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Characterization of Some Nd(III) Sulphonanilide Complexes in terms of Electronic Spectral Parameters

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Nine complexes of Nd(III) with sulphonanilide have been characterized on the basis of various electronic spectral parameters, *viz.*, Judd-Ofelt parameter, symmetry parameter, nephealuxetic ratio and bonding parameters. The study provides useful information about M-L interactions.

Key Words: Electronic spectral parameters, Doped Nd(III) system, Sulphonanilide.

INTRODUCTION

After the publication of Judd-Ofelt theory[1–3] for lanthanide intensities, a great deal of work has been reported on the measurement of *f-f* transitions of free and complexed ions of lanthanides in different chemical environments by several workers[4–7]. Owing to the poor thermodynamic stability of lanthanide complexes, a modified doped model[8] is undertaken to record solution spectra in DMF medium using spectrophotometer.

In the present work, various electronic spectral parameters have been evaluated for Nd(III) systems by using computerized programme, as designed by earlier workers[9]. The study involves various parameters like Judd-Ofelt parametrers (T_λ), bonding parameters (β and $b^{1/2}$) and symmetry parameter (T_4/T_6) which provides important information about M-L interaction and about change in symmetry around Nd(III) ion in different ligand environments.

EXPERIMENTAL

Nine systems were prepared by using $NdCl_3 \cdot 6H_2O$ (provided by Rare Earth Ltd., Kerela) and ligands L_1 to L_9 (Fig. 1) in DMF medium by using standard methods[10]. Solution spectra have been taken by standard spectrophotometer (systronic 106) in the range 520–950 nm.

Ligands (L_1 to L_9)

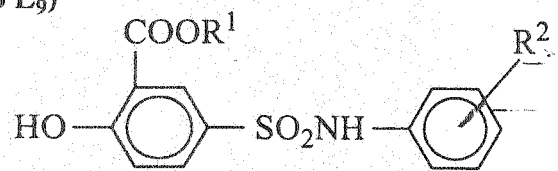

Fig. 1.

where R^1 = H, CH_3, C_2H_5 and R^2 = *o*-NO_2, *m*-NO_2, *p*-NO_2

Calculation of parameters: Value of oscillator strength is calculated by the equation

$$P = 4.6 \times 10^{-9} E_m \Delta\nu_{1/2}$$

where E_m = molar extinction coefficient, $\Delta\nu_{1/2}$ = half band width

Values of Judd-Ofelt parameters have been calculated by using the equation

$$P_{obs.} = [U^2]^2\nu T_2 + [U^4]^2\nu T_4 + [U^6]^2\nu T_6$$

RESULTS AND DISCUSSION

Values of various electronic spectral parameters are presented in Tables 1 to 6. The average value of nephelauxetic ratio (β) has been found to be 0.9929. Using the value of β, the value of bonding parameter ($b^{1/2}$) has been computed and it has been found to be 0.0585. The positive value of $b^{1/2}$ infers covalency in metal-ligand bonding.

TABLE-1
OBSERVED AND CALCULATED VALUES OF OSCILLATOR STRENGTH OF THE BANDS RECORDED FOR Nd(III) ION SYSTEMS INVOLVING LIGAND ENVIRONMENT IN DMF SOLVENT

		Nd(III) ion systems involving ligand environment (1 : 2 molor ratio) in DMF solvent							
S.No.	Levels	Free Nd(III) ion		Nd(III) with L_1		Nd(III) with L_2		Nd(III) with L_3	
		$P_{obs} \times 10^6$	$P_{cal} \times 10^6$	$P_{obs} \times 10^6$	$P_{cal} \times 10^6$	$P_{obs} \times 10^6$	$P_{cal} \times 10^6$	$P_{obs} \times 10^6$	$P_{cal} \times 10^6$
1.	$^4G_{5/2}$	24.42	24.43	44.38	43.72	38.14	38.15	41.37	41.8
2.	$^4F_{9/2}$	0.90	1.67	4.25	2.81	3.71	2.63	3.41	2.86
3.	$^4F_{7/2}$	15.66	14.88	24.12	24.51	21.99	23.14	23.67	24.97
4.	$^4F_{5/2}$	17.96	18.78	34.42	33.01	31.51	30.35	33.94	33.25
5.	$^4F_{3/2}$	8.59	7.92	15.03	15.36	12.68	13.66	14.06	15.17
r.m.s. dev.		$\pm 6.79 \times 10^{-7}$		$\pm 9.73 \times 10^{-7}$		$\pm 9.81 \times 10^{-7}$		$\pm 8.82 \times 10^{-7}$	

