079	0.0630	0.7875
Nd(III): Leu : Ca(II)	329.98	48.20	5.11	928.88	1.0081	0.0634	0.7985
Nd(III): Leu : Zn(II)	329.95	48.19	5.08	928.80	1.0082	0.0640	0.8124
L(-)Hydroxyproline							
Nd(III)	330.02	48.20	5.14	928.79	1.0078	0.0624	0.7717
Nd(III): Hyp	330.00	48.19	5.13	928.76	1.0082	0.0640	0.8116
Nd(III): Hyp : Ca(II)	329.98	48.18	5.12	928.74	1.0083	0.0646	0.8268
Nd(III): Hyp : Zn(II)	329.97	48.16	5.10	928.70	1.0085	0.0650	0.8378
L(+)-Arginine							
Nd(III)	330.07	48.14	5.13	928.99	1.0076	0.0616	0.7534
Nd(III) : Arg	330.06	48.14	5.13	928.97	1.0078	0.0623	0.7707
Nd(III) : Arg : Ca(II)	330.05	48.13	5.13	928.94	1.0079	0.0627	0.7820
Nd(III) : Arg: Zn(II)	330.04	48.12	5.12	928.93	1.0078	0.0631	0.7909
4. Solvent - DMF							
L-Leucine							
Nd(III)	329.86	48.18	5.16	934.56	1.0115	0.0757	1.1342
Nd(III): Leu	329.76	48.17	5.15	934.52	1.0129	0.0804	1.2751
Nd(III): Leu : Ca(II)	329.21	48.59	5.21	934.50	1.0180	0.0947	1.7634
Nd(III): Leu : Zn(II)	329.20	48.59	5.20	934.45	1.0181	0.0952	1.7794
L(-)Hydroxyproline							
Nd(III)	329.89	48.20	5.16	934.84	1.0115	0.0759	1.1381
Nd(III): Hyp	329.82	48.19	5.16	934.82	1.0126	0.0793	1.2405
Nd(III): Hyp : Ca(II)	329.30	48.12	5.13	935.80	1.0175	0.0934	1.7165
Nd(III): Hyp : Zn(II)	329.29	48.10	5.10	935.75	1.0176	0.0937	1.7260

L(+)-Arginine							
Nd(III)	329.94	48.20	5.15	932.94	1.0106	0.0728	1.0487
Nd(III) : Arg	329.71	48.20	5.12	932.90	1.0136	0.0825	1.3419
Nd(III) : Arg : Ca(II)	329.65	48.15	5.09	932.85	1.0194	0.0985	1.9027
Nd(III) : Arg: Zn(II)	329.60	48.12	5.06	932.83	1.0199	0.0997	1.9500
5.Solvent – Dioxane							
L-Leucine							
Nd(III)	329.93	48.13	5.14	931.27	1.0089	0.0668	0.8852
Nd(III): Leu	329.88	48.12	5.14	931.92	1.0094	0.0687	0.9344
Nd(III): Leu : Ca(II)	329.85	48.12	5.14	931.90	1.0097	0.0696	0.9594
Nd(III): Leu : Zn(II)	329.82	48.11	5.13	931.85	1.0099	0.0704	0.9811
L(-)Hydroxyproline							
Nd(III)	329.94	48.17	5.14	930.30	1.0085	0.0652	0.8439
Nd(III): Hyp	329.91	48.17	5.13	930.25	1.0090	0.0670	0.8892
Nd(III): Hyp : Ca(II)	329.85	48.17	5.12	930.20	1.0094	0.0686	0.9317
Nd(III): Hyp : Zn(II)	329.81	48.16	5.10	930.17	1.0097	0.0697	0.9629
L(+)-Arginine							
Nd(III)	329.86	48.15	5.14	931.17	1.0089	0.0665	0.8770
Nd(III) : Arg	329.80	48.12	5.14	931.15	1.0094	0.0687	0.9346
Nd(III) : Arg : Ca(II)	329.75	48.11	5.13	931.12	1.0110	0.0741	1.0870
Nd(III) : Arg: Zn(II)	329.69	48.09	5.12	931.10	1.0130	0.0806	1.2838

$$P_{obs} = 4.6\times10^{-9}\times\varepsilon_{max}\times\Delta\bar{\nu}_{1/2} \quad (11)$$

where, ε_{max} is the molar extinction coefficient and $\Delta\bar{\nu}_{1/2}$ is half band width.

