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Electronic Spectral Characterization of Sulphonanilides with Pr(III) and Nd(III) Ions

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The Pr(III) & Nd(III) doped systems with various sulphonanilide ligands have been studied with respect to electronic spectral parameters. Different parameters prove the covalent nature of M—L bond instead of ionic bond.

Key Words: Electronic spectral parameters, Doped Pr(III) and Nd(III) system, Sulphonanilides.

INTRODUCTION

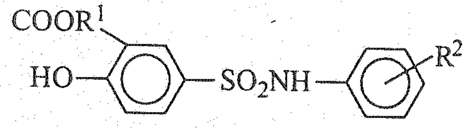
The complexes of *d*-block transition metals with various ligands have been studied extensively, whereas in case of *f*-block lanthanide metal complexes, a limited study has so far been carried out, because of their poor tendency to form complexes[1].

The systematic study of lanthanide complexes began only after the publication of Judd-Ofelt theory[2, 3]. Although the bonding between the ligand and the lanthanide ion is observed sufficiently electrostatic, yet with appreciable interaction between the 4*f*-orbitals and ligand orbitals[4–12]. The interelectronic repulsions and spin-orbit interactions involved in the metal-ligand bond in lanthanide complexes may be given in terms of Slater-Condon-Lande parameters whereas the intensities of various bands observed may be given in terms of Judd-Ofelt parameters[4–12].

In the present paper, some Pr(III) and Nd(III) complexes of sulphonanilides have been characterized in terms of electronic spectral parameters.

EXPERIMENTAL

Standard grade chemicals $PrCl_3 \cdot 6H_2O$ and $NdCl_3 \cdot 6H_2O$ (supplied by Indian Rare Earth Ltd.) have been used for studies. Six sulphonanilide ligands prepared in this laboratory have been used for preparation of systems with Pr(III) and Nd(III) ions. Six (L_1 to L_6) ligands can be represented as follows:



Ligands	Groups and their representation	
	R^2	R^1
L_1	*o*-amino	H
L_2	*p*-amino	H
L_3	*o*-amino	CH_3
L_4	*p*-amino	CH_3
L_5	*o*-amino	C_2H_5
L_6	*p*-amino	C_2H_5

The concentration of ligand has been taken in excess which serves the purpose of modified doped model.

Solution spectra for Pr(III)-ligand and Nd(III)-ligand systems have been taken in the range 400–625 nm and 400–950 nm respectively by using Systronics spectrophotometer (model-106).

RESULTS AND DISCUSSION

Energies of the bands show a red shift when the energy values of the bands are compared with corresponding values of bands for Pr(III) and Nd(III) free ions, which suggests M-L interaction. The present systems show a variation in symmetry environment around Pr(III) and Nd(III) ions when surrounded by different ligands. The symmetry parameter (~~T_4/T_6 ratio~~) for Pr(III) and Nd(III) ion systems clearly show the change in symmetry around these ions (Tables 1–4).

TABLE-1

OBSERVED AND CALCULATED VALUES OF OSCILLATOR STRENGTH (P) AND JUDD OFELT PARAMETER (T_λ) OF THE BANDS RECORDED FOR Pr(III) ION SYSTEMS INVOLVING LIGAND ENVIRONMENT IN DMF SOLVENT

