Calculation of Energy Interaction Parameters for the Complexation of Pr(III) and Nd(III) with 1,10-Phenanthroline and 2,2'-Bipyridyl by *4f*-*4f* Absorption Spectral Analysis

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Absorption difference and comparative absorption spectroscopic studies involving $4f$-$4f$ transitions on Pr(III) and Nd(III) with structurally related 1,10-phenanthroline and 2,2'-bipyridyl complexes in DMF, CH_3CN, dioxane, CH_3OH and their equimolar mixtures have been carried out. Variations in the spectral energy parameters like Slator Condon (F_K), Lande spin orbit coupling (ξ_{4f}), nephelauxetic ratio (β) and bonding parameter ($b^{1/2}$) and per cent covalency (δ) are calculated and correlated with the interaction of Pr(III) and Nd(III) with 1,10-phenanthroline and 2,2'-bipyridyl. The marginal decrease in the values of F_K and $\xi 4_f$ are correlated with the increase in the value of β. The difference in the energy parameters with respect to donor atoms and solvents reveal that the chemical environment around the lanthanide ion has great impact on f-f transition and any change in the environment results in modifications of the spectra.

Key Words: Hypersensitive, Pseudohypersensitive, 1,10-phenanthroline, 2,2'-Bipyridyl, Absorption spectra, Nephelauxetic effect.

INTRODUCTION

The dimensions of lanthanide coordination chemistry in solutions becomes a new age with the increasing use of lanthanides as probes in the exploration of the structural functions of biomolecular reactions[1]. The trivalent lanthanides constitutes a series of hard Lewis acids with similar chemical behaviours and their complexes with anionic ligands containing oxygen as donor atoms have been widely studied[2]. The hard metal acceptors like lanthanide(III) prefer oxygen and nitrogen donor ligands for stable complexes with predominantly ionic character although the affinity for oxygen donar ligand is more. Shah[3] studied comparative $4f$-$4f$ transition spectra of Pr(III) with lysozyme by using energy interaction parameters to

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explain the behaviour of binding between them. Studies on Ln(III) complexes derived from nitrogen donor ligands have shown that the Ln-N interaction is stronger than that previously believed[4]. It has been found that the number of coordinated ligands to the lanthanides depends upon the ability of the anion to compete for the coordination sites and there relative size of the ligands. In present work, the quantitative spectral energy interaction of Pr(III) and Nd(III) with 1,10-phenanthroline (phen) and 2,2'-bipyridyl (bpy) involving $4f$-$4f$ transitions has been carried out in different non-aqueous solvents. We report the sensitivity of the hypersensitive transitions $^4I_{9/2} \to {}^4G_{5/2}$ and ligand mediated pseudo-hypersensitive transitions $^4I_{9/2} \to {}^4F_{3/2}$, $^4I_{9/2} \to {}^4F_{5/2}$, $^4I_{9/2} \to {}^4F_{7/2}$, $^4I_{9/2} \to {}^4G_{7/2}$ of Nd(III) and $^3H_4 \to {}^3P_2$, $^3H_4 \to {}^3P_1$, $^3H_4 \to {}^3P_0$ and $^3H_4 \to {}^1D_2$ of Pr(III) and uses the magnitude and variation of the energy parameters like Slator Condon (F_K), Racah (E^K)and Lande spin orbit coupling ($\xi4_f$), nephelauxetic ratio (β) and bonding parameter ($b^{1/2}$) and per cent covalency (δ) are calculated to discuss the nature of complexation.

EXPERIMENTAL

1,10-Phenanthroline and 2,2′-bipyridyl of analytical grade from qualigens and praseodymium(III) nitrate hexahydrate and neodymium(III) nitrate hexahydrate of 99.9 % purity from M/s Indian Rare Earths Ltd. are used for synthesis and spectral analysis. The solvents used are CH_3OH, CH_3CN, DMF and dioxane which are of AR grade from E. Merk. All the spectra are recorded on a temperature controlled Perkin Elmer Lambda-35 UV-Visible spectrophotometer in the range 350-910 nm in the concentration of 0.01 M at 298 K. The temperature of all the observations is maintained by using water circulating HAAKE DC 10 thermostat. The complexes were synthesized by using the method available in literature[5]. The nephelauxetic effect[6-8], a measure of covalency 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[9-12].

$$\beta = \frac{F_\kappa^C}{F_\kappa^f} \text{ or } \frac{E_c^K}{E_f^K} \tag{1}$$

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 ($b^{1/2}$) is inter-related to nephelauxetic effect as,