TABLE-2
OBSERVED AND CALCULATED VALUES OF OSCILLATOR STRENGTH OF THE BANDS RECORDED FOR Nd(III) ION SYSTEMS INVOLVING LIGAND ENVIRONMENT IN DMF SOLVENT

		Nd(III) ion systems involving ligand environment (1 : 2 molor ratio) in DMF solvent					
S.No.	Levels	Nd(III) with L_4		Nd(III) with L_5		Nd(III) with L_6	
		$P_{obs} \times 10^6$	$P_{cal} \times 10^6$	$P_{obs} \times 10^6$	$P_{cal} \times 10^6$	$P_{obs} \times 10^6$	$P_{cal} \times 10^6$
1.	$^4G_{5/2}$	32.13	30.93	27.45	26.5	29.73	28.69
2.	$^4F_{9/2}$	3.07	2.13	2.26	1.57	2.26	1.85
3.	$^4F_{7/2}$	20.01	18.98	14.45	13.58	17.92	16.60
4.	$^4F_{5/2}$	24.82	24.04	19.02	18.46	20.88	20.65
5.	$^4F_{3/2}$	11.17	10.30	9.45	8.71	9.71	8.61
r.m.s. dev.		$\pm 9.74 \times 10^{-7}$		$\pm 7.74 \times 10^{-7}$		$\pm 9.33 \times 10^{-7}$	

TABLE-3
OBSERVED AND CALCULATED VALUES OF OSCILLATOR STRENGTH OF THE BANDS RECORDED FOR Nd(III) ION SYSTEMS INVOLVING LIGAND ENVIRONMENT IN DMF SOLVENT

		Nd(III) ion systems involving ligand environment (1 : 2 molor ratio) in DMF solvent					
S.No.	Levels	Nd(III) with L_7		Nd(III) with L_8		Nd(III) with L_9	
		$P_{obs} \times 10^6$	$P_{cal} \times 10^6$	$P_{obs} \times 10^6$	$P_{cal} \times 10^6$	$P_{obs} \times 10^6$	$P_{cal} \times 10^6$
1.	$^4G_{5/2}$	30.64	30.07	25.41	25.31	27.46	26.88
2.	$^4F_{9/2}$	1.69	2.00	1.05	1.71	1.37	1.82
3.	$^4F_{7/2}$	19.10	17.85	16.11	15.26	17.67	16.25
4.	$^4F_{5/2}$	22.00	22.43	18.46	19.18	19.89	20.49
5.	$^4F_{3/2}$	10.57	9.50	8.83	8.10	9.93	8.75
r.m.s. dev.		$\pm 8.13 \times 10^{-7}$		$\pm 6.64 \times 10^{-7}$		$\pm 9.38 \times 10^{-7}$	

TABLE-4
COMPUTED VALUES OF T_λ PARAMETERS FOR Nd(III) ION SYSTEMS INVOLVING LIGAND ENVIRONMENT IN DMF SOLVENT

S. No.	Nd(III) System	$T_2 \times 10^9$	$T_4 \times 10^9$	$T_6 \times 10^9$	T_4/T_6
1.	Free Nd(III)ion	0.36	2.46	2.37	1.03
2.	Nd-L_1	0.45	4.99	3.84	1.29
3.	Nd-L_2	0.36	4.37	3.65	1.19
4.	Nd-L_3	0.35	4.91	3.94	1.24
5.	Nd-L_4	0.43	3.23	3.03	1.06
6.	Nd-L_5	0.35	2.83	2.11	1.34
7.	Nd-L_6	0.55	2.67	2.66	1.00
8.	Nd-L_7	0.49	2.95	2.84	1.04
9.	Nd-L_8	0.40	2.51	2.43	1.03
10.	Nd-L_9	0.40	2.72	2.58	1.05