		Pr(III) ion systems involving ligand environment (1 : 2 molar ratio) in DMF solvent							
		Free Pr(III) ion		Pr(III) with L_1		Pr(III) with L_2		Pr(III) with L_3	
		$P_{obs} \times 10^6$	$P_{cal} \times 10^6$	$P_{obs} \times 10^6$	$P_{cal} \times 10^6$	$P_{obs} \times 10^6$	$P_{cal} \times 10^6$	$P_{obs} \times 10^6$	$P_{cal} \times 10^6$
Levels	$^3P_2$	23.3	23.3	28.6	28.6	40.8	40.8	59.1	59.1
	$^3P_1$	3.35	3.35	10.7	10.7	39.7	39.7	57.1	57.1
	$^3P_0$	5.68	5.65	14.4	14.3	26.4	26.3	33.5	33.3
	$^1D_2$	6.19	6.19	8.45	8.45	11.1	11.1	11.6	11.6
	r.m.s. dev.	$\pm 8.32 \times 10^{-6}$		$\pm 2.11 \times 10^{-6}$		$\pm 3.86 \times 10^{-6}$		$\pm 4.90 \times 10^{-6}$	
T_λ Parameter	$T_2 \times 10^{-9}$	–15.5		–1.92		–28.9		–142.0	
	$T_4 \times 10^{-9}$	1.25		3.48		9.11		12.5	
	$T_6 \times 10^{-9}$	7.33		8.46		11.0		16.1	
	T_4/T_6	0.17		0.41		0.83		0.78	

Pr(III) ion in environment of ligands L_1 to L_6

The order of symmetry parameter for systems under study is as follows:

$$L_6 > L_2 > L_3 > L_1 > L_4 > L_5$$

T_4/T_6 changes from 0.94 to 0.17 (Figs. 1 and 2). This ratio shows that the change in the group —COOH, —$COOCH_3$ and —$COOC_2H_5$ affects the ratio. The change in the position of —NH_2 group from *ortho* to *para* also affects the ratio, *i.e.*, change in symmetry around Pr(III) ion.

TABLE-2
OBSERVED AND CALCULATED VALUES OF OSCILLATOR STRENGTH (P) AND JUDD OFELT PARAMETER (T_λ) OF THE BANDS RECORDED FOR Pr(III) ION SYSTEMS INVOLVING LIGAND ENVIRONMENT IN DMF SOLVENT

		Pr(III) ion systems involving ligand environment (1 : 2 molar ~~ratio~~) in DMF solvent					
		Pr(III) with L_4		Pr(III) with L_5		Pr(III) with L_6	
		$P_{obs} \times 10^6$	$P_{cal} \times 10^6$	$P_{obs} \times 10^6$	$P_{cal} \times 10^6$	$P_{obs} \times 10^6$	$P_{cal} \times 10^6$
Levels	$^3P_2$	23.0	23.0	34.2	34.2	23.2	23.2
	$^3P_1$	9.87	9.87	7.41	7.41	23.1	23.1
	$^3P_0$	9.66	9.62	7.28	7.25	18.6	18.5
	$^1D_2$	6.35	6.35	10.0	10.0	6.52	6.52
	r.m.s. dev.	$\pm 1.41 \times 10^{-8}$		$\pm 1.07 \times 10^{-8}$		$\pm 2.72 \times 10^{-8}$	
T_λ Parameter	$T_2 \times 10^{-9}$	–11.4		–1.82		–12.8	
	$T_4 \times 10^{-9}$	2.70		2.03		5.77	
	$T_6 \times 10^{-9}$	6.83		10.7		6.11	
	T_4/T_6	0.40		0.19		0.94	

TABLE-3
OBSERVED AND CALCULATED VALUES OF OSCILLATOR STRENGTH (P) & JUDD OFELT PARAMETER (T_λ) OF THE BANDS RECORDED FOR Nd(III) ION SYSTEMS INVOLVING LIGAND ENVIRONMENT (1 : 2 molar ratio) IN DMF SOLVENT

