

Characterization of Some Rare Earth Complexes in Terms of Thermodynamic & Electronic Spectral Parameters

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Abstract: Electronic-Spectral And Thermodynamic Parameter Of Tm(III) Systems In DMSO Medium Involving Sulphonanilide Ligands Have Been Examined With “O”, “N” And “S” Donor Atoms Ligand On The Basis Of Theories Given By Lande, Carnall & Judd Ofelt. Various Parameters Provide Covalent Character In Metal Ligand Bond.

Keywords: Thulium (III), *f-f* Transition, Electronic Spectral Parameters.

Date Of Submission: 01-08-2017

Date Of Acceptance: 19-08-2017

Introduction

The Deeply Buried 4f-Orbitals Are Not Much Affected By Ligand Environment And Give Rise To Narrow *f-f* Transition, But Their Bonding Tendency With Various Types Of Ligands Is Also Found In Literature⁽¹⁻²⁾. Most Of *f-f* Transitions Of Trivalent Lanthanide Have Intensities, Which Are Little Affected By Environment Of Ligands. A Few However, Are Very Sensitive To Ligand Environment, Are Usually More Intense When Complexed, Such Transitions Have Been Called Hypersensitive Transitions⁽³⁻⁴⁾. After The Publication Of Judd-Ofelt Theory⁽⁵⁻⁷⁾ For Lanthanide Intensities, A Great Deal Of Work Has Been Reported On The Measurement Of *f-f* Transitions Of Free & Complexed Ion Of Lanthanide In Different Chemical Environment By Several Workers⁽⁸⁻¹⁵⁾.

In The Present Paper, Some Tm(III) Complexes Have Been Characterized In Terms Of Electronic Spectral Parameters. To Evaluate Metal-Ligand Interaction, Different Parameters Such As- Intensity Parameters(Oscillator Strength-P, Judd-Ofelt Parameters-T₂, T₄ And T₆ R.M.S. Deviation-σ), Bonding Parameters (Nephelauxetic Ratio-β, Bonding Parameter-b^{1/2}, Sinha’s Covalency Parameter-δ%, Covalency Angular Overlap Parameter-η), Symmetry Parameter-T₄/T₆, Co-ordination Parameter-T₄/T₂, Thermodynamic Parameter(Thermodynamic Efficiency Of Transition-TET, Partition Function Of Transition-Q, Ratio Of Partition-r_p), Formation Constant-K & Peacock Constant-K’ Have Been Examined. On Examining Electronic-Spectral Parameters Of The Systems Under Study, The Interaction In Metal And Ligands Will Be Inferred. The Study Will Also Provide Some Useful Information Regarding Inter-Electronic Repulsions, Spin-Orbit Interaction And Symmetry Changes Around Lanthanide Ion.

Experimental

Six Systems Were Prepared By Using Standard Grade Chemicals TmCl₃.6H₂O & Ligands L₁ To L₆ (Fig. I) In DMSO Medium By Using Standard Method⁽¹⁶⁾. Solution Spectra Have Been Taken For Tm(III) Systems By Standard Spectrophotometer In The Range 400-820 nm. A Simplified Representation Of Six Sulphonanilides Ligands (L₁ To L₆) Is Given In Fig.-I.

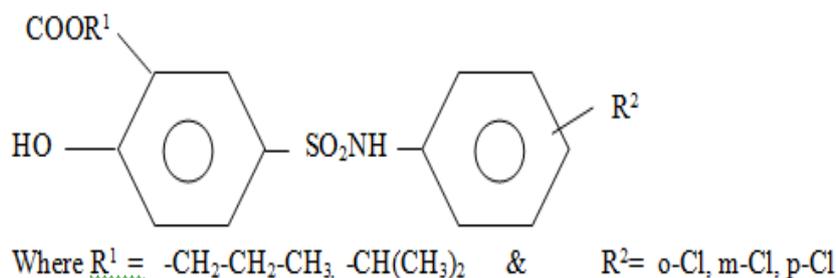


Fig.-I : Representation Of Sulphonanilides

Calculation Of Various Parameters

(I) Intensity Parameters

(A) Oscillator Strength (P):

In Tm(III) Doped Systems, We Observed Four Peaks⁽¹⁷⁻¹⁸⁾ Due To 1G_4 , 3F_2 , 3F_3 & 3H_4 . The Intensity Of An Absorption Band Is Measured By Oscillator Strength, Which Is Directly Proportional To Area Under The Absorption Curve.

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

(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 -

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

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

The Interaction Between M-L Are Predominantly Measured By Three Main Parameter Known As Judd-Ofelt Parameters⁽⁵⁻⁶⁾ (T_2 , T_4 And T_6).

(II) Symmetry Parameter⁽¹⁹⁻²⁰⁾

Judd-Ofelt Parameter Ratio T_4/T_6 Is Called Symmetry-Parameter.