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

The electrostatic term E_0 is expressed in terms of the product of slater radial integral known as Slater-Condon parameter, F_K and is given by

$$E_0 = \sum_{k=0}^{k=6} K^k F_k \tag{3}$$

The Slater-Condon parameters are also known as direct-integral and is decreasing function of K as given by the relation,

$$F_l^K = \int_0^\infty \int_0^\infty \frac{r_<^K}{r_>^{K+1}} R_i^2(r_i) R_j^2(r_j) r_i^2 r_j^2 dr_i dr_j \tag{4}$$

where R is the 4f-radial wave function; $r_<$ and $r_>$ are the radii of near and more distant electrons; i and j are the ith and jth electrons under consideration. Condon and Shortley[12] redefined F_K integrals in terms of reduced integral F_K related to each other and the relation is

$$F_K = \frac{F^K}{D_K} \tag{5}$$

Combining relation (4) and (5), the reduced Slater-Condon integral can be written as:

$$F_K = \frac{1}{D_K} \int_0^\infty \int_0^\infty r_<^k r_>^{k+1} R_i^2(r_i) R_j^2(r_j) T_i^2 r_j^2 dr_i dr_j \tag{6}$$

here, D_K is the denominator and F_K are coefficient of linear combination and represent the angular part of the interaction F_K is the expectation value of scalar product $(C_1^{(K)} C_2^{(K)})$.

The Racah energy interaction parameter E^{Ki}'s are linear combinations of F_K given by

$$E^1 = (70 \times F_2 + 231F_4 + 20.02F_6)/9$$
$$E^2 = (F_2 - 3F_4 + 7F_6)/9$$
$$E^3 = (5F_2 + 6F_4 - 9F_6)/3 \tag{7}$$

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

$$E_{so} = A_{so} \, \xi_{4f} \tag{8}$$

where, A_{so} is the angular part of spin orbit interaction and ξ_{4f} is the radial integral and is known Lande's parameter by first order approximation the energy E_j of the jth level is given by Wong[13,14] as

$$E_j(F_K, \xi_{4f}) = E_{oj}(F_K{}^0, \xi_{4f}) + \frac{\partial E_j}{\partial F_K} \Delta F_K + \frac{\partial E_j}{\partial \xi_{4f}} \Delta \xi_{4f} \tag{9}$$

where E_{oj} is the zero order energy of the jth level. The value of F_K and ξ_{4f} are given by

$$F_K = F_K^0 + \Delta F_K$$
$$\xi_{4f} = \xi_{4f}^0 + \Delta \xi_{4f} \tag{10}$$

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

$$\Delta E_j = \sum_{K=2,4,6} \frac{\partial E_j}{\partial F_K} \Delta F_K + \frac{\partial E_j}{\partial \xi_{4f}} \Delta \xi_{4f} \tag{11}$$

By using the zero order energy and partial derivatives of Pr(III) ion given by Wong[13,14] 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 value of F_2 and ξ_{4f} are found out by using relation (10). The estimated values of F_4 and F_6 are calculated by the relations,

$$\frac{F_4}{F_2} = 0.1380 \quad \text{and} \quad \frac{F_4}{F_2} = 0.0150 \tag{12}$$

The per cent covalency parameter (δ) representing the nephelauxetic effect was given by the relation

$$\delta = \left(\frac{1-\beta}{\beta} \right) \times 100 \tag{13}$$

RESULTS AND DISCUSSION

The $^3H_4 \rightarrow {}^3P_2$, $^3H_4 \rightarrow {}^3P_1$, $^3H_4 \rightarrow {}^3P_0$ and $^3H_4 \rightarrow {}^1D_2$, transitions of Pr(III) and $^4I_{9/2} \rightarrow {}^4F_{3/2}$, $^4I_{9/2} \rightarrow {}^4F_{5/2}$, $^4I_{9/2} \rightarrow {}^4F_{7/2}$, $^4I_{9/2} \rightarrow {}^4G_{7/2}$ transitions of Nd(III) do not obey selection rules but have been found to show substantial sensitivity reflected through wide variation energies and oscillator strengths with even minor changes in the immediate coordination environment around it and even in the presence of structurally related ligand and they are called ligand mediated pseudo-hypersensitive transitions. For Nd(III) the transitions $^4I_{9/2} \rightarrow {}^4G_{5/2}$ obeys the selection rule and show substantial changes even in the minor changes in the coordination environment. Such transition is called hypersensitive transition[15,16]. Karraker[17], showed that the shape, energy and oscillator strengths of hypersensitive and pseudo-hypersensitive transitions can be correlated with coordination number. The comparative absorption spectra as in Figs. 1 and 2 of Pr(III), Pr(III): bpy, Pr(III): phen and Nd(III), Nd(III): bpy, Nd(III): phen (in 1:1 molar ratio) in DMF medium with Tables 1 and 2 shows: (i) the relative affinities of different solvents towards Ln(III) coordination and (ii) relative binding capacity of the two ligands. From these it is observed that red shift occurs as phen/bpy is added to Pr(III)/Nd(III). Tables 1(a) and (b) show the variation of the magnitude of energy interaction parameters like Slator-Condon, F_K (K = 2,4,6), Lande factor (ξ_{4f}), nephelauxetic ratio (β), bonding ($b^{1/2}$) and per cent covalency (δ) of Pr(III); Pr(III): bpy; Pr(III): phen and Nd(III); Nd (III): bpy; Nd(III): phen in different organic solvents. Tables 2(a) and (b)