		Nd(III) ion systems involving ligand environment in DMF solvent							
		Free Nd(III) ion		Nd(III) with L_1		Nd(III) with L_2		Nd(III) with L_3	
		$P_{obs} \times 10^6$	$P_{cal} \times 10^6$	$P_{obs} \times 10^6$	$P_{cal} \times 10^6$	$P_{obs} \times 10^6$	$P_{cal} \times 10^6$	$P_{obs} \times 10^6$	$P_{cal} \times 10^6$
Levels	$^4P_{1/2}$	4.28	0.885	5.69	2.59	4.18	2.27	3.52	1.65
	$^4G_{11/2}$	2.08	0.681	6.75	0.891	5.17	0.996	3.63	0.691
	$^4G_{9/2}$	2.36	4.29	6.56	6.67	4.85	6.95	3.88	4.98
	$^2G_{9/2}$	4.72	1.20	6.05	1.71	4.69	1.84	4.00	1.31
	$^4G_{7/2}$	5.61	8.40	9.79	1.35	7.09	13.5	8.21	10.6
	$^4G_{5/2}$	31.6	36.7	35.5	39.8	33.9	41.6	38.7	44.3
	$^4F_{9/2}$	2.46	2.02	13.4	39.8	33.9	41.6	38.7	44.3
	$^4F_{7/2}$	18.1	19.5	15.2	20.2	19.0	24.9	12.9	17.0
	$^4F_{5/2}$	12.9	19.4	22.2	24.8	21.9	28.0	14.5	19.4
	$^4F_{3/2}$	2.12	4.77	5.08	9.90	2.80	9.45	1.61	6.76
	r.m.s. dev.	$\pm 3.39 \times 10^{-6}$		$\pm 5.24 \times 10^{-6}$		$\pm 5.03 \times 10^{-6}$		$\pm 3.61 \times 10^{-6}$	
T_λ Parameter	$T_2 \times 10^{-9}$	1.78		1.10		1.36		1.90	
	$T_4 \times 10^{-9}$	1.01		2.95		2.58		1.88	
	$T_6 \times 10^{-9}$	3.31		3.24		6.10		2.79	
	T_4/T_6	0.30		0.91		0.62		0.67	

TABLE-4
OBSERVED & CALCULATED VALUES OF OSCILLATOR STRENGTH (P) & JUDD OFELT PARAMETER (T_λ) OF THE BANDS RECORDED FOR Nd(III) ION SYSTEMS INVOLVING LIGAND ENVIRONMENT (1:2 molar ratio) IN DMF SOLVENT

		Nd(III) ion systems involving ligand environment in DMF solvent					
		Nd(III) with L_4		Nd(III) with L_5		Nd(III) with L_6	
		$P_{obs} \times 10^6$	$P_{cal} \times 10^6$	$P_{obs} \times 10^6$	$P_{cal} \times 10^6$	$P_{obs} \times 10^6$	$P_{cal} \times 10^6$
Levels	$^4P_{1/2}$	2.61	1.29	3.92	0.932	3.94	0.875
	$^4G_{11/2}$	3.02	0.424	4.20	0.345	3.99	0.288
	$^4G_{9/2}$	3.39	3.32	4.56	2.67	4.63	2.30
	$^2G_{9/2}$	2.93	0.843	4.86	0.684	4.35	0.582
	$^4G_{7/2}$	5.42	7.70	7.09	6.61	4.87	5.72
	$^4G_{5/2}$	32.0	35.9	36.1	37.9	29.1	31.5
	$^4F_{9/2}$	2.33	1.07	4.26	0.913	1.09	0.737
	$^4F_{7/2}$	6.22	9.40	8.62	8.10	4.44	6.42
	$^4F_{5/2}$	8.64	11.8	5.47	9.67	5.91	8.04
	$^4F_{3/2}$	1.16	4.86	3.19	3.65	0.559	3.30
	r.m.s. dev.	$\pm 2.61 \times 10^{-6}$		$\pm 2.79 \times 10^{-6}$		$\pm 2.56 \times 10^{-6}$	
T_λ Parameter	$T_2 \times 10^{-9}$	1.59		1.92		1.54	
	$T_4 \times 10^{-9}$	1.47		1.06		0.997	
	$T_6 \times 10^{-9}$	1.50		1.31		1.02	
	T_4/T_6	0.98		0.80		0.97	