(III) Co-ordination Parameter⁽¹⁹⁻²⁰⁾

Judd-Ofelt Parameter Ratio T_4/T_2 Is Called Co-Ordination Parameter.

(IV) Hypersensitive Transitions⁽²¹⁻²²⁾

The Bands Having Oscillator Strength $\sim 10^{-5}$ And Found Much Sensitive To The Ligands & Solvents Are Called Hypersensitive Transitions. For Tm(III): $^3H_6 - ^3H_4$ Is Hypersensitive Transitions In Four Bands.

(V) Peacock Constant⁽¹¹⁾ (K')

Oscillator Strength (P) Is Directly Proportional To νT_6 For Hypersensitive Transitions, This Linear Correlation Has Been Proposed By **R. D. Peacock**⁽¹¹⁾.

$$K' = P_{\text{obs}} / \nu T_6.$$

(VI) Bonding Parameters⁽²³⁻²⁵⁾

(A) Nephelauxetic Ratio (β):

The Shifting Of Electronic Spectral Bands During Complexation Can Be Represented In Terms Of Nephelauxetic Ratio (β) As Follows-

$$\beta = \nu_C / \nu_F$$

Where:- ν_C & ν_F Are Wave Numbers Of $f-f$ Transition For 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):

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

(VII) Thermodynamic Parameters⁽²⁶⁻²⁸⁾

(a) Thermodynamic Efficiency = Of Transition (TET)	$\frac{\text{Work Function For Transition}}{\text{Energy Absorbed For Transition}}$
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By Using Thermodynamic Relation-

$$A = E - TS \text{ And } S = K \ln P_{\text{obs}}$$

Following Relation May Be Obtained-

$$A = E - KT \ln P_{\text{obs}}$$

Where:-

A = Work Function (Cm^{-1})

E = Energy Absorbed For Hypersensitive Transition (Cm^{-1})

K = Boltzmann Constant, T = Absolute Temp.

P_{obs} = Oscillator Strength Of Transition, S = Absolute Energy.

(B) Partition Function Of Transition (Q) = $g_i e^{-E/KT}$

Where: For Tm - $g_i = 2J + 1 = 9$

$$(C) \text{ Ratio Of Partition } (r_p) = \frac{Q \text{ For Lanthanide Ion System (Doped)}}{Q \text{ For Lanthanide Ion (Free Ion In Solvent)}}$$

Various Parameters For Tm(III) Systems Were Calculated By Using Partial And Multiple Regression Method, Which Are Tabulated In Tables I To IV .

Table -I
Observed And Calculated Values Of Oscillator Strength (P) And Judd Ofelt Parameters (T_λ) Of The Bands Recorded For Tm(III) Ion Systems Involving Ligand Environment (1:2 Molar Ratio) In DMSO Solvent

Levels	Bands	Tm(III) Ion Systems Involving Ligand Environment In DMSO Solvent					
		Tm(III) With L ₁		Tm(III) With L ₂		Tm(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
	¹ G ₄	2.7407	3.6981	2.5546	3.8467	1.0085	0.3652
	³ F ₂	0.8293	1.5065	0.9966	1.9085	0.8187	0.3638
	³ F ₃	9.6593	10.3090	11.2308	12.1055	2.0294	1.5936
	³ H ₄	8.8275	9.3958	9.3722	10.1394	1.7545	1.3718
	r.m.s. Dev. X 10 ⁷	7.2810		9.8166		4.8921	
T _λ Parameter	T ₂ X 10 ⁹	1.5943		1.5218		0.1750	
	T ₄ X 10 ⁹	1.2209		1.3409		0.0998	
	T ₆ X 10 ⁹	0.3864		0.4901		0.0933	
	T ₄ / T ₆	3.1598		2.7360		1.0701	
	T ₄ / T ₂	0.7658		0.8811		0.5704	

Table –II
Observed And Calculated Values Of Oscillator Strength (P) And Judd Ofelt Parameters (T_λ) Of The Bands Recorded For Tm(III) Ion Systems Involving Ligand Environment (1:2 Molar Ratio) In DMSO Solvent

Levels	Bands	Tm(III) Ion Systems Involving Ligand Environment In DMSO Solvent					
		Tm(III) With L ₄		Tm(III) With L ₅		Tm(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
	¹ G ₄	2.1719	3.2426	0.9464	0.3263	0.8665	0.3009
	³ F ₂	1.0997	1.8529	0.8434	0.4050	0.8362	0.4363
	³ F ₃	9.8657	10.5885	2.0330	1.6129	2.0196	1.6365
	³ H ₄	8.5760	9.2092	1.7767	1.4079	1.7773	1.4409
	r.m.s. Dev. X 10 ⁷	8.1198		4.7146		4.3007	
T _λ Parameter	T ₂ X 10 ⁹	1.3887		0.1716		0.1698	
	T ₄ X 10 ⁹	1.0480		0.0760		0.0598	
	T ₆ X 10 ⁹	0.4766		0.1038		0.1119	
	T ₄ / T ₆	2.1990		0.7321		0.5351	
	T ₄ / T ₂	0.7547		0.4432		0.3525	