From these values the value of T_2, T_4 and T_6 are calculated by using

$$\frac{P_{obs}}{\nu} = [(U^2)]^2.T_2 + [(U^4)]^2.T_4 + [(U^6)]^2.T_6 \quad (12)$$

RESULTS AND DISCUSSION

Five transitions *i.e.*, $^4F_{3/2}$, $^4F_{5/2}$, $^4F_{7/2}$, $^4G_{5/2}$ and $^4G_{7/2}$ originating from symmetry forbidden $^4I_{9/2}$ ground level in the 400-900 nm spectral region are observed in the neodymium complex. Out of the five transitions, the transition $^4I_{9/2} \rightarrow {}^4G_{5/2}$ are very sensitive to the environment and are usually more intense when a lanthanide ion gets complexed than it is in the corresponding aquo ion. Such transitions are called hypersensitive transitions and follow a common set of selection rule $|\Delta J| \leq 2, |\Delta L| \leq 2$ and $|\Delta S| = 0$. In fact, the transitions $^4I_{9/2} \rightarrow {}^4F_{3/2}$, $^4F_{5/2}$, $^4F_{7/2}$ and $^4G_{7/2}$ of Nd(III) do not obey the selection rules for hypersensitive transition[18], but have been found to exhibit substantial sensitivity in the complexes[19]. Such ransitions are called "Ligand Mediated Pseudohypersensitive" or "Pseudohypersensitive" transitions. The comparative absorption spectra of Nd(III), Nd(III): L-leucine/L(-)-hydroxyproline/L(+)-arginine, Nd(III): L-leucine/L(-)-hydroxyproline/L(+)-arginine: Ca(II) and Nd(III): L-leucine/L(-)-hydroxyproline/L(+)-arginine: Zn(II) in DMF is shown in Figs. 2-4. The addition of ligands *i.e.*, L-leucine, L(-)-hydroxyproline and L(+)-arginine to Nd(III) results in the red shift in all the energy bands. Again, the addition of Ca(II) to Nd(III): ligand increases the wavelength further and the addition of Zn(II) to Nd(III): ligand shifts the energy bands to longer wavelength as compared to that of the increase in wavelength on addition of Ca(II) to Nd(III): ligand. From Table-1, one can observe that in all the systems that there is a slight decrease in Slater-Condon (F_K) and spin-orbit interaction or Lande's parameter (ξ_{4f}) as the complexation goes on which lead to increase in the values of nephelauxetic ratio when the ligands are added to Nd(III). Further, in all the systems, the values of nephelauxetic effect (β) ranges from 1.0074-1.0305 and the bonding parameter ($b^{1/2}$) values are found to be positive which indicates covalent bonding between the metal ion and the ligand. The small value and small variation of bonding parameter ($b^{1/2}$) value are indicative of the fact that the 4*f*-orbitals of the metal ion are slightly involved in the formation of bonding between the metal ion and the ligand. It is in accordance with the theory for the origin and the intensity of $f \leftrightarrow f$ transition reported earlier. The same trend is also observed in the case of other ligands *i.e.*, DL-valine, DL-alanine and β-alanine with Nd(III) in our previous work[20]. The corresponding values of oscillator strengths and Judd-Ofelt parameters of Nd(III) with different amino acids *i.e.*, L-leucine, L(-)-hydroxyproline and L(+)-arginine in presence and absence of Ca(II)/Zn(II) in the solvents methanol (CH_3OH), acetonitrile (CH_3CN), dimethylformamide (DMF) and dioxane ($C_4H_8O_2$) are shown in Table-2. From the Table-2, one can observe that the variation of solvent has significant effect on the oscillator strengths of 4*f*-4*f* bands and

