Electronic Spectral Studies on Pr^{3+} Doped Sulphonanilide System, Part II†

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Nine sulphonanilides have been synthesised. Their interaction with Pr^{3+} ion in the form of doped model has been discussed in terms of Slater-Condon, Landé and Judd-Ofelt parameters. The involvement of 4f-orbitals in the Pr^{3+} doped systems including deviation in symmetry have been discussed.

INTRODUCTION

It has been well established that sulphur containing ligands have versatile pharmacological activity, which increases on complexation with metal ions[1]. Most important of them are sulphonanilide derivatives which have immense antibacterial activity. Since the complexing behaviour of lanthanide ions has not been studied extensively, in the present work an attempt has been made to characterise Pr^{3+} doped sulphonanilides on the basis of Judd-Ofelt, Slater-Condon and other theories. Sulphonanilides have been synthesised by the method reported in literature[2-3]. The complexing ability with respect to thermodynamic stability is poor in case of lanthanide complexes, so doped lanthanide ion in saturated solution of ligand has been undertaken as a system for electronic spectral study[4-6]. 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 change in symmetry around lanthanide ion.

EXPERIMENTAL

(A) Synthesis of Sulphonanilides:

(a) Sulphonanilides (L_1 to L_6) were synthesised in two steps.

Step I: In the first step chlorosulphonic acid (0.04 M) was taken in round-bottomed flask, fitted with a stirrer maintaining the temperature from 0–5°C. To it 1-hydroxy-3-methyl naphthoate or 1-hydroxy-3-propyl naphthoate (0.01 N) was added in small lots during the course of 30 min with continued stirring. When fumes of HCl subsided, the reaction mixture was poured into crushed ice. The sulphonyl chloride precipitated out as a white solid was filtered, washed with water, dried and its melting point was recorded.

Step II: Sulphonyl chloride so prepared was refluxed with aromatic amine and anhydrous sodium acetate in dioxane for 8 h. It was cooled and transferred into conc. HCl and left for overnight. On dilution suphonanilide was precipitated.

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It was fitered, washed with water, recrystallised from alcohol-water and its melting point was recorded.

(b) Sulphonanilides (L_7 and L_8) were synthesised as follows:

Step I: Toluene was chlorosulphonated by following the same procedure as given above.

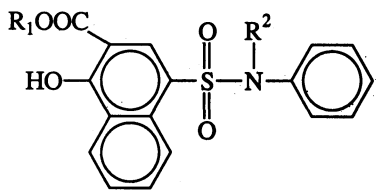
Step II: *p*-Toluene sulphonyl chloride so obtained was dissolved in dioxane and was refluxed with N-ethyl-*p*-toluidine or N-methyl-*p*-anisidine with sodium acetate.

It was then cooled and transferred into the beaker. On dilution sulphonanilide was precipitated. It was filtered, washed with water, crystallised and melting point was recorded.

(c) In the synthesis of L_9 (sulponanilide) benzene sulphonyl chloride was nitrated to give *m*-nitrobenzene sulphonyl chloride. It was condensed with N-methyl-*p*-toluidine and sulphonanilide was prepared by following the same procedure as given earlier.

Formulae of sulphonanilides are as follows:

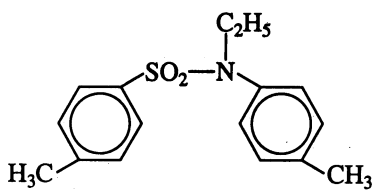
I. L_1 to L_6



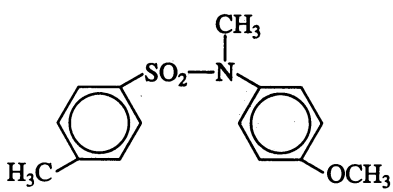
where

L	L_1	L_2	L_3	L_4	L_5	L_6
R^1	CH_3	C_2H_5	nC_3H_7	nC_4H_9	CH_3	C_2H_5
R^2	CH_3	CH_3	CH_3	CH_3	C_2H_5	C_2H_5

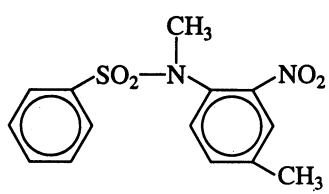
II. L_7



III. L_8



IV. L_9



The names of ligands are as follows:

L_1 3-Carbomethoxy-4-hydroxy-N-methyl naphthalene-1-sulphonanilide
L_2 3-Carboethoxy-4-hydroxy-N-methyl naphthalene-1-sulphonanilide
L_3 3-Carbopropoxy-4-hydroxy-N-methyl naphthalene-1-sulphonanilide
L_4 3-Carbobutoxy-4-hydroxy-N-methyl naphthalene-1-sulphonanilide
L_5 3-Carbomethoxy-4-hydroxy-N-ethyl naphthalene-1-sulphonanilide
L_6 3-Carboethoxy-4-hydroxy-N-ethyl naphthalene-1-sulphonanilide
L_7 4,4′-Dimethyl-N-ethyl benzene sulphonanilide
L_8 4-Methyl-N-methyl-4′-methoxy benzene sulphonanilide
L_9 4-Methyl-N-methyl-3-nitrobenzene sulphonanilide

(B) Preparation of Doped Systems: In the present work nine systems of lanthanide ion doped in saturated solutions of these ligands have been prepared by adding 0.1 g $PrCl_3 \cdot 6H_2O$ salt (supplied by Indian Rare Earth Ltd.) per 10 mL of ligand solution. The solution spectrum of each system has been recorded in the range 600–350 nm by using standard spectrophotometer.

