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

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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).


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.
Calculation Of Various Parameters

(I) Intensity Parameters

(A) Oscillator Strength (P):
In Tm(III) Doped Systems, We Observed Four Peaks due to \(^{1}\text{G}_4, \text{^{3}F}_2, \text{^{3}F}_3\), and \(^{3}H_4\). The Intensity Of An Absorption Band Is Measured By Oscillator Strength, Which Is Directly Proportional To Area Under The Absorption Curve.

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

(B) R.M.S Deviation (\(\sigma\)):
From The Calculated And Observed Values Of Oscillator Strength, The Values Of R.M.S. Deviation For Systems Have Been Computed By Following Equation

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

(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 (19-20) \(T_2, T_4\) And \(T_6\).

(II) Symmetry Parameter (19-20)
Judd-Ofelt Parameter Ratio \(T_2/T_4\) Is Called Symmetry-Parameter.

(III) Co-ordination Parameter (19-20)
Judd-Ofelt Parameter Ratio \(T_2/T_4\) 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), \(^{3}H_6 - ^{3}H_4\) Is Hypersensitive Transitions In Four Bands.

(V) Peacock Constant (10) \(K'\)
Oscillator Strength (P) Is Directly Proportional To \(\nu T_0\) For Hypersensitive Transitions, This Linear Correlation Has Been Proposed By R. D. Peacock (11),

\[
K' = \frac{P_{obs}}{\nu T_0}
\]

(VI) Bonding Parameters (23-25)

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

\[
\beta = \frac{v_C}{v_F}
\]

Where:- \(v_C\) & \(v_F\) Are Wave Numbers Of \(f\sim f\) Transition For Spectra Of Complex And Free Ion Respectively.

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

\[
b^{1/2} = \left[ \frac{1}{2} (1 - \beta) \right]^{1/2}
\]

(C) Sinha's Covalency Parameters (\(\delta\)%):

\[
\delta = \left[1 - \beta / \beta \right] \times 100
\]

(D) Covalency Angular Overlap Parameter (\(\eta\)):

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

(VII) Thermodynamic Parameters (26-28)

(a) Thermodynamic Efficiency =

\[
\text{Work Function For Transition} \quad \text{Energy Absorbed For Transition}
\]

By Using Thermodynamic Relation-

\[
A = E - TS \quad \text{And} \quad S = K \ln P_{obs}
\]

Following Relation May Be Obtained-

\[
A = E - KT \ln P_{obs}
\]

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) = \(g_i e^{-E_i}/kT\)

Where: For Tm, \(g_i = 2J + 1 = 9\)
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(C) 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

<table>
<thead>
<tr>
<th>Levels</th>
<th>Bands</th>
<th>Tm(III) Ion Systems Involving Ligand Environment In DMSO Solvent</th>
<th>Tm(III) With ( \text{L}_1 )</th>
<th>Tm(III) With ( \text{L}_2 )</th>
<th>Tm(III) With ( \text{L}_3 )</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>( \nu )</td>
<td>( P_{\text{obs}} \times 10^6 )</td>
<td>( P_{\text{cal}} \times 10^6 )</td>
<td>( P_{\text{obs}} \times 10^6 )</td>
<td>( P_{\text{cal}} \times 10^6 )</td>
</tr>
<tr>
<td>( ^{3}_\text{G}_1 )</td>
<td>2.7407</td>
<td>2.5546</td>
<td>3.8467</td>
<td>1.0085</td>
<td>0.3652</td>
</tr>
<tr>
<td>( ^{3}_\text{F}_1 )</td>
<td>0.8293</td>
<td>1.5086</td>
<td>0.9966</td>
<td>1.9085</td>
<td>0.8187</td>
</tr>
<tr>
<td>( ^{3}_\text{H}_1 )</td>
<td>9.6593</td>
<td>10.3090</td>
<td>11.2308</td>
<td>12.1055</td>
<td>2.0294</td>
</tr>
<tr>
<td>( ^{1}_\text{G}_1 )</td>
<td>8.8275</td>
<td>9.3958</td>
<td>9.3722</td>
<td>10.1394</td>
<td>1.7545</td>
</tr>
</tbody>
</table>

#### Table - II

<table>
<thead>
<tr>
<th>Levels</th>
<th>Bands</th>
<th>Tm(III) Ion Systems Involving Ligand Environment In DMSO Solvent</th>
<th>Tm(III) With ( \text{L}_1 )</th>
<th>Tm(III) With ( \text{L}_2 )</th>
<th>Tm(III) With ( \text{L}_3 )</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>( \nu )</td>
<td>( P_{\text{obs}} \times 10^6 )</td>
<td>( P_{\text{cal}} \times 10^6 )</td>
<td>( P_{\text{obs}} \times 10^6 )</td>
<td>( P_{\text{cal}} \times 10^6 )</td>
</tr>
<tr>
<td>( ^{3}_\text{G}_1 )</td>
<td>2.1719</td>
<td>0.9464</td>
<td>0.3263</td>
<td>0.8665</td>
<td>0.3099</td>
</tr>
<tr>
<td>( ^{3}_\text{F}_1 )</td>
<td>1.0997</td>
<td>1.8529</td>
<td>0.8434</td>
<td>0.4050</td>
<td>0.8362</td>
</tr>
<tr>
<td>( ^{3}_\text{H}_1 )</td>
<td>9.8657</td>
<td>10.5885</td>
<td>2.0330</td>
<td>1.6129</td>
<td>2.0196</td>
</tr>
<tr>
<td>( ^{1}_\text{G}_1 )</td>
<td>8.5760</td>
<td>9.2092</td>
<td>1.7767</td>
<td>1.4079</td>
<td>1.7773</td>
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</tbody>
</table>