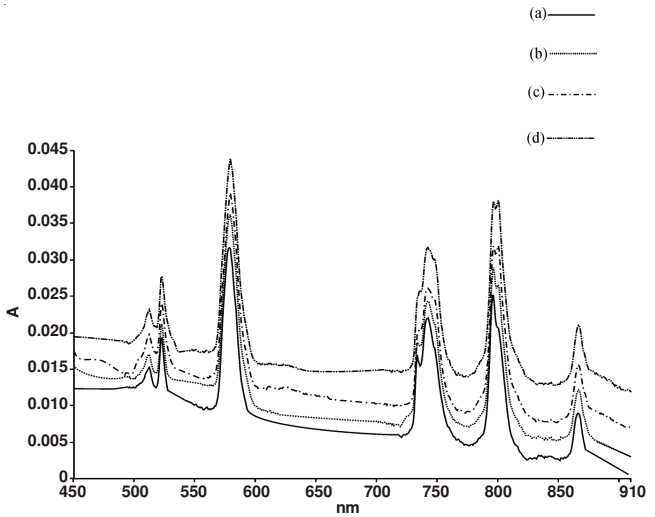


Fig. 2. Comparative absorption spectra of (a) Nd(III); (b) Nd(III): L-leucine; (c) Nd(III): L-leucine: Ca(III); (d) L-leucine: Zn(II) in DMF

TABLE-2
OBSERVED AND COMPUTED VALUES OF OSCILLATOR STRENGTHS ($P \times 10^6$) AND JUDD-OFELT ($T_\lambda \times 10^{10}$) PARAMETERS FOR Nd(III), Nd(III): AMINO ACID (1:1), Nd(III): AMINO ACID: Ca(II) (1:1:1) AND Nd(III): AMINO ACID : Zn(II) (1:1:1) IN AQUEOUS AND DIFFERENT AQUATED ORGANIC SOLVENTS (50:50) AT pH 4

