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Electronic Spectral Characterisation of Pr(III) Systems Involving Sulphonanilide Environment in DMF Medium

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Electronic spectral parameters, *viz.*, nephelauxetic ratio (β), bonding parameter ($b^{1/2}$) and Judd-Ofelt intensity parameter (T_λ) have been computed for some modified doped systems involving Pr(III) surrounded by sulphonanilide ligand. Oscillator strength of all the four bands ($^3P_2$, $^3P_1$, $^3P_0$ and $^1D_2$ levels) in each system has been reported and recalculated using Judd-Ofelt equation. The r.m.s. deviations have been found to be $\pm 1.82 \times 10^{-9}$ to $\pm 9.43 \times 10^{-9}$. A linear correlation between oscillator strength of hypersensitive band ($^3P_2$ level) and νT_6 has been observed.

INTRODUCTION

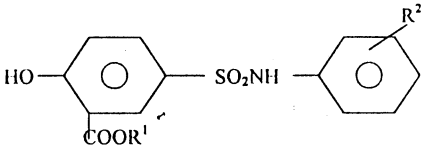
The electronic spectral characterisation of various Pr(III) systems involving sulphonanilide ligands of medicinal importance in DMF medium have been studied. This involves synthesis of twenty-one sulphonanilides using the steps reported in the literature[1, 2]. A modified doped system[3, 4] has been undertaken to record solution spectra in DMF medium using standard spectrophotometer. The various electronic spectral parameters have been computed by using computerised programming method[5]. The calculations involve Judd-Ofelt equation and other relations as described in the literature[6]. The present work infers covalency in metal-ligand bonding in the systems undertaken. The study also provides some useful information regarding metal-ligand interaction and the change in symmetry around lanthanide ion in terms of Judd-Ofelt parameters (T_λ). The systems undertaken have been classified on the basis of T_4/T_6 ratio (symmetry parameter). The validity of the relation $P \propto \nu T_6$ has been examined and found in good agreement in these systems.

EXPERIMENTAL

Synthesis of sulphonanilides[1, 2]: Twenty-one sulphonanilides were synthesized by employing two steps. In the first step, chlorosulphonic acid is taken in a round bottom flask, fitted with an electrical stirrer. Salicylic acid or methyl salicylate or ethyl salicylate is taken in 1 : 2 molar ratio and is added in small lots during the course of 20 min. Temperature is maintained 0–5°C. Stirring is continued for another 1.5 h. The thick reaction mixture is poured into crushed ice. Sulphonyl chloride derivative is obtained as white solid. It is filtered, washed with water and kept immediately for drying as sulphonyl chloride derivative is susceptible for hydrolysis. Crystallisation is done with chloroform. Melting point is recorded.

In the second step, sulphonyl chloride derivative is refluxed with aromatic amine in dioxane solvent in the presence of a pinch of anhydrous sodium acetate for 6–8 h. It is cooled and transferred into conc. HCl. It is left overnight on dilution, sulphonanilide is precipitated. It is filtered, washed with water and crystallised with alcohol-water. Melting point is recorded. AR grade chemicals have been used for synthesis.

All the sulphonanilides may be represented by the formula



where $R^1 = H, CH_3, C_2H_5$, $R^2 =$ *o*-, *m*- and *p*-Cl, *o*- and *p*-OCH_3, *o*-, *m*- and *p*-CH_3.

Standard grade chemical Pr(III) as chloride salt (supplied by Indian Rare Earths Ltd.) has been used for studies. Twenty-one systems have been prepared on doped model with minor modification. 10 mL of 0.12 M Pr(III) solution has been mixed with 10 mL of 0.24 M ligand solution in DMF medium. In this way the concentration of ligand has been taken in excess which serves the purpose of modified doped model. Solution spectrum for the Pr(III)-ligand system has been taken in the range 400–625 nm by using Systronic spectrophotometer (Model-106).