TABLE -1(a)

COMPUTED VALUES OF ENERGY INTERACTION SLATOR CONDON (F_K) AND LANDE SPIN ORBIT COUPLING ($\Xi 4_F$), NEPHELAUXETIC RATIO (β) AND BONDING PARAMETER ($b^{1/2}$) AND COVALENCY PARAMETERS (δ) OF Pr(III), Pr(III): Bpy AND Pr(III): Phen IN DMF, CH_3CN, CH_3OH, DIOXANE AND THEIR EQUIMOLAR BINARY MIXTURES

System	F_2	F_4	F_6	ξ_{4f}	β	$b^{1/2}$	δ
Solvent-CH_3OH							
Pr(III)	308.8467	42.6363	4.6636	719.6274	0.9444	0.1668	5.8904
Pr(III) + Bpy	308.8586	42.6379	4.6638	719.8563	0.9445	0.1665	5.8709
Pr(III) + Phen	308.8850	42.5638	4.6557	721.0336	0.9446	0.1665	5.8686
Solvent - CH_3CN							
Pr(III)	308.3532	42.5682	4.6561	723.8837	0.9466	0.1635	5.6453
Pr(III) + Bpy	307.2411	42.4146	4.6393	721.9964	0.9436	0.1679	5.9720
Pr(III) + Phen	306.0091	42.2446	4.6207	722.3418	0.9421	0.1702	6.1482
Solvent - Dioxane							
Pr(III)	308.1013	42.5334	4.6523	722.6680	0.9454	0.1653	5.7794
Pr(III) + Bpy	307.9974	42.5190	4.6508	722.0624	0.9448	0.1661	5.8429
Pr(III) + Phen	306.9069	42.3685	4.6343	720.7680	0.9432	0.1698	6.1216
Solvent - DMF							
Pr(III)	308.1064	42.5341	4.6524	719.3425	0.9431	0.1687	6.0339
Pr(III) + Bpy	308.2119	42.5487	4.6540	718.9176	0.9430	0.1689	6.0493
Pr(III) + Phen	308.0735	42.5296	4.6519	719.2725	0.9430	0.1688	6.0447
Solvent - CH_3OH + CH_3CN							
Pr(III)	308.2608	42.5554	4.6547	720.0623	0.9438	0.1676	5.9532
Pr(III) + Bpy	308.2599	42.5553	4.6547	720.9904	0.9444	0.1667	5.8821
Pr(III) + Phen	307.0358	42.5863	4.6362	721.2242	0.9428	0.1691	6.0652
Solvent - CH_3OH + Dioxane							
Pr(III)	308.0788	42.5303	4.650	721.4075	0.9445	0.1666	5.8798
Pr(III) + Bpy	308.2658	42.5561	4.6548	721.3876	0.947	0.1662	5.8506
Pr(III) + Phen	307.2837	42.4205	4.6400	721.3444	0.9433	0.1684	6.0152
Solvent - CH_3OH + DMF							
Pr(III)	308.3668	42.5700	4.6563	719.6374	0.9437	0.1678	5.9684
Pr(III) + Bpy	308.3394	42.5663	4.6559	719.3452	0.9434	0.1682	5.9954
Pr(III) + Phen	308.2668	42.5562	4.6548	719.0844	0.9432	0.1686	6.0274
Solvent - DMF + CH_3CN							
Pr(III)	308.1657	42.5423	4.6533	719.5563	0.9433	0.1683	6.0077
Pr(III) + Bpy	308.1514	42.5403	4.6531	719.3057	0.9431	0.1686	6.0294
Pr(III) + Phen	307.8109	42.4933	4.6479	720.0342	0.9431	0.1686	6.0293
Solvent - DMF + Dioxane							
Pr(III)	308.2380	42.5523	4.6544	720.0548	0.9438	0.1677	5.9575
Pr(III) + Bpy	308.2832	42.5585	4.6551	720.6835	0.9443	0.1669	5.9018
Pr(III) + Phen	307.9737	42.5158	4.6504	721.0008	0.9440	0.1673	5.9282
Solvent Dioxane + CH_3CN							
Pr(III)	308.1142	42.5352	4.6525	723.3610	0.9459	0.1645	5.7243
Pr(III) + Bpy	305.8562	42.2235	4.6184	719.5063	0.9399	0.1733	6.3926
Pr(III) + Phen	305.8562	42.2235	4.6184	719.5063	0.9399	0.1733	6.3926

TABLE-1(b)

COMPUTED VALUES OF ENERGY INTERACTION SLATOR CONDON (F_K) AND LANDE SPIN ORBIT COUPLING (Ξ_F), NEPHELAUXETIC RATIO (β) AND BONDING PARAMETER ($b^{\frac{1}{2}}$) AND COVALENCY PARAMETERS (δ) OF Nd(III), Nd(III): Bpy AND Nd(III): Phen IN DMF, CH_3CN, CH_3OH, DIOXANE AND THEIR EQUIMOLAR BINARY MIXTURES

