Variation in Symmetry Around Doped Pr(III) ion in Saturated Solution of Biologically Important Ligands

Samata Jain[*] and Sushma Jain

Department of Chemistry, Government Dungar Post Graduate College, Bikaner-334 001, India

*Corresponding author: E-mail: jainche23@gmail.com

The absorption spectra of doped Pr(III) ion with some biologically important ligands (*viz.* indole acetic acid, indole-3-butyric acid, gibberalic acid, ascorbic acid and pyridoxine) have been studied in aqueous and organic solvents (DMSO, DMF, EtOH, H_2O). The doped model involves small concentration of Pr(III) ion salt (0.0435 g) in saturated solution of ligand in various solvent at 298 K. The electronic spectral parameters *viz.* Judd-Ofelt (T_λ), Racah parameter (E_k), Slater-Condon parameter (F_k), Lande parameter (ζ_{4F}), bonding parameters ($b^{1/2}$), naphelauxetic ratio (β), covalency (%) (δ), rms deviation (σ) and Peacock constant (K) have been evaluated. The study infers the change in symmetry around doped Pr(III) ion and metal-ligand interaction. The greater change in symmetry observed when DMSO is taken as solvent in study. The Peacock proportionality constant (K) has been found to constant in almost all systems under study.

Key Words: Pr(III), Electronic spectra.

INTRODUCTION

Lanthanides complexes have attracted many researchers due to their numerous applications such as laser material, electroluminescent devices, biological indicator, immunoassay sensors and shift reagent for NMR spectroscopy[1-3]. The biological action of lanthanide ion is almost entirely based upon the use of rare earth ion as a substitute or antagonist of Ca^{2+} in variety of cellular and sub cellular reactions[4]. Therefore paramagnetic Pr(III) ion can be utilized as an absorption spectral probe in biological reactions[5]. Recently electronic spectral studies of lanthanides ion complexes with reference to Judd-Ofelt parameters have been found to have due significance[6]. This is because of strong validity of the theory given by Judd-Ofelt have been used to explain mostly covalency and symmetry around lanthanide ion. The complexing ability with respect to thermodynamic stability is poor in case of lanthanide complexes, so recently doped lanthanide in saturated solution of ligand has been undertaken as system in the present electronic spectral study[7].

In the present study, five compounds *viz.*, indole acetic acid (IAA), indole-3-butyric acid (IBA), gibberalic acid (GA), ascorbic acid (AscA) and pyridoxine (Py) have been used as ligands. A constant amount of $Pr(NO_3)_3 \cdot 6H_2O$ has been added to each of the saturated solution of ligand in different solvent media and spectra is measured in 390-650 nm region. Pr(III) ion yields four bands in visible region corresponding to $^3P_2$,

$^3P_1$, $^3P_0$ and $^1D_2$ levels. A red shift is observed in the ligand solution doped with Pr(III) ion compared to free ion. The calculation involves the Judd-Ofelt equation and the other relation described in literature[8,9]. On examining electronic spectral parameters of the systems under study the covalency is inferred to some extent to metal-ligand bonding. The study also provides some useful information regarding validity of Judd-Ofelt equation and relation proposed by Peacock[10] ($P\alpha \bar{\nu} T_6$). The study also provides beneficial information about interelectronic repulsion, spin orbit interaction and symmetry changes around Pr(III) ion.

EXPERIMENTAL

Standard grade chemicals $Pr(NO_3)_3 \cdot 6H_2O$ (99.9 % purity) (procured from Indian Rare Earths) and biologically important compounds indole acetic acid, indole-3-butyric acid, gibberalic acid, ascorbic acid and pyridoxine (SD fine) were used. The solvents used in the present study are distilled water, EtOH, DMF, DMSO. Saturated solutions of ligands were prepared in each solvent and 0.0435 g of $Pr(NO_3)_3 \cdot 6H_2O$ was added to each saturated solution of ligand (10 mL). Spectra of these solutions were recorded by using standard spectrophotometer (SL 164 double beam UV visible) in the 390-650 nm range at 298 K. In this range four peaks corresponding to $^3H_4 \rightarrow {}^3P_2$, $^3H_4 \rightarrow {}^3P_1$, $^3H_4 \rightarrow {}^3P_0$ and $^3H_4 \rightarrow {}^1D_2$ transition have been obtained.