#### Table - III

<table>
<thead>
<tr>
<th>S. No.</th>
<th>Tm(III) Doped Systems</th>
<th>Average Energy [ \text{In Cm}^{-1} ]</th>
<th>( \beta )</th>
<th>( b^{1/2} )</th>
<th>( \delta )</th>
<th>( \eta )</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>Tm(III)-\text{L}_1</td>
<td>1267.20</td>
<td>0.996557</td>
<td>0.041493</td>
<td>0.345536</td>
<td>0.001726</td>
</tr>
<tr>
<td>2</td>
<td>Tm(III)-\text{L}_2</td>
<td>12693.94</td>
<td>0.997951</td>
<td>0.032008</td>
<td>0.205323</td>
<td>0.001026</td>
</tr>
<tr>
<td>3</td>
<td>Tm(III)-\text{L}_3</td>
<td>12712.03</td>
<td>0.999373</td>
<td>0.017702</td>
<td>0.062715</td>
<td>0.000313</td>
</tr>
<tr>
<td>4</td>
<td>Tm(III)-\text{L}_4</td>
<td>12663.73</td>
<td>0.995577</td>
<td>0.047029</td>
<td>0.443515</td>
<td>0.002219</td>
</tr>
<tr>
<td>5</td>
<td>Tm(III)-\text{L}_5</td>
<td>12706.47</td>
<td>0.998936</td>
<td>0.023060</td>
<td>0.106471</td>
<td>0.000532</td>
</tr>
<tr>
<td>6</td>
<td>Tm(III)-\text{L}_6</td>
<td>12706.35</td>
<td>0.998297</td>
<td>0.023164</td>
<td>0.107430</td>
<td>0.000537</td>
</tr>
</tbody>
</table>
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### Table- IV 
**Thermodynamic Property**

<table>
<thead>
<tr>
<th>S. N.</th>
<th>Tm(III) Doped Systems</th>
<th>Energy for Hypersensitive Transition ($^1T_H$) (cm⁻¹)</th>
<th>Oscillator Strength for Hypersensitive Transition ($^1T_H$) (X 10^16)</th>
<th>Work Function (A) (Cm⁻¹)</th>
<th>Thermo Dynamic Efficiency Of The Transition (TET)</th>
<th>Partition Function $Q_{g=0}^{EXT}$ (X 10^26)</th>
<th>Ratio Of Partition Function ($t_o$)</th>
<th>Peacock Relation $(K') = P_{as} / vT_o$</th>
</tr>
</thead>
<tbody>
<tr>
<td>1.</td>
<td>Tm(III) + L₁</td>
<td>12676.20</td>
<td>8.827541</td>
<td>15100.90</td>
<td>1.191280</td>
<td>3.399227</td>
<td>1.233958</td>
<td>1.802226</td>
</tr>
<tr>
<td>2.</td>
<td>Tm(III) + L₂</td>
<td>12693.94</td>
<td>9.372284</td>
<td>15106.16</td>
<td>1.190030</td>
<td>3.121821</td>
<td>1.132557</td>
<td>1.506483</td>
</tr>
<tr>
<td>3.</td>
<td>Tm(III) + L₃</td>
<td>12712.03</td>
<td>1.754592</td>
<td>15473.35</td>
<td>1.217221</td>
<td>2.685215</td>
<td>1.039006</td>
<td>1.579171</td>
</tr>
<tr>
<td>4.</td>
<td>Tm(III) + L₄</td>
<td>12663.73</td>
<td>8.576030</td>
<td>15094.46</td>
<td>1.191944</td>
<td>3.608818</td>
<td>1.310042</td>
<td>1.420916</td>
</tr>
<tr>
<td>5.</td>
<td>Tm(III) + L₅</td>
<td>12706.47</td>
<td>1.776719</td>
<td>15465.18</td>
<td>1.217111</td>
<td>2.939540</td>
<td>1.067087</td>
<td>1.345819</td>
</tr>
<tr>
<td>6.</td>
<td>Tm(III) + L₆</td>
<td>12706.35</td>
<td>1.777357</td>
<td>15464.98</td>
<td>1.217107</td>
<td>2.941239</td>
<td>1.067711</td>
<td>1.249775</td>
</tr>
</tbody>
</table>