Table –III
Computed Values Of β, b^{1/2}, δ & η For Tm(III) Doped Systems

S. No.	Tm(III) Doped Systems	Average Energy [In Cm ⁻¹]	β	b ^{1/2}	δ	η
1	Tm(III)-L ₁	12676.20	0.996557	0.041493	0.345536	0.001726
2	Tm(III)-L ₂	12693.94	0.997951	0.032008	0.205323	0.001026
3	Tm(III)-L ₃	12712.03	0.999373	0.017702	0.062715	0.000313
4	Tm(III)-L ₄	12663.73	0.995577	0.047029	0.444315	0.002219
5	Tm(III)-L ₅	12706.47	0.998936	0.023060	0.106471	0.000532
6	Tm(III)-L ₆	12706.35	0.998927	0.023164	0.107430	0.000537

Table- IV
Thermodynamic Property

S. N.	Tm(III) Doped Systems	Energy For Hypersensitive Transition (${}^3\text{H}_4$) (Cm^{-1})	Oscillator Strength For Hypersensitive Transition (${}^3\text{H}_4$) ($\times 10^6$)	Work Function (A) (Cm^{-1})	Thermo Dynamic Efficiency Of The Transition (TET)	Partition Function $Q = g_e e^{-E/KT}$ ($\times 10^{26}$)	Ratio Of Partition Function (r_p)	Peacock Relation ($K' = P_{\text{obs}} / \nu T_6$)
1.	Tm(III) + L ₁	12676.20	8.827541	15100.90	1.191280	3.399227	1.233958	1.802226
2.	Tm(III) + L ₂	12693.94	9.372254	15106.16	1.190030	3.121821	1.133257	1.506483
3.	Tm(III) + L ₃	12712.03	1.754592	15473.35	1.217221	2.862185	1.039006	1.479171
4.	Tm(III) + L ₄	12663.73	8.576030	15094.46	1.191944	3.608818	1.310042	1.420916
5.	Tm(III) + L ₅	12706.47	1.776719	15465.18	1.217111	2.939540	1.067087	1.345819
6.	Tm(III) + L ₆	12706.35	1.777357	15464.98	1.217107	2.941259	1.067711	1.249775

Where:- K = 0.6945, T = 300K

Result And Discussion

Electronic Spectral Parameter:

The Values Of Various Electronic Spectral Parameters And Thermodynamic Parameter Have Been Reported In Table- I To IV .

From The Calculated And Observed Values Of Oscillator Strength, The Values Of r.m.s. Deviation For All Systems Have Been Computed, Low Value Of r.m.s. Deviation Prove Judd Ofelt Theory .

- The Calculated Oscillator Strength Values For ${}^1\text{G}_4$, ${}^3\text{F}_2$, ${}^3\text{F}_3$, ${}^3\text{H}_4$ Band Were Found Between 0.3009×10^{-6} & 3.8467×10^{-6} , 0.3638×10^{-6} & 1.9085×10^{-6} , 1.5936×10^{-6} & 12.1055×10^{-6} And 1.3718×10^{-6} & 10.1394×10^{-6} Respectively .

- The Values Of rms Deviation (σ) For Tm(III) Systems Were Found Between 4.3007×10^{-7} & 9.8166×10^{-7} And The Order Of rms Deviation Was Found As Given Below-

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

Judd -Ofelt Parameters Are Indicative Of Degree Of Metal Ligand (M-L) Interaction (T_2), Refractive Index Of Medium (T_4) And Change In Symmetry Around The Cation (T_6).

- T_2 Values For Tm(III) Systems Were Found Between 0.1698×10^{-9} & 1.5943×10^{-9} And The Order Of T_2 Values Were Found As Given Below-

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

- T_4 Values For Tm(III) Systems Were Found Between 0.0598×10^{-9} & 1.3409×10^{-9} And The Order Of T_4 Values Was Found As Given Below-

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

- T_6 Values For Tm(III) Systems Were Found Between 0.1875×10^{-9} & 0.2002×10^{-9} And The Order Of T_6 Values Was Found As Given Below-

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

Variation In Symmetry Parameter (T_4/T_6) & Co-Ordination Parameter (T_4/T_2) Values Show The Change In Symmetry & Co-Ordination Environment Around Central Metal Ion.

