



ELECTRONIC SPECTRAL CHARACTERIZATION OF Dy(III) SYSTEMS INVOLVING ENVIRONMENT OF 'N' & 'O' DONOR ATOM LIGANDS IN POLAR APROTIC SOLVENT

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ABSTRACT

Electronic spectral parameters viz. intensity parameters (P , T_2 , T_4 , T_6 , σ), bonding parameters (β , $b^{1/2}$, $\delta\%$, η), symmetry parameter- T_4/T_6 , co-ordination parameter- T_4/T_6 , Peacock constant- K' and thermodynamic parameter (A , TET , Q , r_p) have been analyzed for Dy(III) systems with 'N' and 'O' donor atom ligands, on the basis of theories given by Lande, Carnall and Judd Ofelt. Various electronic spectral parameters and thermodynamic parameter provide some extent of covalent characters in M-L bond in lanthanide complexes.

Key words: Dysprosium (III) ion, Electronic spectral parameters, thermodynamic parameter lanthanide complex.

Introduction

Lanthanide coordination chemistry is very important and one of the most focused areas of research⁽¹⁻³⁾. The intriguing structures⁽⁴⁻⁶⁾ and the potential uses in a wide and diverse areas like diagnosis tools in biology⁽⁷⁾, catalysis⁽⁸⁾, luminescence⁽⁹⁾ and magnetism⁽¹⁰⁾ reinforce to interest in the field of chemical science especially in lanthanide coordination chemistry.

The complexing behavior of lanthanide ions has not been studied extensively as compared to the transition metal ions. Despite the biological importance and potential applications of lanthanide complexes⁽¹¹⁻¹³⁾, they have not received proper attention because the complexation behavior of lanthanide (III) ions is differing from the d-block elements.

But after the publication of Judd – Ofelt theory⁽¹⁴⁻¹⁵⁾ for the lanthanide complexes, a great deal of work has been reported on the measurement of f-f transitions for free and aquo/solvent ions of lanthanide in different chemical environment by several workers⁽¹⁶⁻¹⁹⁾.

In the present study, six sulphonanilide ligands having N & O as donor atoms have been selected for complexation with Dy(III) ion and complexes were characterized through various electronic spectral parameters like intensity parameters (oscillator strength-P, Judd-Ofelt parameters- T_2 , T_4 and T_6 , r.m.s. deviation- σ), bonding parameters (Nephelauxetic ratio- β , bonding parameter- $b^{1/2}$, Sinha's covalency parameter- $\delta\%$, covalency angular overlap parameter- η), symmetry parameter- T_4/T_6 , co-ordination parameter- T_4/T_6 , thermodynamic parameter (thermodynamic efficiency of transition-TET, partition function of transition-Q, ratio of partition- r_p) & Peacock constant- K' . Partial and multiple regression method involving theories given by Slater-Condon, Lande, Carnall and Judd Ofelt used for determination of these parameters. The studies give valuable information regarding metal-Ligand bonding, spin-orbit interaction and inter electronic repulsion.

Experimental

In this method, standard grade chemicals-DyCl₃.6H₂O (molecular weight-376.95) and six sulphonanilide ligands (table-1) have been used for studies. Modified doped model technique have been used for preparation of systems with Dy(III) ions in which metal & ligand ratio has been taken as 1:2.

The solution spectrum of each system has been recorded in the range 355-950 nm by using standard spectrophotometer. All the systems were characterized by various electronic spectral & thermodynamic parameters. Different parameters were calculated by using partial and multiple regression method by using following formulae –

(I) Intensity Parameters

(A) Oscillator Strength (P):

In Dy(III) Doped Systems, we observed six peaks due to ${}^6F_{7/2}$, ${}^6F_{5/2}$, ${}^6F_{3/2}$, ${}^4I_{15/2}$, ${}^4F_{7/2}$ and ${}^4M_{19/2}$. The intensity of an absorption band is measured by oscillator strength, which is directly proportional to area under the absorption curve.

$$P = 4.315 \times 10^{-9} \int \epsilon \, dv \quad \text{Where } \epsilon = \text{Molar Absorptivity}$$

(B) R.M.S Deviation (σ):

From the calculated and observed values of oscillator strength, the values of r.m.s. deviation for systems have been computed by following equation-

$$\sigma = [\sum(P_{\text{cal}} - P_{\text{obs}})^2 / N]^{1/2}$$

(C) Judd-Ofelt Parameters (T_2, T_4, T_6):

The interaction between M-L are predominantly measured by three parameters known as Judd-Ofelt Parameters.