TABLE-1
COMPUTRIZED VALUES OF OSILLATOR STRENGTH, T_λ, *etc.*

Compound		Oscillator strength × 10⁵				$P_{cal.}$ 10⁵	$P_{obs.}$ 10⁵	T_λ × 10⁸				rms σ × 10⁸	$\overline{\nu}$ of ³P₂ band	$P_{obs}/\overline{\nu}$ T_6 × 10²
System	Solvent	³P₂ band	³P₁ band	³P₀ band	²D₁ band			T_2	T_4	T_6	T_4/T_6			
Pr + IAA	H_2O	7.628	3.540	2.020	2.250	7.682	7.682	-0.208	0.771	2.310	0.3346	4.700	22573	14.62
Pr + IAA	EtOH	10.17	5.672	2.759	2.717	9.469	9.469	-6.610	1.160	3.020	0.3856	6.390	22523	14.95
Pr + IAA	DMSO	8.077	7.181	3.400	2.270	8.077	8.077	-2.760	1.470	2.260	0.6487	7.870	22472	15.90
Pr + IAA	DMF	9.680	5.840	2.710	2.440	9.689	9.689	-9.430	1.180	2.900	0.4130	6.290	22472	14.85
Pr + IBA	H_2O	8.380	3.160	2.350	2.449	8.388	8.388	-0.387	0.760	2.550	0.2984	5.440	22523	14.58
Pr + IBA	EtOH	9.375	4.800	2.624	2.720	12.57	12.57	-0.640	1.030	3.000	0.3651	6.070	22422	14.87
Pr + IBA	DMSO	12.57	6.701	3.227	3.674	9.375	9.375	-0.194	1.370	3.750	0.3658	7.470	22523	14.88
Pr + IBA	DMF	9.940	4.800	2.400	2.900	9.947	9.947	-0.297	1.010	2.810	0.3373	5.570	22472	14.74
Pr + GA	H_2O	7.080	3.390	1.560	2.070	7.089	7.089	-0.266	0.684	2.130	0.3204	3.610	22573	14.72
Pr + GA	EtOH	6.570	2.029	1.292	1.909	6.578	6.578	-0.106	0.459	2.030	0.2256	2.990	22523	14.36
Pr + GA	DMSO	8.960	4.340	2.480	2.600	8.961	8.961	-0.106	0.940	2.700	0.3512	5.740	22422	14.80
Pr + GA	DMF	10.10	2.070	1.760	2.950	10.81	10.81	-0.264	0.533	3.200	0.1664	4.090	22472	14.04
Pr + AscA	H_2O	11.50	5.138	2.577	2.973	8.278	8.278	-9.290	1.070	3.480	0.3063	5.970	22523	14.66
Pr + AscA	EtOH	5.50	2.331	1.251	1.526	6.624	6.624	-1.850	0.496	1.670	0.2962	2.900	22472	14.65
Pr + AscA	DMSO	11.34	5.870	3.343	3.313	8.419	8.419	-0.373	1.270	3.390	0.3756	7.740	22422	14.91
Pr + AscA	DMF	9.12	2.919	2.046	2.611	8.272	8.272	-1.320	0.680	2.820	0.2414	4.740	22472	14.40
Pr + Py	H_2O	8.28	3.504	1.484	2.398	11.50	11.50	-0.741	0.680	2.530	0.2718	3.440	22523	14.49
Pr + Py	EtOH	6.62	2.202	1.504	1.918	5.501	5.501	-0.137	0.513	2.030	0.2525	3.480	22523	14.48
Pr + Py	DMSO	8.41	4.109	2.488	2.452	11.34	11.34	-0.870	0.915	2.500	0.3629	5.760	22472	14.98
Pr + Py	DMF	8.27	3.105	1.507	2.400	9.128	9.128	-0.338	0.638	2.550	0.2505	3.490	22472	14.40