RESULTS AND DISCUSSION

In the present Pr(III)-ligand systems, the solution spectra yield four bands, *viz.*, $^3H_4 \rightarrow {}^3P_2$; $^3H_4 \rightarrow {}^3P_1$; $^3H_4 \rightarrow {}^3P_0$ and $^3H_4 \rightarrow {}^1D_2$. The energies of these bands have been found to be in between 22470–22730 cm^{-1}, 21370–21550 cm^{-1}, 20530–20830 cm^{-1} and 16950 cm^{-1}, respectively. The value of nephelauxetic ratio (β) has been computed by involving hypersensitive band ($^3P_2$) using the following relationship.

$$\beta = \frac{\text{Average value of energy for } {}^3P_2 \text{ band in the system (in cm}^{-1}\text{)}}{\text{Value of energy}^8 \text{ for } {}^3P_2 \text{ band in Pr(III) free ion (23161 cm}^{-1}\text{)}}$$

The bonding parameter $b^{1/2}$ has been computed by using the following equation. $b^{1/2} = [\frac{1}{2}(1 - \beta)]^{1/2}$

Using the Judd-Ofelt equation,

$$P_{obs} = [U^{(2)}]\nu \times T_2 + [U^{(4)}]^2\nu \times T_4 + [U^{(6)}]^2\nu \times T_6,$$

the intensity parameters (T_2, T_4 and T_6) have been computed and reported in Table-1. Assuming hydrogen-like wave function, the value of T_2 has been found

TABLE-1: COMPUTED VALUES OF VARIOUS PARAMETERS FOR Pr(III) SYSTEMS INVOLVING SULPHONANILIDE LIGANDS

	Parameters	O.S.(P) of $^3P_2$ band $P \times 10^6$		O.S.(P) of $^3P_1$ band $P \times 10^6$		O.S.(P) of $^3P_0$ band $P \times 10^6$		O.S. (P) of $^1D_2$ band $P \times 10^6$		r.m.s. dev. (σ) $\pm 1.0 \times 10^{-9}$	$T_2 \times 10^9$	$T_4 \times 10^9$	$T_6 \times 10^9$	T_4/T_6	$vT_6 \times 10^9$	$K = \frac{P}{vT_6}$
	Systems	Exp.	Cal.	Exp.	Cal.	Exp.	Cal.	Exp.	Cal.							
Catg A 1	Pr-SMeS-MT [Pr(III)-L5]	15.5	15.5	4.94	4.94	2.68	2.67	1.18	1.18	3.93	–76	1.05	4.8	0.22	107856	14.48×10^{-2}
2	Pr-SMeS-PT [Pr(III)-L6]	25.7	25.7	9.70	9.70	5.28	5.25	1.43	1.43	7.73	–137	2.06	7.78	0.26	176839	14.53×10^{-2}
3	Pr-SEtS-OCA [Pr(III)-L13]	15.24	15.24	5.82	5.82	1.98	1.97	1.04	1.04	2.90	–78	1.07	4.72	0.23	106058	14.33×10^{-2}
4	Pr-SMeS-PA [Pr(III)-L19]	20.40	20.41	7.58	7.58	3.86	3.85	1.56	1.56	5.66	–100	1.57	3.99	0.25	141111	14.45×10^{-2}
5	Pr-SEtS-OA [Pr(III)-L20]	12.66	12.66	3.50	3.50	1.25	1.24	1.18	1.18	1.82	–57	0.65	4.20	0.16	89655	14.17×10^{-2}
Catg B 1	Pr-SSA-OT [Pr(III)-L1]	12.12	12.12	5.82	5.82	3.00	2.99	1.69	1.69	4.39	–43	1.22	3.65	0.33	82015	14.75×10^{-2}
2	Pr-SSA-MT [Pr(III)-L2]	11.73	11.73	6.10	6.10	2.40	2.38	1.40	1.40	3.51	–47	1.17	3.54	0.33	79544	14.71×10^{-2}
3	Pr-SSA-PT [Pr(III)-L3]	10.94	10.94	5.82	5.82	2.61	2.59	1.27	1.27	3.82	–44	1.16	3.27	0.35	73804	14.75×10^{-2}
4	Pr-SMeS-OT [Pr(III)-L4]	11.92	11.92	5.64	5.64	2.64	2.63	1.84	1.84	3.86	–38	1.14	3.59	0.32	81026	14.69×10^{-2}
5	Pr-SSA-OCA [Pr(III)-L7]	18.03	18.03	8.05	8.05	5.64	5.61	3.99	3.99	8.25	–29	1.89	5.35	0.35	121605	14.80×10^{-2}
6	Pr-SMeS-OCA [Pr(III)-L10]	12.11	12.11	6.60	6.60	2.20	2.19	1.72	1.72	3.23	–42	1.21	3.66	0.33	82240	14.72×10^{-2}
7	Pr-SMeS-MCA [Pr(III)-L11]	12.31	12.31	5.80	5.80	2.78	2.77	1.50	1.50	4.07	–48	1.18	3.73	0.32	83813	14.67×10^{-2}