II. Bonding Parameters :

(A) Nephelauxetic ratio (β)

$$\beta = \nu_c / \nu_f$$

(Where ν_c & ν_f = wave numbers of f-f transition in spectra of complex and free ion respectively)

(B) Bonding Parameter ($b^{1/2}$)

$$b^{1/2} = [1/2 (1-\beta)]^{1/2}$$

(C) Sinha's Covalency parameters ($\delta\%$) :

$$\delta = [1 - \beta / \beta] \times 100$$

(D) Covalency angular overlap parameter (η) :

$$\eta = [1 - \beta^{1/2} / \beta^{1/2}]$$

III. Symmetry Parameter:

Judd-Ofelt parameter ratio T_4/T_6 is called Symmetry-parameter.

(iv) Co-ordination Parameter:

Judd-Ofelt parameter ratio T_4/T_2 is called Co-ordination parameter.

(v) Thermodynamic Parameters:

(A) Thermodynamic Efficiency = $\frac{\text{Work Function for transition}}{\text{Energy absorbed for transition}}$
of transition (**TET**)

(B) Partition Function of Transition (**Q**) = $g_i e^{-E/kT}$

(where $g_i = 2J + 1=16$)

(C) Ratio of Partition (**r_p**) = $\frac{\text{Q for lanthanide ion system (doped)}}{\text{Q for lanthanide ion (free ion in solvent)}}$

(vii) Peacock Constant (K') = $P_{\text{obs}} / \nu T_6$

Results and Discussion

Electronic Spectral Parameter:

The values of various electronic spectral parameters and thermodynamic parameter have been reported in table-2 to 5.

The calculated oscillator strength values of ${}^6F_{7/2}$, ${}^6F_{5/2}$, ${}^6F_{3/2}$, ${}^4I_{15/2}$, ${}^4F_{7/2}$ and ${}^4M_{19/2}$ bands were reported between 6.0933×10^{-6} & 14.8235×10^{-6} , 2.6456×10^{-6} & 7.1292×10^{-6} , 0.4991×10^{-6} & 1.3482×10^{-6} , 1.4131×10^{-6} & 3.0857×10^{-6} , 1.0908×10^{-6} & 3.3869×10^{-6} , 2.1363×10^{-6} & 5.2064×10^{-6} respectively.

The values of r.m.s. deviation for all systems have been computed from the calculated and observed values of oscillator strength. Low value of r.m.s. deviation prove Judd Ofelt theory. The r.m.s. values varies from 1.2297×10^{-9} to 2.3037×10^{-9} in systems. The order of the r.m.s. deviation was found as given below:

Dy(III)-L₄ < Dy(III)-L₁ < Dy(III)-L₅ < Dy(III)-L₆ < Dy(III)-L₃ < Dy(III)-L₂

Judd-Ofelt Parameters are indicative of degree of metal ligand (M-L) interaction (T₂), refractive Index of medium (T₄) and change in symmetry around the cation (T₆). The T₂, T₄, and T₆ values were found between 0.3113 x 10⁻⁹ & 4.2148 x 10⁻⁹, 0.0591 x 10⁻⁹ & 1.1396 x 10⁻⁹, 0.6181 x 10⁻⁹ & 1.6687 x 10⁻⁹ respectively.

Variation in symmetry parameter (T₄/T₆) & co-ordination parameter (T₄/T₂) values show the change in symmetry & co-ordination environment around central metal ion. The T₄/T₆ values were found between 0.0410 & 1.3381 whereas the T₄/T₂ values were observed between 0.1841 & 0.6065.

A constant value of peacock relation signifies the validity of Judd Ofelt theory. The peacock constant (K') for Dy(III) systems varies from 0.0733 to 0.3097. The average values of all systems were observed to be 0.1371.

Low and high value of bonding parameters (β, b^{1/2}, δ%, η) indicate weak and strong covalent character in metal-ligand bond. Nephelauxetic Ratio (β) depicts that how effectively bands of metal ions are shifted in presence of ligand environment. The positive value of bonding parameters (b^{1/2}) indicate covalent character in metal-ligand bonds while negative value show ionic character in metal-ligand interaction.