System	F_2	F_4	F_6	ξ_{4f}	β	$b^{\frac{1}{2}}$	δ
Solvent – CH_3OH							
Nd(III)	330.4711	48.8324	5.2180	928.0190	1.0124	0.0787	1.2234
Nd(III) + Bpy	331.5382	48.6693	4.1445	908.9684	0.9995	0.0161	0.0516
Nd(III) + Phen	330.1656	48.7617	5.2376	935.3941	1.0167	0.0914	1.9419
Solvent - CH_3CN							
Nd(III)	330.9891	47.9501	5.2177	939.9116	1.0162	0.0900	1.5943
Nd(III) + Bpy	330.2140	47.8949	5.2793	939.9965	1.0278	0.1179	2.7041
Nd(III) + Phen	330.9197	46.3489	5.3591	940.6230	1.0413	0.7878	55.3820
Solvent – Dioxane							
Nd(III)	331.0930	48.0224	5.1727	929.6993	1.0094	0.0686	0.9325
Nd(III) + Bpy	330.9727	47.9673	5.1712	931.4548	1.0101	0.0710	0.9986
Nd(III) + Phen	330.8379	47.9308	5.1739	933.7305	1.0112	0.0750	1.1113
Solvent – DMF							
Nd(III)	329.2090	48.9722	5.2851	947.9922	1.0254	0.1127	2.4783
Nd(III) + Bpy	329.1920	48.9673	5.2881	948.7397	1.0259	0.1138	2.5241
Nd(III) + Phen	329.1244	48.9664	5.2918	949.9862	1.0267	0.1155	2.5974
Solvent – CH_3OH + CH_3CN							
Nd(III)	330.7031	48.0553	5.1873	934.9344	1.0127	0.0797	1.2530
Nd(III) + Bpy	330.7454	48.0047	5.1887	935.7481	1.0130	0.0807	1.2863
Nd(III) + Phen	330.3134	48.1984	5.2464	946.1504	1.0211	0.1026	2.0638
Solvent – CH_3OH + Dioxane							
Nd(III)	331.0597	48.0292	5.1715	929.6246	1.0093	0.0683	0.9254
Nd(III) + Bpy	331.0733	48.0068	5.1663	929.0040	1.0088	0.0662	0.8684
Nd(III) + Phen	330.8028	48.0918	5.2252	940.2236	1.0170	0.0922	1.6721
Solvent - CH_3OH + DMF							
Nd(III)	329.5118	49.0732	5.2795	942.6172	1.0228	0.1067	2.2253
Nd(III) + Bpy	329.4840	19.0735	4.2807	943.0545	1.0230	0.1073	2.2508
Nd(III) + Phen	329.3759	49.0200	5.2783	944.5208	1.0235	0.1085	2.2982
Solvent - DMF + CH_3CN							
Nd(III)	329.2127	48.9168	5.2848	948.9169	1.0257	0.1134	2.5080
Nd(III) + Bpy	329.0178	48.9802	5.2941	951.0658	1.0273	0.1169	2.6603
Nd(III) + Phen	329.0346	48.8567	5.2932	953.0192	1.0280	0.1183	2.7205
Solvent - DMF + Dioxane							
Nd(III)	329.9816	48.3809	5.2601	947.9740	1.0230	0.1072	2.2458
Nd(III) + Bpy	329.9756	48.3781	5.2591	947.9124	1.0229	0.1070	2.2384
Nd(III) + Phen	329.9507	48.3708	5.2588	948.2127	1.0230	0.1073	2.2499
Solvent - Dioxane + CH_3CN							
Nd(III)	330.8596	47.8945	5.1922	937.4835	1.0138	0.0830	1.3597
Nd(III) + Bpy	330.4857	47.8910	5.2226	946.1149	1.0193	0.0983	1.8964
Nd(III) + Phen	328.8047	46.8589	5.2491	983.7479	1.0366	0.1353	3.5310

TABLE-2(a)

COMPUTED AND OBSERVED VALUES OF ENERGIES (cm⁻¹) AND RMS VALUES IN DMF, CH₃CN, CH₃OH, DIOXANE AND THEIR EQUIMOLAR BINARY MIXTURES FOR Pr(III), Pr(III): Bpy AND Pr(III): Phen