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 $^4T_{2g}$,$^1E_{2g}$,$^3T_{2g}$ Band Were Found Between 0.3009 X 10⁻⁶ & 3.8467 X 10⁻⁶, 0.3638 X 10⁻⁶ & 1.9085 X 10⁻⁶, 1.5936 X 10⁻⁶ & 1.21055 X 10⁻⁶ And 1.3718 X 10⁻⁶ & 10.1394 X 10⁻⁶ Respectively .
- The Values Of rms Deviation ($\sigma$) For Tm(III) Systems Were Found Between 4.3007 X 10⁻⁷ & 9.8166 X 10⁻⁷ And The Order Of rms Deviation Was Found As Given Below-
  - Tm(III)-L₄ < Tm (III)-L₅ < Tm (III)-L₆ < Tm (III)-L₇ < Tm (III)-L₈ < Tm (III)-L₉ < Tm (III)-L₁₀

**Judd-Ofelt Parameters Are Indicative Degree Of Metal Ligand (M-L) Interaction ($T_2$), Refractive Index Of Medium ($T_d$) And Change In Symmetry Around The Cation ($T_o$).**
- $T_2$ Values For Tm(III) Systems Were Found Between 0.1698 X 10⁻⁹ & 1.5943 X 10⁻⁹ And The Order Of $T_2$ Values Were Found As Given Below-
  - Tm(III)-L₆ < Tm (III)-L₉ < Tm (III)-L₁₀ < Tm (III)-L₁ < Tm (III)-L₄ < Tm (III)-L₅ < Tm (III)-L₇
- $T_d$ Values For Tm(III) Systems Were Found Between 0.5958 X 10⁻⁹ & 1.3409 X 10⁻⁹ And The Order Of $T_d$ Values Was Found As Given Below-
  - Tm(III)-L₆ < Tm (III)-L₅ < Tm (III)-L₉ < Tm (III)-L₇ < Tm (III)-L₄ < Tm (III)-L₈ < Tm (III)-L₁
- $T_o$ Values For Tm(III) Systems Were Found Between 0.1875 X 10⁻⁹ & 0.2002 X 10⁻⁹ And The Order Of $T_o$ Values Was Found As Given Below-
  - Tm(III)-L₅ < Tm (III)-L₄ < Tm (III)-L₉ < Tm (III)-L₇ < Tm (III)-L₆ < Tm (III)-L₁ < Tm (III)-L₂

**Variation In Symmetry Parameter ($T_d/T_o$) & Co-Ordination Parameter ($T_d/T_2$)Values Show The Change In Symmetry & Co-Ordination Environment Around Central Metal Ion.**
- $T_d/T_2$ Values For Tm(III) Systems Were Found Between 0.5351 & 3.1598 And The Order Of $T_d/T_2$ Values Was Found As Given Below-
  - Tm(III)-L₆ < Tm (III)-L₉ < Tm (III)-L₁₀ < Tm (III)-L₄ < Tm (III)-L₅ < Tm (III)-L₇
- $T_d/T_o$ Values For Tm(III) Systems Were Found Between 0.3525 & 0.8811 And The Order Of $T_d/T_o$ Values Was Found As Given Below-
  - Tm(III)-L₆ < Tm (III)-L₅ < Tm (III)-L₉ < Tm (III)-L₇ < Tm (III)-L₄ < Tm (III)-L₁ < Tm (III)-L₂

**Constant Values Of Peacock Relation Signifies The Validity Of Judd-Ofelt Theory.**
- The Peacock Constant ($K_{o}^{'}$) 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 $K_{o}^{'}$ And Also With Mean Value.

**Nephelauxetic Ratio ($\beta$) Depicts That How Effectively Bands Of Metal Ions Are Shifted In Presence Of Ligand Environment, Low And High Value Of Bonding Parameters ($\beta$, $\delta$ & $\eta$) Indicate Weak & Strong Covalent Character In Metal-Ligand Bond Respectively.**

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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)-L₅ < Tm(III)-L₆ < Tm(III)-L₃ < Tm(III)-L₇

Positive Value Of Bonding Parameter(b¹/²) Indicates Covalent Character In Metal-Ligand Bond While Negative Value Shows Ionic Character In Metal-Ligand Interaction. The Values Of Bonding Parameter (b¹/²) For Tm(III) Systems Were Found Between 0.017702 & 0.047029 And The Order Of b¹/² Value Was Found As Given Below: Tm(III)-L₃ < Tm (III)-L₅ < Tm(III)-L₆ < Tm (III)-L₄ < Tm (III)-L₁ < Tm (III)-L₄

Percentage Covalent Character In Metal Ligand Bond Can Be Expressed By Sinha’s Covalency Parameter (δ%). Covalency Angular Overlap Parameter (η) Represents Extent Of Overlapping Between Metal Ion Orbital And Ligand Orbital. Sinha’s Covalency Parameter-δ% & Covalency Angular Overlap Parameter-η Also Indicate The Covalent Character In Metal Ligand Bond.

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)-L₅ < Tm(III)-L₆ < 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 (rₚ) For Tm(III) Systems Were Found Between 2.862185 X 10⁻²⁶ & 3.608818 X 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.

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References
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