The values of nephelauxetic ratio (β) for Dy(III) systems were reported between 0.991216 & 0.997773 and the order of this ratio was found as given below:

Dy(III)-L₂ < Dy(III)-L₁ = Dy(III)-L₄ < Dy(III)-L₅ < Dy(III)-L₃ = Dy(III)-L₆

The values of bonding parameters (b^{1/2}) were observed between 0.033371 & 0.066274 and the order of this ratio was found as given below:

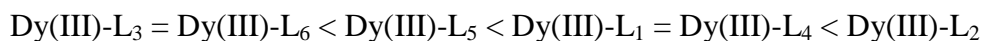
Dy(III)-L₃ = Dy(III)-L₆ < Dy(III)-L₅ < Dy(III)-L₁ = Dy(III)-L₄ < Dy(III)-L₂

The percentage covalent character in metal ligand bond can be expressed by sinha's covalency parameter (δ%). Covalency angular overlap parameters (η) represents extent of overlapping between metal ion orbital and ligand orbital. Both parameters also indicate the covalent character in metal ligand bond. The values of sinha's covalency parameter (δ%) were found between 0.2232 & 0.8862 and the values of covalency angular overlap parameters (η) were found between 0.001116 & 0.004421.

Thermodynamic parameters

The values of work function (A) for Dy(III) systems were recorded between 24485.6 & 24681.05 whereas the values of TET were observed from 1.1167 to 1.1218. The values of

partition function (Q) and ratio of partition function (r_p) were found between 1.7401×10^{-45} & 3.4885×10^{-45} and 1.2665 & 2.5390 , respectively. The order of partition function and ratio of partition function are found as given below:



The thermodynamic parameters resulting from spectroscopic data support the covalency between Dy(III) ion and the surrounding ligand. The significance of thermodynamic parameters are well understood but their computation from spectroscopic data proposes the microscopic behavior of the f-f transition.

Acknowledgement

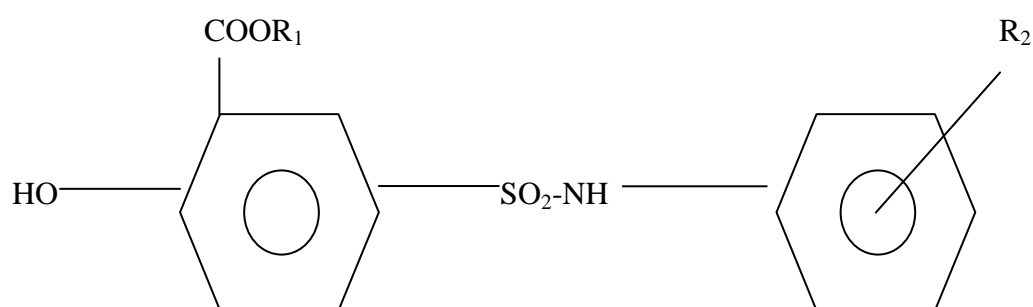
The authors are thankful to Dr. G. K. Barupal (Department of Botany, Govt. Dungar College, Bikaner), Dr. J. S. Acharya, Dr. A. Gupta and Dr. H. S. Bhandari (Department of Chemistry, Govt. Dungar College, Bikaner) for their whole hearted cooperation.

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Table –1. Representation of Sulphonanilides



Sulphonanilides	Groups and their Position	
	R ¹	R ²
L ₁	H	o-NO ₂
L ₂	H	m-NO ₂
L ₃	H	p-NO ₂
L ₄	CH ₃	o-NO ₂
L ₅	CH ₃	m-NO ₂
L ₆	CH ₃	p-NO ₂

Table-2. Observed and Calculated Values of Oscillator Strength (P) and Judd Ofelt Parameters (T_λ) of the Bands Recorded for Dy(III) Ion Systems (Dy-L₁ to Dy-L₃) involving Ligand Environment (1:2 Molar Ratio) in DMF Solvent

levels	Dy(III) ion systems involving ligand environment in DMF solvent						
	Bands	Dy(III) with L ₁		Dy(III) with L ₂		Dy(III) with L ₃	
		P _{obs} X 10 ⁶	P _{cal} X 10 ⁶	P _{obs} X 10 ⁶	P _{cal} X 10 ⁶	P _{obs} X 10 ⁶	P _{cal} X 10 ⁶
⁶ F _{7/2}	14.1067	14.3273	7.4290	6.0933	12.1992	11.4028	
⁶ F _{5/2}	7.4750	6.9043	4.3608	2.6456	8.0960	6.1518	
⁶ F _{3/2}	1.3378	1.3057	2.8405	0.4991	2.6412	1.1618	
⁴ I _{15/2}	2.6067	2.6198	4.1934	1.4131	4.2780	2.1283	
⁴ F _{7/2}	4.2763	3.2422	5.7316	2.0535	4.9680	1.0908	
⁴ M _{19/2}	2.1836	5.0221	2.7499	2.1363	2.6496	4.0567	
r.m.s. dev.X 10 ⁶		1.2584		2.3037		2.1694	
T _λ parameter	T ₂ X 10 ⁹	1.7883		3.2650		0.3113	
	T ₄ X 10 ⁹	1.0846		0.8271		0.0591	
	T ₆ X 10 ⁹	1.6161		0.6181		1.4408	
	T ₄ / T ₆	0.6711		1.3381		0.0410	
	T ₄ / T ₂	0.6065		0.2533		0.1898	