System	$^3H_4 \rightarrow {}^3P_2$		$^3H_4 \rightarrow {}^3P_1$		$^3H_4 \rightarrow {}^3P_0$		$^3H_4 \rightarrow {}^1D_2$		R.M.S.
	E_{obs}	E_{cal}	E_{obs}	E_{cal}	E_{obs}	E_{cal}	E_{obs}	E_{cal}	
Solvent – CH₃OH									
Pr(III)	22490.10	22425.21	21311.51	21216.33	20737.42	20661.21	16893.89	17117.24	131.30
Pr(III) + Bpy	22490.61	22427.16	21313.33	21218.07	20736.99	20662.48	16898.46	17118.45	129.47
Pr(III) + Phen	22464.34	22396.81	21283.84	21185.13	20693.22	20627.05	16885.05	17097.19	126.18
Solvent - CH₃CN									
Pr(III)	22519.99	22413.27	21311.96	21198.67	20681.67	20634.69	16890.75	17106.92	135.24
Pr(III) + Bpy	22439.13	22328.65	21240.89	21113.24	20613.03	20553.06	16801.64	17050.31	136.25
Pr(III) + Phen	22357.36	22247.14	21129.14	21028.28	20525.87	20467.26	16767.83	16994.68	138.94
Solvent – Dioxane									
Pr(III)	22508.33	22390.14	21316.51	21176.19	20669.70	20614.70	16837.00	17091.81	137.38
Pr(III) + Bpy	22510.36	22380.07	21312.42	21166.50	20665.85	20606.26	16812.38	17085.27	135.51
Pr(III) + Phen	22427.05	22299.89	21228.27	21084.94	20596.05	20527.27	16748.17	17031.38	136.89
Solvent – DMF									
Pr(III)	22432.09	22373.76	21255.34	21163.32	20686.80	20608.72	16862.27	17082.38	128.85
Pr(III) + Bpy	22435.61	22378.75	21264.38	21169.03	20696.22	20615.32	16859.99	17085.99	130.75
Pr(III) + Phen	22429.07	22370.97	21256.24	21160.54	20684.66	20606.12	16748.17	17031.38	130.96
Solvent – CH₃OH+ CH₃CN									
Pr(III)	22470.90	22387.81	21290.19	21177.01	20694.08	20620.93	16849.20	17091.57	137.75
Pr(III) + Bpy	22473.43	22392.42	21297.44	21180.63	20688.94	20622.63	16860.85	17094.22	135..60
Pr(III) + Phen	22416.50	22310.89	21244.50	21095.79	20601.57	20537.18	16770.64	17038.63	136.25

System	$^3H_4 \rightarrow {}^3P_2$		$^3H_4 \rightarrow {}^3P_1$		$^3H_4 \rightarrow {}^3P_0$		$^3H_4 \rightarrow {}^1D_2$		R.M.S.
	E_{obs}	E_{cal}	E_{obs}	E_{cal}	E_{obs}	E_{cal}	E_{obs}	E_{cal}	
Solvent – CH$_3$CN + Dioxane									
Pr(III)	22489.60	22382.28	21305.61	21169.60	20674.40	20610.72	16828.50	17087.11	138.86
Pr(III) + Bpy	22492.13	22394.81	21296.99	21182.62	20688.09	20623.80	16857.72	17095.65	132.30
Pr(III) + Phen	22454.25	22328.24	21257.60	21113.63	20619.41	20554.80	16773.74	17050.38	131.25
Solvent - CH$_3$OH+ DMF									
Pr(III)	22451.22	22392.83	21275.69	21182.74	20703.50	20627.55	16877.64	17095.21	127.63
Pr(III) + Bpy	22450.22	22389.51	21275.69	21179.66	20703.08	20625.08	16868.81	17093.10	131.62
Pr(III) + Phen	22440.14	22383.29	21268345	21173.54	20699.22	20619.48	16865.11	17089.00	131.08
Solvent DMF + CH$_3$CN									
Pr(III)	22434.60	22378.84	21258.96	21168.33	20689.80	20613.29	16870.52	17085.72	125.99
Pr(III) + Bpy	22435.11	22376.61	21256.70	21166.33	20690.23	20611.81	16864.83	17084.34	128.38
Pr(III) + Phen	22420.52	22357.27	21243.15	21145.37	20662.44	20589.30	16851.19	17070.80	129.56
Solvent DMF + Dioxane									
Pr(III)	22454.75	22386.23	21277.05	21175.38	20692.37	20619.31	16865.11	17090.50	133.39
Pr(III) + Bpy	22458.29	22392.45	21277.50	21181.05	20692.37	20623.69	16881.06	17064.40	132.07
Pr(III) + Phen	22444.67	22373.13	21266.64	21160.62	20668.84	20602.57	16861.13	17081.10	131.47
Solvent - Dioxane + CH$_3$CN									
Pr(III)	22520.49	22394.49	21293.81	21179.84	20668.42	20616.92	16859.71	17094.41	135.14
Pr(III) + Bpy	22360.53	22278.50	21148.68	21075.32	20575.13	20483.72	16673.92	16993.63	133.08
Pr(III) + Phen	22354.36	22222.56	21125.57	21006.31	20530.09	20451.14	16695.61	16979.41	132.03

TABLE-2(b)
COMPUTED AND OBSERVED VALUES OF ENERGIES (cm^{-1}) AND RMS VALUES IN DMF, CH$_3$CN, CH$_3$OH, DIOXANE AND THEIR EQUIMOLAR BINARY MIXTURES FOR Nd(III), Nd(III): Bpy AND Nd(III): Phen