Nd(III) ion in environment of ligands L_1 to L_6

The order of symmetry parameter for systems under study is as follows:

$$L_4 > L_6 > L_1 > L_5 > L_3 > L_2$$

T_4/T_6 changes from 0.981 to 0.628 (Figs. 1 and 2). T_4/T_6 ratio shows that

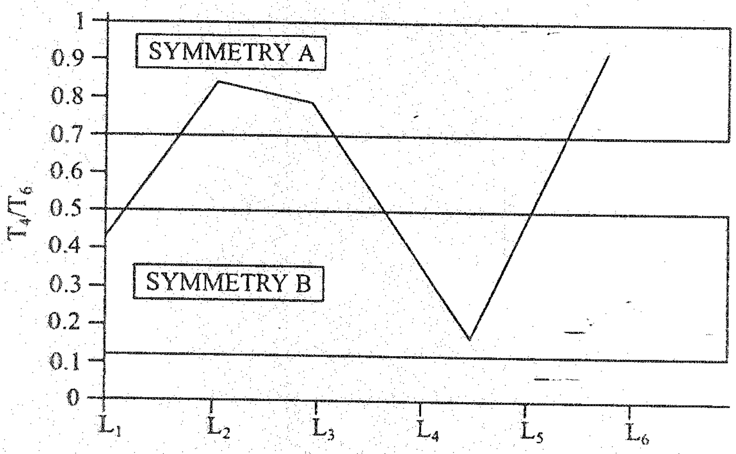


Fig. 1. Symmetery variation with reference to T_4/T_6 ratio value of various Pr(III) ion systems in DMF solvent

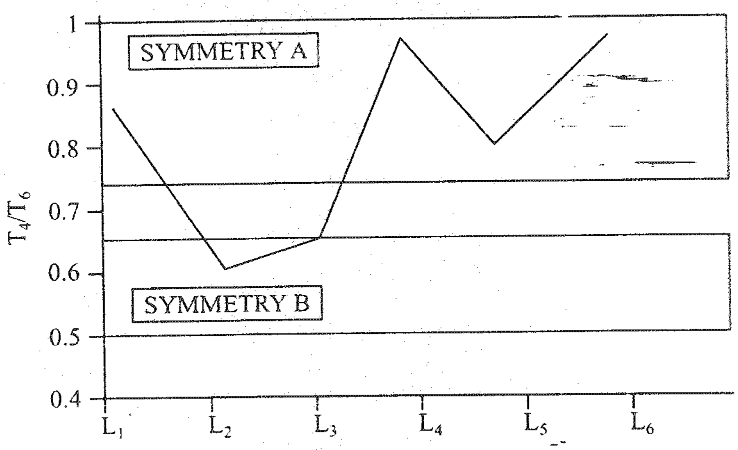


Fig. 2. Symmetery variation with reference to T_4/T_6 ratio value of various Nd(III) ion systems in DMF solvent

change in group (—COOH, —$COOCH_3$ and —$COOC_2H_5$) does not make appreciable change in the value of T_4/T_6, but the change in position of NH_2 group from *ortho* to *para* position significantly changes the ratio, *i.e.*, change in symmetry around Nd(III) ion.

	Pr (III)					Nd(III)					
	$P_{obs.}$	T_4	T_6	T_4/T_6	r.m.s. dev.	$P_{obs.}$	T_2	T_4	T_6	T_4/T_6	r.m.s. dev.
Max	L_3	L_3	L_3	L_6	L_3	L_3	L_5	L_1	L_2	L_4	L_1
Min	L_4	L_5	L_6	L_5	L_5	L_6	L_1	L_6	L_6	L_2	L_6

The small rms deviation in observed oscillator strength value (P_{obs}) and calculated oscillator strength value (P_{cal}) for both Pr(III) and Nd(III) systems indicate the applicability of Judd-Ofelt theory for the interpretation of the spectra.

The highest value of the oscillator strength has been found for 1 : 2 metal-ligand stoichiometry in DMF solvent. The M-L stoichiometry and solvent interaction affect the oscillator strength. The complexation and covalency have been found related to spectral intensity in terms of oscillator strength. Higher the value of oscillator strength, higher will be complextion and covalency. Hence it may be concluded that interaction of the lanthanide, *i.e.*, Pr(III) and Nd(III) ions with ligands has not been ionic but covalent in nature.

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