Table-3. Observed and Calculated Values of Oscillator Strength (P) and Judd Ofelt Parameters (T_λ) of the Bands Recorded for Dy(III) Ion Systems (Dy-L₄ to Dy-L₆) involving Ligand Environment (1:2 Molar Ratio) in DMF Solvent

levels	Dy(III) ion systems involving ligand environment in DMF solvent						
	Bands	Dy(III) with L ₄		Dy(III) with L ₅		Dy(III) with L ₆	
		P _{obs} X 10 ⁶	P _{cal} X 10 ⁶	P _{obs} X 10 ⁶	P _{cal} X 10 ⁶	P _{obs} X 10 ⁶	P _{cal} X 10 ⁶
⁶ F _{7/2}	14.8005	14.8235	12.7458	12.7816	13.9196	13.3517	
⁶ F _{5/2}	7.5440	7.1292	7.4750	6.4206	8.1803	6.8112	
⁶ F _{3/2}	1.9435	1.3482	1.3378	1.2135	2.6818	1.2863	
⁴ I _{15/2}	3.2775	3.0857	3.0667	2.5695	4.3255	2.7953	
⁴ F _{7/2}	4.2780	3.3869	4.2550	2.3194	4.9956	2.1843	
⁴ M _{19/2}	2.4288	5.2064	2.1160	4.5229	2.6717	4.7468	
r.m.s. dev.X 10 ⁶		1.2297		1.3488		1.7652	
T _λ parameter	T ₂ X 10 ⁹	4.2148		2.4978		3.0501	
	T ₄ X 10 ⁹	1.1396		0.6559		0.5615	
	T ₆ X 10 ⁹	1.6687		1.5019		1.5953	
	T ₄ / T ₆	0.6829		0.4367		0.3519	
	T ₄ / T ₂	0.2704		0.2626		0.1841	

Table-4. Computed Values Of β , $b^{1/2}$, δ and η for Dy(III) Doped Systems

S. No.	Dy(III) doped systems	Average energy [in cm^{-1}]	β	$b^{1/2}$	δ	η
1.	Dy(III)-L ₁	22002.20	0.995577	0.047025	0.4442	0.002219
2.	Dy(III)-L ₂	21905.81	0.991216	0.066274	0.8862	0.004421
3.	Dy(III)-L ₃	22050.72	0.997773	0.033371	0.2232	0.001116
4.	Dy(III)-L ₄	22002.20	0.995577	0.047025	0.4442	0.002219
5.	Dy(III)-L ₅	22026.43	0.996674	0.040781	0.3337	0.001667
6.	Dy(III)-L ₆	22050.72	0.997773	0.033371	0.2232	0.001116

Table-5. Thermodynamic Properties for Dy(III) Doped Systems

S. No	Dy(III) doped systems	Energy for hypersensitive transition (${}^4\text{I}_{15/2}$) (cm^{-1})	Oscillator strength for hypersensitive transition (${}^4\text{I}_{15/2}$)($\times 10^6$)	Work function (A) (cm^{-1})	Thermo dynamic efficiency of the transition (TET)	Partition function $Q = \sum g_i e^{-E_i/KT}$ ($\times 10^{45}$)	Ratio of partition function (r_p)	Peacock constant (K') = $P_{\text{obs}} / \nu T_6$
1.	Dy(III)-L ₁	22002.20	2.6067	24681.05	1.1218	2.1964	1.5986	0.0733
2.	Dy(III)-L ₂	21905.81	4.1934	24485.60	1.1178	3.4885	2.5390	0.3097
3.	Dy(III)-L ₃	22050.72	4.2780	24626.34	1.1168	1.7401	1.2665	0.1346
4.	Dy(III)-L ₄	22002.20	3.2775	24633.33	1.1196	2.1964	1.5986	0.0893
5.	Dy(III)-L ₅	22026.43	3.0667	24671.42	1.1201	1.9552	1.4231	0.0927
6.	Dy(III)-L ₆	22050.72	4.3255	24624.04	1.1167	1.7401	1.2665	0.1229

Where: $K = 0.6945$, $T = 300\text{K}$