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Electronic Spectral Parameters of the Saturated Solutions of Some Amino Acids and Some Bioactive N-heterocyclic Compounds Doped with Pr(III) ion

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Electronic spectral parameters, *viz.*, Judd-Ofelt parameter (T_λ), Racah (E^k), Slater-Condon (F^k), Landé (ζ_{4f}) and bonding parameters (β, $b^{1/2}$ and δ) have been evaluated for the saturated solutions of some amino acids (L-cystine, L-leucine, L-proline, L-threonine, arginine, β-alanine and DL-aspartic acid) and some bio-active N-heterocyclics (indole, 4-aminoantipyrine, 1,2,3-benzotriazole and uracil) doped with Pr(III) ion. The change in symmetry around Pr(III) ion and covalency in M-L interactions is observed. A linear relationship between oscillator strength (P_{ed}) and $\bar{\nu}T_6$ has beeen observed for hypersensitive transition ($^3H_4 \rightarrow {}^3P_2$).

INTRODUCTION

Electronic spectra of lanthanides have earned much interest due to their biological applications. In continuation of the earlier work an electronic spectral investigation of the saturated solutions of some amino acids and some bio-active N-heterocyclic compounds, doped with Pr(III) ion is undertaken.

In the present study seven amino acids (L-leucine, L-cystine, L-threonine arginine, β-alanine, L-proline, DL-aspartic acid) and four bioactive N-heterocyclics (indole, uracil, 4-aminoantipyrine, and 1,2,3-benzotriazole) have been used as ligands.

Pr(III) ion yields four bands[1–3] in the visible region corresponding to $^3P_2$, $^3P_1$, $^3P_0$ and $^1D_2$ levels. A saturated solution of ligand is prepared in 50% aqueous ethanol and a constant amount of Pr(III) ion has been added to this solution and spectra is measured in 400–625 nm region. A red shift is observed in the ligands solution doped with Pr(III) ion compared to aqua ion.

EXPERIMENTAL

Standard grade chemicals $PrCl_3$ (99.9% purity) (procured from Indian Rare Earths) and amino acids and N-heterocyclic compounds (S.D. fine) were used.

Ligands were dissolved in 50% aqueous ethanol at room temperature (30°C). Saturated solutions of ligands were prepared and 0.05 g of $PrCl_3$ was added to 10 cm^3 of each saturated solution of ligand. Solution spectra of these solutions were recorded by using standard spectrophotometer (Systronic-106) in the 400–625 nm range. In this range four peaks corresponding to $^3H_4 \rightarrow {}^3P_2$, $^3H_4 \rightarrow {}^3P_1$, $^3H_4 \rightarrow {}^3P_0$ and $^3H_4 \rightarrow {}^1D_2$ transitions have been obtained.

With the help of electronic spectra, oscillator strength of each band was obtained by the relation[4–6]

$$P_{ed} = 4.60 \times 10^{-9} \times \Delta\nu_{1/2} \times \varepsilon_{max}$$

where $\Delta\nu_{1/2}$ = half band width

ε_{max} = molar extinction coefficient

P_{ed} = oscillator strength.

The calculations of other parameters, *viz.*, Judd-Ofelt (T_2, T_4, T_6), Landé (ζ_{4f}), Slater-Condon (F^k) and Racah (E^k) have been made by computerized programme used by earlier workers.[7–10]

The nephelauxetic ratio (β) has been calculated by using the relation:

$$\beta = \frac{\bar{\nu}_{complex}}{\bar{\nu}_{aqua\ ion}}$$

The bonding parameter ($b^{1/2}$) and Sinha's parameter (δ) have been computed by using the following relations:

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

$$\delta = \left(\frac{1-\beta}{2}\right) \times 100\%$$

β = nephelauxetic ratio.

RESULTS AND DISCUSSION

Evaluated values of oscillator strengths, Judd-Ofelt parameters (T_2, T_4, T_6), Racah parameter (E^1, E^2, E^3), Slater-Condon-Shortly parameter (F^2, F^4, and F^6) and Landé (ζ_{4f}) and nephelauxetic ratio (β) values are tabulated in Tables 1 and 2.

The parametric values reveal a remarkable variation in spin-orbit interaction parameter (Landé). Its value ranges from 658 to 697. The percentage reduction in ζ_{4f} (% $r\zeta_{4f}$) values comes to be from 6.45 to 11.14. This indicates decrease in spin-orbit interaction in metal-ligand bonding.

The values of F^2 parameter (Slater-Condon-Shortly) in the present study decrease from free ion value, this indicates decrease in inter-electronic repulsion due to complexation, even though almost similar values are obtained (the value ranges from 309.07 to 311.43).

The oscillator stength (P_{ed}) values vary from 17.6×10^{-6} to 36.4×10^{-6} for hypersensitive transitions ($^3H_4 \rightarrow {}^3P_2$). There is much variation in Judd-Ofelt parameters (T_2, T_4 and T_6). The values of T_2 have been found to be negative for all the systems. The values of T_2, T_4 and T_6 show the sequence $T_2 < T_4 < T_6$ which is in good agreement with the lanthanide metal ion characteristics[2]. The deep lying 4f subshells experiencing intense shielding make these orbitals less available for bonding, thereby leading to lesser degree of metal-ligand interactions. The ratio T_4/T_6 indicating symmetry around cation. The ratio T_4/T_6 varies from 0.25–0.33 indicates very slight change in symmetry around Pr(III) ion in the present systems under study.