8	Pr-SEts-MCA [Pr(III)-L14]	9.66	9.66	3.54	3.54	2.97	2.95	2.65	2.65	4.34	–38	0.89	2.90	0.31	65917	14.65×10^{-2}
9	Pr-SEts-PCA [Pr(III)-L15]	13.36	13.36	5.87	5.87	2.68	2.67	2.45	2.45	3.93	–32	1.17	4.02	0.29	91375	14.63×10^{-2}
10	Pr-SEtS-PA [Pr(III)-L21]	14.26	14.26	7.76	7.76	3.91	3.89	2.35	2.35	5.72	–41	1.60	4.20	0.31	95466	14.98×10^{-2}
Catg C 1	Pr-SSA-MCA [Pr(III)-L8]	12.31	12.31	7.94	7.94	3.52	3.50	2.58	2.58	5.15	–23	1.58	3.58	0.44	81373	15.11×10^{-2}
2	Pr-SSA-PCA [Pr(III)-L9]	14.75	14.75	9.02	9.02	6.44	6.41	3.78	3.78	9.43	–13	2.13	4.22	0.55	95921	15.38×10^{-2}
3	Pr-SMeS-PCA [Pr(III)-L12]	27.33	27.33	18.40	18.40	4.83	4.81	3.91	3.91	7.07	–94	3.20	8.08	0.40	182366	14.97×10^{-2}
4	Pr-SSA-OA [Pr(III)-L16]	11.34	11.34	8.43	8.43	3.38	3.37	1.16	1.61	4.95	–40	1.63	3.29	0.49	73926	15.34×10^{-2}
5	Pr-SSA-PA [Pr(III)-L17]	10.16	10.16	6.85	6.85	3.22	3.21	1.17	1.17	4.71	–42	1.38	2.97	0.47	66736	15.29×10^{-2}
6	Pr-SMeS-OA [Pr(III)-L18]	11.46	11.46	7.76	7.76	2.36	2.35	2.21	2.22	3.46	–27	1.39	3.39	0.41	76177	15.11×10^{-2}

where SSA = Sulphonyl chloride of salicylic acid, SMeS = Sulphonyl chloride of methyl salicylate, SEtS = Sulphonyl chloride of ethyl salicylate, OT = *o*-toluidine MT = *m*-toluidine, PT = *p*-toluidine OCA = *o*-chloroaniline, MCA = *m*-chloroaniline, PCA = *p*-chloroaniline, OA = *o*-anisidine, PA = *p*-anisidene

Category	β	$b^{1/2}$
A	0.9742	0.1174
B	0.9755	0.1107
C	0.9746	0.1127

to be negative. The systems undertaken have been classified on the basis of symmetry parameter (T_4/T_6) into three categories, *viz.*, A, B and C. The value of T_4/T_6 for these three categories ranges from 0.15 to 0.27, 0.27 to 0.39 and 0.39 to 0.51 respectively.

The intensity of the bands observed has been given in terms of oscillator strength (P). The values of oscillator strength of these bands have been recalculated by applying the Judd-Ofelt equation using computed values of T_λ parameters. The r.m.s. deviation in between experimental and recalculated values for the oscillator strength varies from $\pm 1.82 \times 10^{-9}$ to $\pm 9.43 \times 10^{-9}$ as reported in Table-1.

Various relations have been suggested to correlate intensity of hypersensitive band in terms of oscillator strength with νT_2 or νT_4 or νT_6 or νb^2. In the present work, the relation $P \propto \nu T_6$ for hypersensitive band has been examined for its validity. The value of $K = O.S.(P)/\nu T_6$ for various categories have been computed and reported in Table-1. It has been observed that the value of K remains almost constant for all systems of one category.

The values of β and $b^{1/2}$ suggest that the covalency in metal-ligand bond in three categories of the systems undertaken follows the order: $A > C > B$.

The present study shows that the change in T_4/T_6 value indicates the change in stereo environment (or coordination number) around Pr(III) ion.

The hypersensitive transition ($^3P_2$ band) shows variation of high order as compared to other bands in oscillator strength (P) value which varies from 9.66×10^{-6} to 27.33×10^{-6} in the present systems.

A linear relationship between O.S.(P) and νT_6 has been shown which is indicated by the values of K in different categories of the systems.

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