System	$^4I_{9/2} \rightarrow {}^4F_{3/2}$		$^4I_{9/2} \rightarrow {}^4F_{5/2}$		$^4I_{9/2} \rightarrow {}^4F_{7/2}$		$^4I_{9/2} \rightarrow {}^4G_{5/2}$		$^4I_{9/2} \rightarrow {}^4G_{7/2}$		R.M.S.
	E_{obs}	E_{cal}	E_{obs}	E_{cal}	E_{obs}	E_{cal}	E_{obs}	E_{cal}	E_{obs}	E_{cal}	
Solvent - CH$_3$OH											
Nd(III)	19127.77	19181.25	17252.98	17263.96	13460.40	13448.54	12561.08	12586.14	11535.36	11469.99	40.06
Nd(III) + Bpy	19156.72	19176.40	17335.23	17360.65	13499.65	13461.79	12578.77	12614.26	11555.62	11525.06	30.53
Nd(III) + Phen	19112.05	19179.57	17214.67	7232.84	13459.13	13447.05	12553.35	12579.36	11534.96	11452.43	50.05
Solvent - CH$_3$CN											
Nd(III)	19102.56	19162.60	17201.93	17252.51	13562.82	13469.20	12537.30	12600.39	11518.08	11465.73	65.80
Nd(III) + Bpy	19075.23	19162.41	17129.45	17169.13	13539.68	13462.43	12534.94	12579.83	11485.01	11418.74	65.65
Nd(III) + Phen	19075.96	19703.90	1707.09	9773.49	13523.75	13363.17	12531.64	11070.44	11478.95	7413.50	65.83
Solvent - Dioxane											
Nd(III)	19102.20	19160.08	17251.49	17294.22	13553.81	13469.84	1254595	12608.94	11543.47	11488.35	62.02
Nd(III) + Bpy	19093.08	19157.58	17251.78	17287.84	13553.44	13469.93	12545.63	12608.01	11540.81	11484.57	62.43
Nd(III) + Phen	19085.06	19155.94	17247.03	17278.39	13551.61	13469.46	12544.69	12606.64	11538.02	11479.11	63.35
Solvent - DMF											
Nd(III)	19085.79	19183.35	17186.86	17162.63	13425.88	13434.36	12529.76	12556.71	11514.10	11411.86	65.35
Nd(III) + Bpy	19085.43	19183.41	17185.38	17159.45	13425.88	13434.23	12529.60	12556.01	11510.92	11410.10	65.12
Nd(III) + Phen	19082.88	19183.30	17183.02	17153.57	13424.44	13433.60	12528.34	12554.46	11507.88	11406.75	66.25
Solvent - CH$_3$OH + CH$_3$CN											
Nd(III)	19088.71	19159.59	17242.57	17267.09	13535.28	13465.67	12547.99	12600.87	11531.23	11472.61	57.80
Nd(III) + Bpy	19088.34	19158.75	17239.30	17265.95	13540.96	13466.90	12547.68	12601.61	11528.31	11472.14	58.68
Nd(III) + Phen	19087.25	19167.47	17179.77	17210.64	13534.55	13458.67	12516.11	12584.56	11521.13	11441.19	69.60