TABLE-1
COMPUTERIZED VALUES OF OSCILLATOR STRENGTH, T_λ etc.

Compounds	Oscillator strength				$T_\lambda \times 10^9$			T_4/T_6	$\bar{\nu}$ for $^3P_2$ band	$K = \frac{P_{ed}}{\bar{\nu}T_6}$ ($\times 10^{-2}$)
	$^3P_2$-band ($\times 10^{-6}$)	$^3P_1$-band ($\times 10^{-6}$)	$^3P_0$-band ($\times 10^{-6}$)	$^1D_2$-band ($\times 10^{-6}$)	T_2	T_4	T_6			
Pr^{3+}-L-Cystine	33.3	16.0	6.24	9.36	–9.35	3.07	10.20	0.30	22321	14.62
Pr^{3+}-L-Leucine	30.3	14.6	5.52	8.52	–8.89	2.78	9.23	0.30	22421	14.64
Pr^{3+}-Proline	23.7	10.3	5.25	6.82	–3.20	2.15	7.25	0.30	22371	14.61
Pr^{3+}-Threonine	17.6	9.51	3.01	4.97	–4.25	1.73	5.31	0.33	22523	14.71
Pr^{3+}-β-Alanine	23.9	11.0	3.35	6.83	–4.41	1.98	7.33	0.27	22422	14.54
Pr^{3+}-Arginine	36.4	20.1	6.51	10.7	–2.08	3.68	11.00	0.33	22371	14.79
Pr^{3+}-Aspartic acid	23.3	10.7	3.97	6.49	–7.37	2.03	7.13	0.28	22421	14.57
Pr^{3+}-Indole	27.7	13.3	5.01	8.01	–2.76	2.52	8.45	0.30	22422	14.62
Pr^{3+}-4-Amino antipyrine	25.6	10.3	4.00	7.48	–2.35	1.97	7.88	0.25	22472	14.45
Pr^{3+}-Benzotriazole	29.2	14.9	5.60	8.33	–4.58	2.83	8.78	0.32	22573	14.73
Pr^{3+}-Uracil	32.5	17.3	5.66	9.31	–5.84	3.17	9.86	0.32	22420	14.70

Mean = 14.63

TABLE-2
COMPUTED VALUES OF VARIOUS PARAMETERS

Compounds (Systems)	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^{3+}-Free ion	322.09	44.46	4.87	–	738	–	4729	24.78	478.13	–	–	–
Pr^{3+}-L-Cystine	310.51	42.86	4.69	3.59	662	10.62	4558	23.84	460.92	0.9867	0.0815	1.347
Pr^{3+}-L-Leucine	309.64	42.72	4.67	3.86	692	6.52	4546	23.78	459.64	0.9912	0.0663	0.887
Pr^{3+}-Proline	309.07	42.66	4.67	4.03	693	6.45	4537	23.73	458.79	0.9889	0.0741	1.122
Pr^{3+}-Threonine	310.41	42.85	4.69	3.62	683	7.79	4557	23.84	460.78	0.9957	0.0469	0.441
Pr^{3+}-β-Alanine	310.38	42.84	4.68	3.63	687	7.15	4556	23.83	460.73	0.9912	0.0663	0.887
Pr^{3+}-Arginine	309.91	42.78	4.68	3.78	681	8.05	4550	23.80	460.03	0.9889	0.0741	1.122
Pr^{3+}-Aspartic acid	309.26	42.69	4.67	3.98	682	7.95	4540	23.75	459.03	0.9912	0.0663	0.887
Pr^{3+}-Indole	311.43	42.99	4.70	3.30	658	11.14	4572	23.91	462.29	0.9912	0.0663	0.887
Pr^{3+}-4-Aminoantipyrine	310.32	42.84	4.68	3.65	689	6.95	4556	23.83	460.64	0.9934	0.0574	0.664
Pr^{3+}-Benzotriazole	310.03	42.79	4.68	3.74	697	5.82	4551	23.81	460.20	0.9979	0.0331	0.210
Pr^{3+}-Uracil	309.62	42.74	4.67	3.54	693	6.46	4545	23.77	459.60	0.9911	0.0663	0.888

The transition $^3H_4 \rightarrow {}^3P_2$ behaves as a hypersensitive transition and it follows the relation $P_{ed} \propto \bar{\nu}T_6$ in the present study. The values of proportionality constant (K) with respect to $\bar{\nu}T_6$ have been tabulated in Table-1. Its value comes to be almost constant (Mean value 14.63×10^{-2}). This confirms the relation $P \propto \bar{\nu}T_6$ as proposed by Peacock[11].

The value of nephelauxetic ratio (β) has been found to be less than one in all the systems. Positive value of $b^{1/2}$ indicates some covalent character in metal-ligand bond.

Sinha's parameter (δ) is usually taken as a measure of covalency[3]. The value of δ% ranges from 0.210 to 1.347 for the present system, indicative of very weak covalent bonding. Because the deep lying 4f subshells are strongly shielded and are less available for bonding, the Ln(III)-L bonds are thus expected to be ionic with probable partial covalency.

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