TABLE-2
COMPUTRIZED VALUES OF VARIOUS PARAMETERS

System	Solvent	F_2	F_4	F_6	rF_2 (%)	ζ_{4F}	$r\zeta_{4F}$ (%)	E^1	E^2	E^3	β	$b^{1/2}$	δ (%)
Pr free ion	-	322.09	44.46	4.87	-	738.00	-	4729.00	24.78	478.43	-	-	-
Pr + IAA	H_2O	309.65	42.74	4.67	3.86	709.94	4.19	4546.30	23.78	459.65	0.9613	0.1389	1.935
Pr + IAA	EtOH	310.34	42.84	4.68	3.64	685.85	7.44	4556.49	23.83	460.68	0.9635	0.1350	1.825
Pr + IAA	DMF	310.56	42.87	4.69	3.57	678.77	8.39	4559.69	23.85	461.00	0.9642	0.1337	1.790
Pr + IAA	DMSO	309.21	42.68	4.67	3.99	683.10	7.81	4539.90	23.74	459.00	0.9600	0.1413	2.000
Pr + IBA	H_2O	311.77	43.03	4.71	3.20	680.57	8.15	4577.34	23.94	462.79	0.9679	0.1265	1.605
Pr + IBA	EtOH	308.49	42.58	4.66	4.22	711.32	4.00	4529.29	23.69	457.93	0.9577	0.1452	2.115
Pr + IBA	DMF	308.96	42.65	4.66	4.07	693.65	6.39	4536.20	23.72	458.63	0.9592	0.1427	2.040
Pr + IBA	DMSO	310.84	42.91	4.69	3.49	667.96	9.85	4563.69	23.87	461.41	0.9650	0.1321	1.750
Pr + GA	H_2O	309.69	42.75	4.67	3.84	709.52	4.24	4546.85	23.78	459.70	0.9615	0.1387	1.925
Pr + GA	EtOH	312.57	43.15	4.72	2.95	648.22	12.5	4589.10	24.00	463.98	0.9554	0.1215	2.230
Pr + GA	DMF	308.21	42.54	4.65	4.30	722.14	2.54	4525.17	23.67	457.51	0.9569	0.1467	2.155
Pr + GA	DMSO	310.65	42.88	4.69	3.54	650.42	12.2	4560.90	23.85	461.13	0.9645	0.1332	1.770
Pr + AscA	H_2O	312.34	43.12	4.72	3.03	632.20	14.68	4585.17	23.98	463.63	0.9697	0.1230	1.150
Pr + AscA	EtOH	308.79	42.63	4.66	4.13	699.71	5.57	4533.60	23.72	458.36	0.9587	0.1436	2.060
Pr + AscA	DMF	308.59	42.60	4.66	4.19	722.00	2.56	4530.74	23.70	458.08	0.9581	0.1447	2.090
Pr + AscA	DMSO	312.34	43.12	4.72	3.02	634.24	14.40	4585.83	23.99	463.65	0.9697	0.1229	1.510
Pr + Py	H_2O	312.12	43.08	4.72	3.09	642.49	13.29	4582.51	23.97	463.31	0.9690	0.1244	1.550
Pr + Py	EtOH	310.88	42.92	4.70	3.48	664.42	10.33	4564.22	23.87	461.46	0.9652	0.1319	1.740
Pr + Py	DMF	308.52	42.59	4.66	4.21	726.79	1.99	4529.66	23.69	457.97	0.9679	0.1451	2.100
Pr + Py	DMSO	311.74	43.04	4.71	3.21	630.05	14.97	4576.90	23.94	462.75	0.9679	0.1267	1.600