System	$^4I_{9/2} \rightarrow {}^4F_{3/2}$		$^4I_{9/2} \rightarrow {}^4F_{5/2}$		$^4I_{9/2} \rightarrow {}^4F_{7/2}$		$^4I_{9/2} \rightarrow {}^4G_{5/2}$		$^4I_{9/2} \rightarrow {}^4G_{7/2}$		R.M.S.
	E_{obs}	E_{cal}	E_{obs}	E_{cal}	E_{obs}	E_{cal}	E_{obs}	E_{cal}	E_{obs}	E_{cal}	
Solvent – CH₃OH + Dioxane											
Nd(III)	19101.10	19159.79	17262.81	17293.87	13552.89	13469.41	12545.48	12608.58	11536.95	11488.05	59.58
Nd(III) + Bpy	19099.28	19158.75	17263.11	17297.57	13553.99	1347009	12546.42	12609.86	11541.75	11490.08	60.76
Nd(III) + Phen	19102.20	19165.80	17200.75	17244.12	13550.14	13464.96	12530.86	12595.50	11521.40	11460.63	64.89
Solvent - CH₃OH + DMF											
Nd(III)	19104.75	19185.63	17190.40	17184.31	13426.78	13435.10	12533.70	12560.97	11526.05	11424.37	59.55
Nd(III) + Bpy	19103.66	19187.56	17190.11	17182.18	13426.24	13434.54	12533.06	12560.38	11524.85	11423.15	60.43
Nd(III) + Phen	19094.90	19185.11	17188.92	17177.11	13426.06	13435.04	12532.74	12559.78	11524.72	11420.11	63.3
Solvent - DMF + CH₃CN											
Nd(III)	19082.88	19181.90	17184.49	17160.88	13430.21	13435.43	12529.60	12557.27	11512.25	11410.95	65.45
Nd(III) + Bpy	19077.78	19183.25	17180.95	17147.67	13428.23	13432.53	12516.43	12552.60	11511.45	11403.27	71.08
Nd(III) + Phen	19072.32	19180.05	17165.91	17144.27	13429.13	13434.95	12527.40	12553.97	11510.92	11401.53	70.4
Solvent -DMF + Dioxane											
Nd(III)	19085.43	19171.14	17167.68	17192.67	13495.09	13452.50	12533.53	12576.21	11518.78	11430.49	62.29
Nd(III) + Bpy	19084.70	19170.92	17167.38	17193.02	13495.09	13452.24	12533.37	12576.32	11519.81	11430.66	62.8
Nd(III) + Phen	19082.88	19170.54	17164.73	17191.85	13494.73	13452.20	12533.06	12576.11	11521.70	11429.96	64.03
Solvent - Dioxane + CH₃CN											
Nd(III)	19087.24	19157.34	17225.34	17264.06	13563.00	13469.90	12534.78	12603.53	11530.96	11471.53	68.32
Nd(III) + Bpy	19074.87	19158.04	17181.24	17224.23	13550.87	13466.28	12531.96	12593.37	11523.39	11449.07	71.01
Nd(III) + Phen	18946.21	19121.57	17070.09	17089.05	13525.58	13471.01	12577.51	12574.39	11473.28	11371.79	94.23
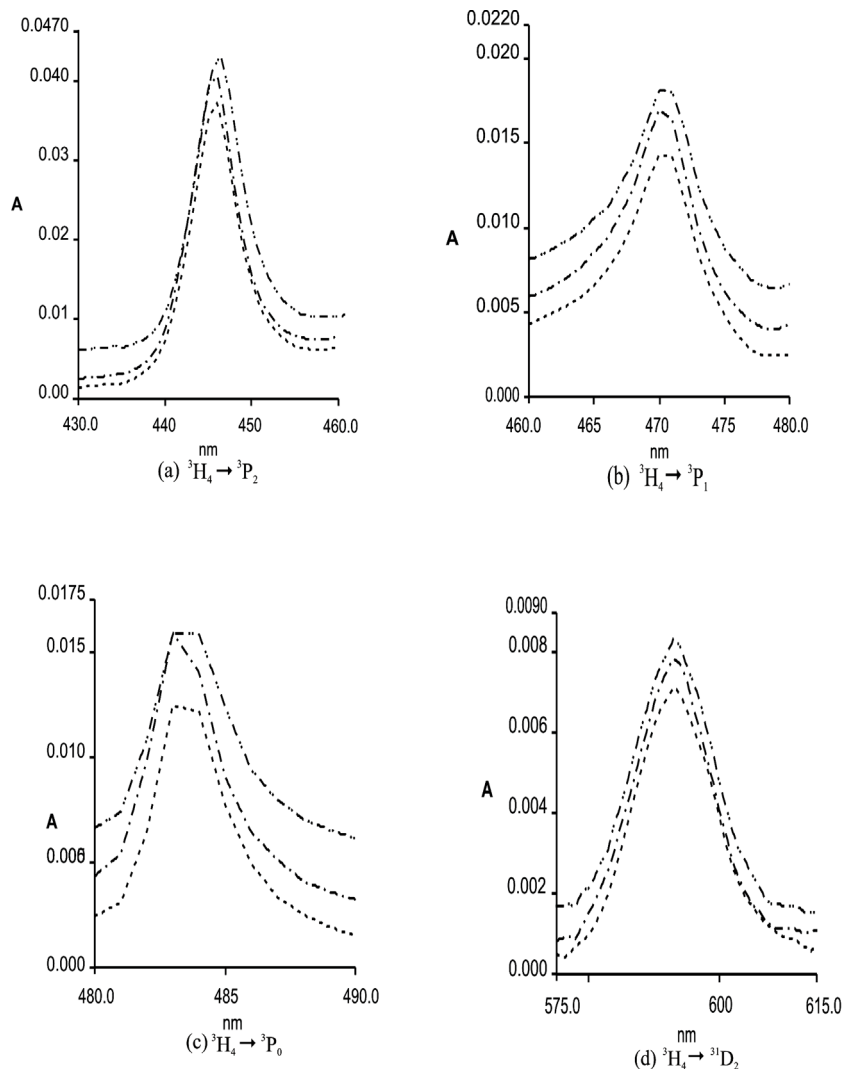
Fig. 1.   Comparative absorption spectra of (a) Pr(III) .... (b) Pr(III):Bpy _._._._.
and (c) Pr(III):Phen _.._.._._ in DMF

gives the computed and observed values of energies for the various transition bands and root mean square (RMS) deviation showing the correctness of the various energy parameters. The marginal decrease in the value of F_K and ξ_{4f} indicating complexation led to the increase in the values of nephelauxetic ratio and percentage covalency.