The covalency in M-L bond is indicated by red-shift in energies of various bands as compared to lanthanide ion free value (Table-5). These values have been considered to calculate nephelauxetic ratio (β) and bonding parameter ($b^{1/2}$). Symmetry parameter (T_4/T_6) values for Nd(III) systems have been found to vary from 1.00 to 1.34. The change in T_4/T_6 values suggests the change in stereo-environment around lanthanide ion. Oscillator strength for hypersensitive transition varies from 25.31×10^{-6} to 43.72×10^{-6}. This increase in intensity of hypersensitive band also suggests M-L interaction.

TABLE-5
OBSERVED VALUES OF ENERGIES (cm^{-1}) OF FOUR BANDS FOR VARIOUS Nd(III) ION SYSTEMS IN DMF SOLVENT

S. No.	Levels Nd(III) System	$^4G_{5/2}$	$^4F_{9/2}$	$^4F_{7/2}$	$^4F_{5/2}$	$^4F_{3/2}$
1.	Free Nd(III) ion	16920	14490	13300	12200	11310
2.	Nd-L1	16980	14510	13330	12220	11340
3.	Nd-L2	16950	14490	13280	12210	11300
4.	Nd-L3	17010	14530	13350	12240	11350
5.	Nd-L4	17060	14580	13400	12270	11380
6.	Nd-L5	17040	14560	13370	12250	11360
7.	Nd-L6	17120	14600	13420	12290	11390
8.	Nd-L7	17210	14640	13420	12320	11430
9.	Nd-L8	17150	14620	13420	12290	11390
10.	Nd-L9	17240	14660	13420	12350	11420

TABLE-6
COMPUTED VALUES OF β and $b^{1/2}$ FOR Nd(III) SYSTEMS

S. No.	Band	Average energy [in cm^{-1}]	β	$b^{1/2}$
1.	$^4G_{5/2}$	17048.88	0.9889	0.0744
2.	$^4F_{9/2}$	14555.55	0.9928	0.0600
3.	$^4F_{7/2}$	13365.55	0.9959	0.0452
4.	$^4F_{5/2}$	12254.44	0.9922	0.0624
5.	$^4F_{3/2}$	11361.11	0.9948	0.0509
		Mean	0.9929	0.0585

Free ion values for different bands of Nd(III) ion: For $^4G_{5/2}$ band: 17240 cm^{-1}; for $^4F_{9/2}$: 14660 cm^{-1}; for $^4F_{7/2}$: 13420 cm^{-1}; for $^4F_{5/2}$: 12350 cm^{-1}; for $^4F_{3/2}$: 11420 cm^{-1}.

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REFERENCES

1. B.R. Judd, *Phys. Rev. (USA)*, **127**, 750 (1962).
2. G.S. Ofelt, *J. Chem. Phys. (USA)*, **37**, 511 (1962).
3. W.T. Carnall, P.R. Fields and B.G. Wybourne, *J. Chem. Phys. (USA)*, **42**, 3797 (1965).
4. S.P. Tandon and P.C. Mehta, *J. Chem. Phys. (USA)*, **52**, 4313 (1970).
5. S.N. Mishra and G.K. Joshi, *Indian J. Pure Appl. Phys.*, **19**, 279 (1981).
6. S.S.L. Surana, M. Singh and S.N. Misra, *J. Inorg. Nucl. Chem.*, **42**, 61 (1980).
7. R.D. Peacock, *J. Chem. Soc. A.*, 2028 (1971); *Molec. Phys.*, **25**, 817 (1973); *Chem. Phys. Lett.*, **16**, 590 (1970).
8. B.K. Gupta, G.K. Joshi and P.R. Bhati, *Indian J. Pure Appl. Phys.*, **28**, 525 (1990).
9. P.R. Bhati, K.P. Soni, G.K. Joshi and S.N. Swami, *Asian J. Chem.*, **4**, 828 (1992).
10. G.K. Joshi, *Indian J. Pure Appl. Phys.*, **21**, 224 (1983).

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