System	$^4F_{3/2}$	$^4F_{5/2}$	$^4F_{7/2}$	$^4G_{5/2}$	$^4G_{7/2}$	T_2	T_4	T_6
	P_{obs} (P_{cal})	P_{obs} (P_{cal})	P_{obs} (P_{cal})	P_{obs} (P_{cal})	P_{obs} (P_{cal})			
1. Solvent-water								
L = L-Leucine								
Nd(III)	0.3350 (0.3200)	1.9905 (2.0924)	2.4222 (2.2302)	3.8265 (3.8393)	0.8203 (0.6506)	2.2054	0.2473	4.0572
Nd(III): L	0.3746 (0.3614)	2.2108 (2.5438)	2.6210 (2.5441)	3.8950 (3.9056)	0.8372 (0.6969)	2.2020	0.3167	4.4257
Nd(III) : L: Ca(II)	0.3138 (0.3222)	2.0914 (2.1221)	2.3956 (2.3675)	3.3089 (3.3153)	0.6867 (0.6030)	1.8683	0.2396	4.1246
Nd(III): L: Zn(II)	0.3289 (0.3321)	2.1605 (2.2043)	2.5025 (2.4627)	3.3566 (3.3640)	0.7133 (0.6160)	1.8942	0.2375	4.2921
L = L(-)-Hydroxyproline								
Nd(III): L	0.4136 (0.3341)	2.1234 (2.2855)	2.7111 (2.5966)	3.9128 (3.9227)	0.7966 (0.6678)	2.2638	0.2012	4.4726
Nd(III): L : Ca(II)	0.3773 (0.3394)	2.2000 (2.3214)	2.7149 (2.6060)	3.5103 (3.5217)	0.7862 (0.6350)	2.0050	0.2047	4.5445
Nd(III): L : Zn(II)	0.3811 (0.3535)	2.2178 (2.3496)	2.7440 (2.6736)	3.6491 (3.6643)	0.8619 (0.6633)	2.0702	0.2515	2.5747
L = L(+)-Arginine								
Nd(III) : L	0.3278 (0.3146)	1.9586 (2.0022)	2.2594 (2.2202)	3.4233 (3.4276)	0.6645 (0.6080)	1.9346	0.2739	3.8615
Nd(III) : L : Ca(II)	0.3200 (0.3066)	1.9789 (2.0456)	2.3474 (2.2874)	3.3519 (3.3597)	0.6939 (0.5905)	1.9138	0.2139	3.9854
Nd(III) : L: Zn(II)	0.3172 (0.2713)	1.9370 (2.0567)	2.2838 (2.3438)	3.2683 (3.2784)	0.6786 (0.5464)	1.9271	0.0599	4.0996
2. Solvent - Methanol								
L = L-Leucine								
Nd(III)	0.4554 (0.3180)	1.9646 (2.1906)	2.6618 (2.4611)	4.1198 (4.1283)	0.7863 (0.6706)	2.4047	0.1815	4.2727
Nd(III): L	0.4071 (0.3072)	1.9912 (2.1896)	2.6302 (2.4616)	4.0046 (4.0148)	0.7813 (0.6484)	2.3512	0.1395	4.2787
Nd(III) : L :Ca(II)	0.4339 (0.3815)	2.1917 (2.3739)	2.7848 (2.6213)	4.2046 (4.2227)	0.9228 (0.7447)	2.3753	0.3580	4.5361
Nd(III): L : Zn(II)	0.3844 (0.3492)	2.1750 (2.2745)	2.6210 (2.5319)	4.0684 (4.0770)	0.8117 (0.6982)	2.3269	0.2715	4.3887
L = L(-)-Hydroxyproline								
Nd(III): L	0.3989 (0.2938)	1.9654 (2.1879)	2.6877 (2.4892)	3.9839 (3.9982)	0.8182 (0.6316)	2.3666	0.0755	4.3290
Nd(III): L : Ca(II)	0.3876 (0.3267)	2.0509 (2.2499)	2.7078 (2.5292)	3.9227 (3.1496)	0.9129 (0.6621)	2.2845	0.1873	4.3882
Nd(III): L : Zn(II)	0.3881 (0.3245)	2.1100 (2.2908)	2.7469 (2.5850)	3.9903 (4.0061)	0.8710 (0.6644)	2.3369	0.1550	4.4892
L = L(+)-Arginine								
Nd(III) : L	0.4467 (0.3540)	2.0283 (2.2272)	2.6428 (2.4653)	4.2107 (4.2236)	0.8900 (0.7198)	2.4108	0.3196	4.2650
Nd(III) : L : Ca(II)	0.4457 (0.3469)	2.0716 (2.2909)	2.7518 (2.5561)	4.1221 (4.1370)	0.8979 (0.7018)	2.3792	0.2532	4.4324
Nd(III) : L: Zn(II)	0.4333 (0.3574)	2.0926 (2.2757)	2.6870 (2.5233)	4.1982 (4.2119)	0.9017 (0.7212)	2.4054	0.3079	4.3698
3. Solvent - acetonitrile								
L = L-Leucine								
Nd(III)	0.5130 (0.3488)	1.9551 (2.1642)	2.5712 (2.3868)	3.8202 (3.8210)	0.6877 (0.6776)	2.1439	0.3322	4.1299
Nd(III): L	0.4572 (0.3156)	1.9723 (2.2539)	2.5776 (2.4164)	3.8564 (3.8573)	0.6579 (0.6440)	2.2289	0.1916	4.1952
Nd(III) : L :Ca(II)	0.4171 (0.3249)	2.0901 (2.2584)	2.6892 (2.5395)	3.9166 (3.9249)	0.7668 (0.6575)	2.2714	0.1752	4.4118
Nd(III): L : Zn(II)	0.3850 (0.2985)	2.0116 (2.1769)	2.6133 (2.4662)	3.6272 (3.6361)	0.7212 (0.6036)	2.1226	0.1044	4.2912