RESULTS AND DISCUSSION

Evaluated values of oscillator strength (P), Judd-Ofelt parameters T_λ (T_2, T_4, T_6), symmetry parameter ratio T_4/T_6 Racah parameters (E^1, E^2, E^3), Slater-Condon parameters (F_2, F_4, F_6), Lande parameter ζ_{4F}, percent reduction (% rF_2) and bonding parameters *viz.*, naphelauxetic ratio (β), bonding parameter ($b^{1/2}$), Sinha covalency parameter (δ %), rms deviation (σ), peacock constant (K) are tabulated in Tables 1 and 2. The calculations of these parameters have been computed by the programme developed by earlier workers[11].
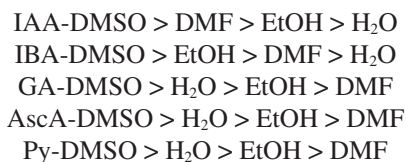
In the present study, transition $^3H_4 \rightarrow {}^3P_2$ is regarded as pseudo hypersensitive transition[12,13]. The complexation and covalency have been found to relate to spectral intensity (oscillator strength) of hypersensitive transition. The values of oscillator strength (P) of the complex system are found to be higher as compared to free ion, which shows higher complexation and covalency. From the study it has been found that the better complexation is occur in DMSO (8.077 × 10⁻⁵ to 12.57 × 10⁻⁵) in the systems. The higher magnitude of oscillator strength (12.57 × 10⁻⁵) indicate inner sphere complexation. The rms deviation with respect to oscillator strength (P) (7.870 × 10⁻⁸ to 2.940 × 10⁻⁸) has been reported in Table-1. The small deviation for calculated and observed P value suggests the validity of Judd-Ofelt equation for *f-f* transition. The value of Peacock proportionality constant (K) from relation $P_{obs} \alpha \overline{\nu} T_6$

(P for hypersensitive transition) comes to be almost constant (14×10^2). This confirms the relation proposed by Peacock[10].

There is much variation in Judd-Ofelt parameters T_2, T_4, T_6, which lies in the ordered $T_2 < T_4 < T_6$. These data is in good agreement with the Pr(III) ion characterization[6]. Judd-Ofelt intensity parameters T_λ (T_2, T_4, T_6) have also been computed from the Judd-Ofelt expression by using partial and multiple regression method. These parameters have been used for the determination of calculated values of Oscillator strength (P_{cal}). Judd-Ofelt intensity parameters T_4 and T_6 values are greater than zero and supported to Judd-Ofelt theory of *f-f* transition for Pr(III) complexes. From Table, one can find that the T_6 is much more sensitive to the coordination environment than the T_4, but T_2 occasionally showed negative values, which are physically unacceptable. The ratio T_4/T_6 indicates symmetry around cation. The ratio T_4/T_6 value varies from (0.1664 to 0.6487) indicate remarkable changes in symmetry around Pr(III) ion in the all systems.

The order of T_4/T_6 ratio for all the systems in four solvents is given as:

IAA-DMSO > DMF > EtOH > H_2O
IBA-DMSO > EtOH > DMF > H_2O
GA-DMSO > H_2O > EtOH > DMF
AscA-DMSO > H_2O > EtOH > DMF
Py-DMSO > H_2O > EtOH > DMF

The higher value of T_4/T_6 ratio in DMSO solvent in all ligands doped with Pr(III) ion support greater change in coordination environment around the central metal atom.

The red shift in all the energy bands compared with the free ion value supports interaction between metal cation with bonding anion due to an expansion of wave function. The value of nephelauxetic ratio β has been found less than one (0.9554 to 0.9697) in all the systems. Positive value of bonding parameter $b^{1/2}$ (0.1215 to 0.1467) suggests that the 4f orbital are slightly involve in the bonding in the saturated solution of ligands, indicating covalent bonding to same extent in doped Pr(III) ion. The values of Sinha covalency parameter δ % (1.51 to 2.23 %) also support covalent nature of metal-ligand bonding[10,14].

The parametric values reveal a remarkable variation in spin-orbit interaction parameter (Lande parameter) ζ_{4F} (630.05 to 726.79). There is decrease in values of Slater-Condon parameter (F_k) (308.21 to 312.57) than free ion value (322.09) indicates decrease in interelectronic repulsion due to complexation. This is in corroboration with the expansion of the central metal ion orbital when chelation of Pr(III) ion with the ligand in the surrounding environment[15].

The decrease in F_2 value and ζ_{4F} value is more affected in DMSO solvent in all the systems indicating better complexation in this solvent with ligands under study and greater variation in symmetry around Pr(III) ion.

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