For spectral studies on the structures of coordination compounds of lanthanides in solution, any evidence of the relationship between the nephelauxetic band shift and the structure is of special interest. Jorgensen and Ryan[18] suggested that shortening in the metal ligand distance occurs
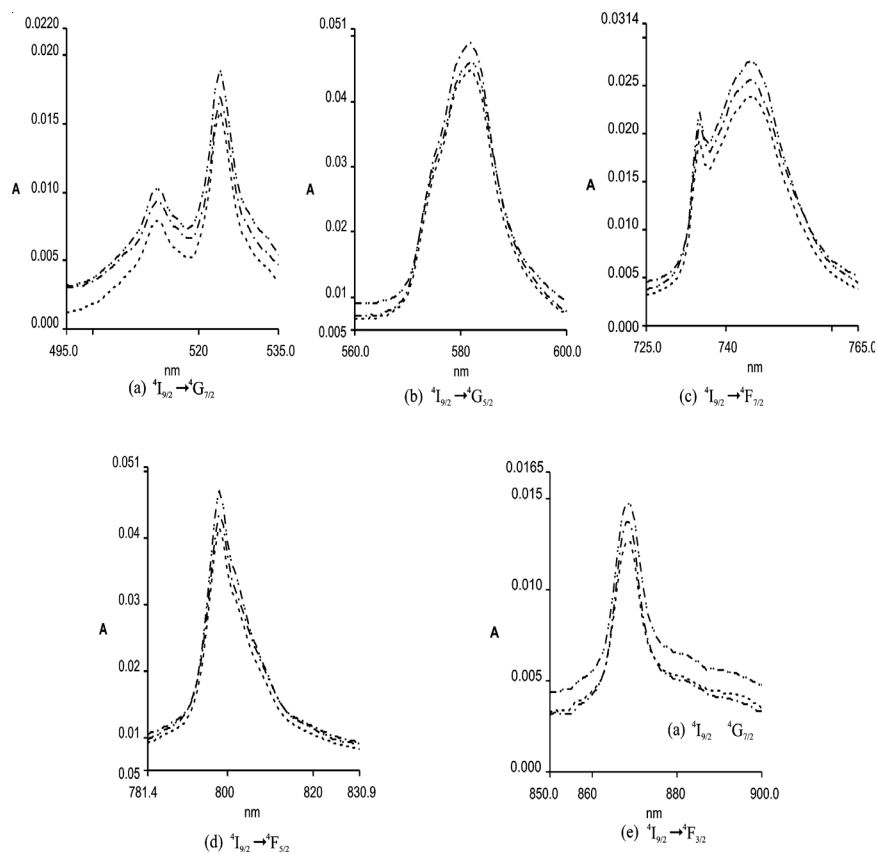
Fig. 1. Comparative absorption spectra of (a) Nd(III) ‒‒‒‒‒‒ (b) Nd(III):Bpy ‒·‒·‒· and (c) Nd(III):Phen ‒··‒··‒ in DMF

with decrease in the coordination number. To interpret the correlation and analysis of the relationship between nephelauxetic effect and geometry, energy parameters have been derived and evaluated as reported earlier[19-22] for complex compound using the angular overlap model. The value of 'n' is proportional to the nephelauxetic effect as

$$n = \left[\frac{(1 - \beta^{½})}{\beta^{½}} \right] \tag{14}$$

It may also be expressed as

$$n = \frac{H_L^2}{\left(H_M - H_L \right)^2} \cdot \left(S^* R \right)^2 N \tag{15}$$

where N is the coordination number, H_M and H_L are coulomb integrals of atomic orbital, S is the overlap integral and R is the radius of the orbit. For

compounds with ligand coordinated through identical donor atoms, the term of eqn. 15 is a constant and eqn. 15 becomes

$$n = \text{constant.} \ (S^*R)^2 \ N \qquad (16)$$

The eqn. 16 represents the nephelauxetic effect as a function of two variable. S*R and N which vary with changes in lanthanides-ligand distance in opposite directions. However any variation in the value of R leads to a larger change in $(S^*R)^2$ compared to that in N. The nephelauxetic effect increases as the coordination number decreases. The Ln–N distance shortens in spite of the addition nature of β and decrease in the number of the coordinating ligand. The variation in the value of E^K (K = 2,4,6); corresponds to that in the value of F^K, since they are inter-related. Misra et al.[23,24] observed a general decrease in the values of F_K, E^K and ξ_{4f} parameters as compared to the corresponding parameters of the free ion. The values of nephelauxetic effect (β) in all the system is less then unity and the values of bonding parameters ($b^{½}$) are positive which indicates covalent bonding. In Fig. 1 and 2 addition of Bpy/Phen in Pr(III)/Nd(III) resulted in a marginal red shift of 4f-4f transition bands. The enhancement is more in case of Phen indicating a better ligand than Bpy when recorded in identical solvent. The weak Ln-N interaction is enhanced by the presence of extra π-electrons as in the case of Phen than in Bpy, increasing the ligand character of the donor N-atom. The redshift is maximum in case when solvent is DMF or one of the solvent is DMF. It has been shown that the non-aqueous solvents with weak basic properties offer a powerful means for the synthesis of Ln(III) complexes with neutral ligands with N (or even S) donor atoms.

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