L = L(-)-Hydroxyproline								
Nd(III): L	0.4550 (0.3644)	2.0642 (2.2191)	2.5777 (2.4400)	3.9616 (3.9682)	0.7932 (0.7071)	2.2180	0.3701	4.2183
Nd(III): L : Ca(II)	0.4021 (0.3406)	2.0948 (2.2461)	2.6402 (2.5049)	3.8286 (3.8402)	0.8198 (0.6676)	2.1854	0.2505	4.3435
Nd(III): L : Zn(II)	0.3924 (0.3474)	2.0970 (2.2505)	2.6398 (2.5021)	3.8144 (3.8295)	0.8726 (0.6742)	2.1662	0.2782	4.3360
L = L(+)-Arginine								
Nd(III) : L	0.4741 (0.3671)	1.9753 (2.1574)	2.5174 (2.3558)	4.1414 (4.1489)	0.8284 (0.7287)	2.3206	0.4155	4.0671
Nd(III) : L : Ca(II)	0.4334 (0.3732)	2.1537 (2.3120)	2.6914 (2.5498)	4.2361 (4.2490)	0.9096 (0.7399)	2.3983	0.3566	4.4116
Nd(III) : L: Zn(II)	0.4308 (0.3560)	2.0652 (2.2053)	2.5568 (2.4322)	4.0238 (4.0311)	0.7996 (0.7038)	2.2736	0.3403	4.2082
4. Solvent – DMF								
L = L-Leucine								
Nd(III)	0.3085 (0.1323)	1.7538 (1.9725)	2.6013 (2.4082)	3.8336 (3.8336)	0.4432 (0.4428)	2.5394	-0.5128	4.2495
Nd(III): L	0.3676 (0.2198)	1.8934 (2.0626)	2.5664 (2.4175)	4.1253 (4.1231)	0.5362 (0.5651)	2.5758	-0.1791	4.2334
Nd(III) : L :Ca(II)	0.4656 (0.3502)	2.1151 (2.2681)	2.6740 (2.5191)	4.5796 (4.5813)	0.7682 (0.7470)	2.6593	0.2727	4.3992
Nd(III): L : Zn(II)	0.4422 (0.3402)	2.0764 (2.2208)	2.6170 (2.4885)	4.4163 (4.4192)	0.7600 (0.7223)	2.5659	0.2555	4.3145
L = L(-)-Hydroxyproline								
Nd(III): L	0.3942 (0.2476)	2.0447 (2.2379)	2.7829 (2.6122)	4.4280 (4.2970)	0.6422 (0.6194)	2.7488	-0.1542	4.5695
Nd(III): L : Ca(II)	0.4859 (0.4083)	2.2309 (2.3776)	2.7412 (2.6098)	4.8120 (4.8198)	0.9350 (0.8310)	2.7205	0.4667	4.5041
Nd(III): L : Zn(II)	0.4588 (0.3622)	2.0433 (2.2304)	2.6418 (2.4742)	4.5389 (4.3864)	0.8973 (0.7589)	2.6097	0.3465	4.2796
L = L(+)-Arginine								
Nd(III) : L	0.3440 (0.9256)	3.7887 (4.9174)	5.4116 (5.2626)	8.5340 (1.0451)	1.2694 (0.7407)	5.7779	1.3371	9.0461
Nd(III) : L : Ca(II)	0.3082 (0.4062)	4.1163 (4.3516)	5.4121 (5.1949)	9.7310 (9.7862)	1.9570 (1.2289)	6.2497	-0.6412	9.1303
Nd(III) : L: Zn(II)	0.3016 (0.3398)	3.9223 (4.1317)	5.1799 (4.9881)	9.1916 (9.2317)	1.6342 (0.7851)	5.9821	-0.8098	8.7884
5. Solvent - Dioxane								
L = L-Leucine								
Nd(III)	0.4089 (0.2629)	1.8472 (2.0904)	2.6154 (2.3994)	3.6830 (3.6925)	0.6971 (0.5716)	2.2146	-0.0047	4.1835
Nd(III): L	0.4307 (0.3338)	2.0142 (2.2197)	2.6633 (2.4636)	3.9632 (3.9764)	0.8463 (0.6734)	2.2836	0.2348	4.3006
Nd(III) : L :Ca(II)	0.3887 (0.3266)	2.0037 (2.1851)	2.6059 (2.4433)	3.7954 (3.8118)	0.8629 (0.6511)	2.1856	0.2224	4.2391
Nd(III): L : Zn(II)	0.3832 (0.3569)	1.9814 (2.2748)	2.6275 (2.5225)	3.7715 (3.7845)	0.8504 (0.6796)	2.1251	0.3057	4.3694
L = L(-)-Hydroxyproline								
Nd(III): L	0.4386 (0.2984)	1.9931 (2.1989)	2.6796 (2.4973)	3.7787 (3.8036)	0.6823 (0.6182)	2.2358	0.0908	4.3452
Nd(III): L : Ca(II)	0.3863 (0.2949)	1.9431 (2.0824)	2.4730 (2.3495)	3.6756 (3.6795)	0.6588 (0.6065)	2.1434	0.1403	4.0829
Nd(III): L : Zn(II)	0.4313 (0.3522)	1.9976 (2.1615)	2.5271 (2.3809)	3.8720 (3.8821)	0.8207 (0.6871)	2.1776	0.3483	4.1177
L = L(+)-Arginine								
Nd(III) : L	0.3912 (0.2913)	1.9309 (2.1458)	2.6280 (2.4362)	3.9960 (4.0100)	0.8154 (0.6310)	2.3727	0.0893	4.2396
Nd(III) : L : Ca(II)	0.4370 (0.3424)	1.9540 (2.1663)	2.5889 (2.3993)	4.1415 (4.1561)	0.8941 (0.7016)	2.3754	0.3024	4.1544
Nd(III) : L: Zn(II)	0.3914 (0.3143)	1.9024 (2.0977)	2.5193 (2.3447)	3.9062 (3.9715)	0.8579 (0.6556)	2.3021	0.2174	4.0676