- T_4/T_6 Values For Tm(III) Systems Were Found Between 0.5351 & 3.1598 And The Order Of T_4/T_6 Values Was Found As Given Below-

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

- T_4/T_2 Values For Tm(III) Systems Were Found Between 0.3525 & 0.8811 And The Order Of T_4/T_2 Values Was Found As Given Below-

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

Constant Values Of Peacock Relation Signifies The Validity Of Judd-Ofelt Theory.

- The Peacock Constant (K_1') For Tm(III) Systems Varies From 1.249775 To 1.802226 And Its Average Value Is 1.467398 . Most Of The Systems Exhibit Constancy In Value Of K_1' And Also With Mean Value.

Nephelauxetic Ratio (β) Depicts That How Effectively Bands Of Metal Ions Are Shifted In Presence Of Ligand Environment. Low And High Value Of Bonding Parameters (β , δ , η) Indicate Weak & Strong Covalent Character In Metal-Ligand Bond Respectively.

- The Values Of Nephelauxetic Ratio (β) For Tm(III) Systems Were Found Between 0.995577 & 0.999373 And The Order Of Nephelauxetic Ratio Was Found As Given Below-
Tm(III)-L₄ < Tm(III)-L₁ < Tm(III)-L₂ < Tm(III)-L₆ < Tm(III)-L₅ < Tm(III)-L₃

Positive Value Of Bonding Parameter ($b^{1/2}$) Indicates Covalent Character In Metal-Ligand Bond While Negative Value Shows Ionic Character In Metal-Ligand Interaction.

- The Values Of Bonding Parameter ($b^{1/2}$) For Tm(III) Systems Were Found Between 0.017702 & 0.047029 And The Order Of $b^{1/2}$ - Value Was Found As Given Below-
Tm(III)-L₃ < Tm(III)-L₅ < Tm(III)-L₆ < Tm(III)-L₂ < Tm(III)-L₁ < Tm(III)-L₄

Percentage Covalent Character In Metal Ligand Bond Can Be Expressed By Sinha's Covalency Parameter ($\delta\%$). Covalency Angular Overlap Parameter (η) Represents Extent Of Overlapping Between Metal Ion Orbital And Ligand Orbital.

Sinha's Covalency Parameter- $\delta\%$ & Covalency Angular Overlap Parameter- η Also Indicate The Covalent Character In Metal Ligand Bond.

- The Values Of Sinha's Covalency Parameter ($\delta\%$) Were Found Between 0.062715 To 0.444315 And Values Of Covalency Angular Overlap Parameter (η) Were Found Between 0.000313 To 0.002219. The Order Of Sinha's Covalency Parameter ($\delta\%$) And Covalency Angular Overlap Parameter (η) For Tm(III) Systems Were Found As Given Below-
Tm(III)-L₃ < Tm(III)-L₅ < Tm(III)-L₆ < Tm(III)-L₂ < Tm(III)-L₁ < Tm(III)-L₄

Thermodynamic Parameters:

- The Values Of Work Function (A) For Tm(III) Systems Were Found Between 15094.46 & 15473.35 And The Order Of Work Function Was Found As Given Below-
Tm(III)-L₄ < Tm(III)-L₁ < Tm(III)-L₂ < Tm(III)-L₆ < Tm(III)-L₅ < Tm(III)-L₃
- The Values Of TET For Tm(III) Systems Were Found Between 1.190030 & 1.217221, And The Order Of TET Values Was Found As Given Below-
Tm(III)-L₂ < Tm(III)-L₁ < Tm(III)-L₄ < Tm(III)-L₆ < Tm(III)-L₅ < Tm(III)-L₃

The Values Of Partition Function (Q) And Ratio Of Partition Function (r_p) For Tm(III) Systems Were Found Between 2.862185×10^{-26} & 3.608818×10^{-26} And 1.039006 & 1.310042 Respectively.

Thus, The Order Of Partition Function And Ratio Of Partition Function Are Found As Given Below-
Tm(III)-L₃ < Tm(III)-L₅ < Tm(III)-L₆ < Tm(III)-L₂ < Tm(III)-L₁ < Tm(III)-L₄

The Thermodynamic Parameters Resulting From Spectroscopic Data Support The Covalency Between Lanthanide 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 Grateful To Principal Dungar College, Bikaner For Providing Necessary Facilities And To Dr H. K. Pandey, Dr R. P. Mathur, Dr R. S. Verma, Dr H .P. Yadav Dr M. Bhatnagar, Dr S. Jain, Dr S. Gupta, Dr N. Bhojak, Dr S. Sharma And Dr A. Gupta For Fruitful Discussion And Keen Interest In The Work.

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IOSR Journal of Computer Engineering (IOSR-JCE) is UGC approved Journal with Sl. No. 5019, Journal no. 49102.

Gourav Chawla . “Characterization of Some Rare Earth Complexes in Terms of Thermodynamic & Electronic Spectral Parameters.” International Journal of Engineering Science Invention (IJESI), vol. 6, no. 8, 2017, pp. 56–61.