RESULTS AND DISCUSSION

The values of various spectral parameters including oscillator strength, energy, Slater-Condon nephelauxetic ratio, Landé and bonding parameters, etc. have been reported in Tables 1 and 2. The observed change in the various energy and intensity parameters shows that the $f \leftrightarrow f$ transition resulting from spin-orbit interaction in Pr^{3+} ion is due to the interaction of f-orbital with the ligand present in the saturated solution. The calculation of various parameters involve Slater-Condon-Landé Judd-Ofelt theories as reported by earlier workers[4, 5]. Red-shift has been observed in all energy bands as compared to the free ion thereby establishing the validity of Stater-Condon-Landé theory. The r.m.s. deviation in energy (c.f. Table-1) varies from ±88 to ±169 in all the systems. The intensities

TABLE-1
VALUES OF ENERGY AND OSCILLATOR STRENGTH (P) FOR VARIOUS Pr^{3+} DOPED SULPHONANILIDES

Level	$^3P_2$		$^3P_1$		$^3P_0$		$^1D_2$		r.m.s.	Dev (±)
Ligand	E_{exp} (cm^{-1})	P_{exp} $\times 10^6$	E_{exp} (cm^{-1})	P_{exp} $\times 10^6$	E_{exp} (cm^{-1})	P_{exp} $\times 10^6$	E_{exp} (cm^{-1})	P_{exp} $\times 10^6$	ln E	ln P ($\sigma * 10^9$)
L_1	22470	6.77	21510	2.87	20700	1.68	16950	1.67	141	2.45
L_2	22470	8.89	21570	3.65	20703	1.68	16891	1.69	162	2.45
L_3	22470	17.9	21460	8.39	20703	1.90	16920	2.86	136	2.78
L_4	22470	6.17	21367	2.41	20746	1.03	16949	1.05	101	1.52
L_5	22573	9.12	21570	1.83	20790	1.49	16949	2.08	142	2.19
L_6	22573	4.88	21510	1.83	20790	1.44	16891	1.35	169	2.10
L_7	22470	8.15	21231	3.25	20703	1.95	16920	1.42	98	2.86
L_8	22490	8.85	21186	3.64	20860	1.01	16950	1.89	125	1.48
L_9	22470	9.03	21486	3.98	20700	1.58	16950	1.70	88	2.32

of observed bands have been given in terms of oscillator strength (P). The r.m.s. deviation is very small varying from $\pm 1.48 \times 10^{-9}$ to 2.86×10^{-9} suggesting the validity of Judd-Ofelt theory for f-f transition.

The T_4/T_6 ratio (c.f. Table-2) varies from 0.16 to 0.31. It indicates variation in symmetry around doped Pr^{3+} ion in saturated ligand solution. The % rF_2 varies from 2.619 to 3.835 indicating decrease in inter-electronic repulsion between metal-ligand. The values of nephelauxetic ratio (β) and bonding parameter ($b^{1/2}$) and little variation in it suggests that the 4f-orbitals are very slightly involved in the bonding in saturated solutions doped with Pr^{3+} ion. The % $r\zeta_{4f}$ varies from 3.85 to 12.46 indicating decrease in spin-orbit interactions in metal-ligand bonding.

TABLE-2
VALUES OF T_λ AND OTHER PARAMETERS FOR VARIOUS Pr^{3+} DOPED SULPHONANILIDES

Ligand	$T_2 \times 10^{10}$	$T_4 \times 10^{10}$	$T_6 \times 10^{10}$	T_4/T_6	F_2	F_4	F_6	ζ_{4F}	% $r(\zeta)_{4F}$	% rF_2	β	$b^{1/2}$
L_1	–73.3	6.25	20.60	0.30	309.74	42.76	4.68	712.44	3.85	3.84	0.962	0.138
L_2	–209	7.32	27.30	0.27	310.11	42.81	4.69	699.97	5.54	3.72	0.963	0.136
L_3	–543	14.10	55.00	0.26	310.08	42.81	4.69	699.89	5.55	3.73	0.963	0.137
L_4	–172	4.74	19.00	0.25	311.19	42.96	4.70	678.89	6.38	3.38	0.966	0.130
L_5	–129	4.58	28.60	0.16	311.47	42.99	4.71	693.03	6.47	3.29	0.967	0.128
L_6	–17.2	4.50	14.70	0.31	311.76	43.04	4.71	681.87	7.98	3.21	0.968	0.127
L_7	–221	7.22	24.80	0.29	310.63	42.88	4.69	673.99	9.09	5.56	0.964	0.133
L_8	–159	6.38	27.30	0.23	313.65	43.29	4.74	648.68	12.46	2.62	0.974	0.114
L_9	–216	7.71	27.60	0.28	310.57	42.87	4.69	675.79	8.79	3.59	0.964	0.134

Other parameters have also been computed so as to indicate variation in electronic-spectral characterization.

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