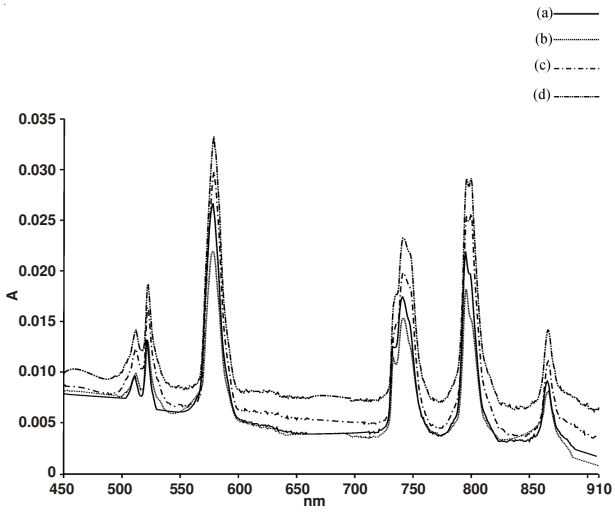


Fig. 3. Comparative absorption spectra of (a) Nd(III); (b) Nd(III): L(-)-hydroxyproline; (c) Nd(III): L(-)-hydroxyproline: Ca(II); (d) Nd(III): L(-)-hydroxyproline: Zn(II) in DMF

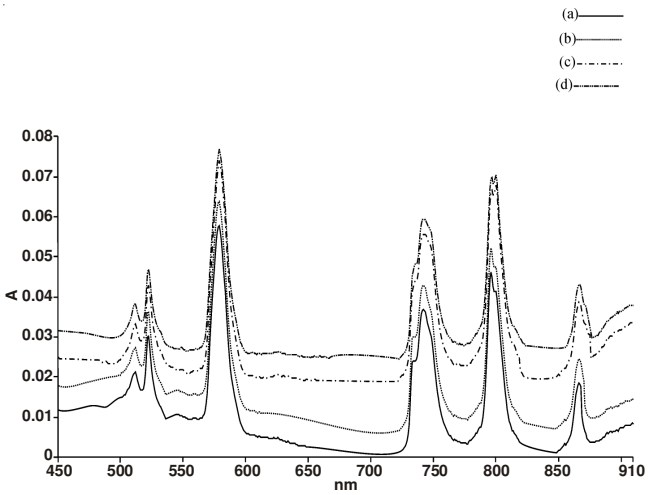


Fig. 4. Comparative absorption spectra of (a) Nd(III); (b) Nd(III); L(+)-arginine; (c) Nd(III): L(+)-arginine: Ca(II); (d) Nd(III): L(+)-arginine: Zn(II) in DMF

this leads to variation in the magnitudes of Judd-Ofelt ((T_λ) parameters. The oscillator strength values of hypersensitive and pseudohypersensitive transitions are found to be highest in acetonitrile (CH_3CN) and dimethylformamide (DMF). Different band shapes for the hypersensitive and Pseudo-hypersensitive transitions have been observed in different solvents *i.e.*, methanol (CH_3OH), acetonitrile (CH_3CN), dimethylformamide (DMF) and dioxane ($C_4H_8O_2$) medium relative to the complex Nd(III): L-leucine. The intensification of the 4*f*-4*f* bands is maximum in DMF medium for all the ligands. This is because when DMF coordinates to hard acids like lanthanide ions, it generally binds through oxygen and not nitrogen. This shows that oxygen has a stronger binding capacity than nitrogen. Acetonitrile (CH_3CN) binds through nitrogen whereas methanol is a very weak donor which in some cases does coordinate and otherwise not.

Karraker[21,22] compared the spectra of several Nd(III) complexes of different coordination numbers with the spectra of complexes having known structures. He pointed out that the shape, energy and oscillator strength of the hypersensitive transition can be correlated with the coordination number of neodymium in the complex species. Misra[23] has observed that intensification of the hypersensitive band is generally accompanied by a lowering in coordination of lanthanide and a greater involvement of metal 4*f*-orbitals in their bonding in the ligating atom. The intensification of 4*f*-4*f* band specially hypersensitive and peudohypersensitive transitions are reflected in the magnitude of T_λ ($\lambda = 2, 4, 6$) parameters. Intensification of the bands is due to the introduction of covalency in the metal-ligand bond as the oscillator strength of intra 4*f*-4*f* transitions and magnitude of T_λ increase with the increase in the nephelauxetic effect.

When Nd(III) is added to different ligands *i.e.*, L-leucine, L(-)-hydroxyproline and L(+)-arginine in DMF medium, it has been found that the sensitivity of the binding of different ligands to Nd(III) are in the order L(+)-arginine > L(-)-hydroxyproline > L-leucine.This sensitivity of the binding of different ligands to Nd(III) is shown in Fig. 5.

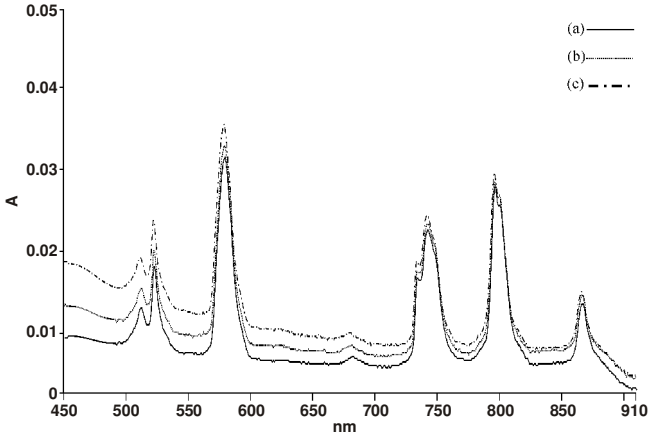


Fig. 5. Comparative absorption spectra of (a) Nd(III): L-leucine; (b) Nd(III): L(-)-hydroxyproline; (c) Nd(III): L(+)-arginine in DMF

Conclusion

From the above investigation it has been observed that the 4*f*-4*f* transition of Nd(III) can be used to investigate the nature of binding of some biologically important amino acid ligands. There is expansion of the central metal ion orbital when amino acids are added to Nd(III) and also on further addition of Ca(II) and Zn(II). This information is supported by the decrease in the values of inter-electronic repulsion parameter, Slater-Condon parameter (F_K) and spin-orbit coupling constant (ξ_{4f}) and increase in the value of nephelauxetic ratio (β). There is lowering of coordination number and shortening of metal-ligand distance when the Ln(III) is coordinated with amino acid ligands in the absence and presence of Ca(II)/Zn(II). Same changes is also observed in intensity parameters-oscillator strength (P) and Judd-Ofelt parameter, T_λ ($\lambda = 2, 4, 6$). From the study of interaction of Nd(III) with some biologically important amino acid ligands, it is observed that the variation of solvent has significant effect on the oscillator strength (P) and Judd-Ofelt parameter, T_λ ($\lambda = 2, 4, 6$). Among the solvents used, dimethylformamide (DMF) is the most favored solvent as maximum intensification is observed in this particular solvent. It is also observed that the sensitivity of the binding of some biologically important amino acid ligands to

Nd(III) is in the order L(+)-arginine > L(-)-hydroxyproline > L-leucine.

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