



# Characterization of Tm (III) -sulphonanilide systems in terms of thermodynamic and electronic-spectral parameters

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## Introduction

The complexes of d-block transition metals with various ligands have been studied extensively. However, in case of f-block lanthanide metal complexes, a limited study has so far been carried out. Systematic study of lanthanide complexes began only after the publication of **Judd-Ofelt theory** in 1962. Several lanthanide complexes were prepared with the ligands possessing “O” and “N” as donor atoms and examined for various electronic-spectral parameters resulting from f-f transitions.

In the present work, electronic-spectral characterization of various Tm(III) systems in DMF medium involving sulphonilide ligands having “O”, “N” and “S” donor atoms will be examined on the basis of theories given by **Lande, Carnall & Judd-Ofelt**

**The complexing ability has been reported poor in case of lanthanide complexes and also the stability of lanthanide complexes is found similar to  $[\text{Ag}(\text{NH}_3)_2]^+$  type of complex, which makes the isolation of these complexes in solid state difficult. Owing to the poor thermodynamic stability of lanthanide complexes, a modified doped model technique will be taken as system in the present electronic-spectral study.**

## Importance of the Work

The 4f-inner transition metals (from cerium to lutetium) are known as lanthanides or lanthanones.

Lanthanides are known to form complexes less readily due to deeply buried f-orbitals and the shielding of 4f-orbitals by 5d, 6s and 6p-orbitals is responsible for difference in properties of transition metals and lanthanide metals.

These 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

As explained above, 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<sup>(16-17)</sup>. The intensity of hypersensitive transitions can be up to 200 times greater than corresponding aqua ion transition depending upon particular complex.

The energy aspect of transition has been explained in terms of energy bands.

## Review of Previous work

A number of studies have been carried out so far pertaining to lanthanide complexes on the basis of elemental analysis, spectroscopic method and electronic-spectral analysis along with their biological & medicinal significance.

**K Mohanan et al** formed bis hydrazone from the condensation of isatin mono hydrazone and salicylaldehyde reacted with lanthanide (III) chloride to form complexes of the type  $[\text{Ln}(\text{HISA})_2\text{Cl}_3]$ , where,  $\text{Ln}=\text{La}(\text{III}), \text{Ce}(\text{III}), \text{Pr}(\text{III}), \text{Nd}(\text{III}), \text{Sm}(\text{III}), \text{Eu}(\text{III}),$  or  $\text{Gd}(\text{III})$  and  $\text{HISA}=[(2\text{-hydroxybenzaldehyde})\text{-}3\text{-isatin}]\text{bishydrazone}$ . Both reactions were carried out under microwave conditions. The ligand and the metal complexes were characterized on the basis of elemental analysis, molar conductance, magnetic susceptibility measurements, UV, visible, infrared, far infrared, and proton NMR spectral data. The ligands and the metal complexes were screened for their antifungal activities.

**Vlasoula Bekiari et al** measured the photophysical behaviour of 2,2'-bipyrimidine alone and in the presence of several lanthanides or other metal ions. This substance, which is employed as bridging ligand in homo- and hetero-binuclear complexes, can form stable complexes with luminescent lanthanide ions like  $\text{Eu}^{3+}$  and  $\text{Tb}^{3+}$ .

**Stefan Lis et al** investigated spectroscopic properties of  $\text{Ln}(\text{III})$  complexes with diethyl benzylphosphonate ( $\text{PhCH}_2\text{P}(\text{O})(\text{EtO})_2$ ) and diethyl (carboxymethyl) phosphonate ( $(\text{EtO})_2\text{P}(\text{O})\text{CH}_2\text{COOH}$ ) using absorption and luminescence spectroscopy. Absorption spectra of organophosphorus ligands with  $\text{Nd}(\text{III})$  were measured in acetonitrile solution and oscillator strength values and Judd–Ofelt parameters were calculated. The  $\text{La}(\text{III})$  and  $\text{Pr}(\text{III})$  complexes with the studied ligands were synthesized and their structures were confirmed by elemental analysis, IR spectra and also  $^{13}\text{C}$  and  $^{31}\text{P}$  NMR.

## Calculation of Parameters

This chapter deals with calculation of various electronic spectral parameters like intensity parameter, bonding parameter, symmetry parameter, co-ordination parameter, thermodynamic parameter, Peacock's relation & formation constant, along with their computation method.

Systems of Tm(III) with sulphanilides have been prepared on doped model pattern in DMF medium and characterized spectrophotometrically.

This work is related with synthesis and electronic spectral study of Tm(III) systems with substituted sulphonilides.

To evaluate metal-ligand interaction, different parameters such as- **intensity parameters** (oscillator strength-P, Judd-Ofelt parameters- $T_2$ ,  $T_4$  and  $T_6$  r.m.s. deviation- $\sigma$ ), **bonding parameters** (Nephelauxetic ratio- $\beta$ , bonding parameter- $b^{1/2}$ , Sinha's covalency parameter- $\delta\%$ , covalency angular overlap parameter- $\eta$ ), **symmetry parameter**- $T_4/T_6$ , **co-ordination parameter**- $T_4/T_2$ , **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 can be inferred.

Various parameters have been determined with the help of computerized programmed and following formulae:

### (I) Intensity parameters

#### (a) Oscillator strength (P):

In Tm(III) doped systems, we observed four peaks<sup>(4-5)</sup> 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.

$$P = 4.315 \times 10^{-9} \int \epsilon \, d\nu$$

Where  $\epsilon$  = molar absorptivity

$$= \text{Absorbance} / (\text{Concentration} \times \text{Path length})$$

$$\nu = \text{Frequency in wave number}$$

The equation may be expressed in terms half band width :

$$P_{\text{obs}} \approx 4.6 \times 10^{-9} \times \epsilon_{\text{max}} \Delta \nu_{1/2} \dots \dots \dots \text{eq.1}$$

Where:-

$$\epsilon_{\text{max}} = \text{molar extinction coefficient} = \text{OD} / (\text{C} \times \text{L})$$

OD=optical density (Absorbance)

C=concentration in mole / litre

L=path length =1cm

$\nu$  = frequency in wave number

$$\Delta \nu_{1/2} = \text{half band width} = \{1/(\lambda - 0.5bw) - 1/(\lambda + 0.5bw)\} \times 10^{-7}$$

$P_{\text{obs}}$  and  $\nu$  are different for different levels

Each observed absorption band was resolved into Gaussian curve to enable evolution of P.

The observed oscillator strength  $P_{\text{obs}}$ , may have contribution from the induced electronic dipole  $P_{\text{el}}$ , magnetic dipole  $P_{\text{md}}$  and electric quadrupole mode  $P_{\text{eq}}$ .

Hence,

$$P_{\text{obs}} = P_{\text{el}} + P_{\text{md}} + P_{\text{eq}}$$

The  $P_{\text{el}}$  and  $P_{\text{md}}$  values are found to be  $\sim 10^{-10}$  and  $10^{-8}$  respectively, so can be neglected in comparison to  $P_{\text{eq}}$  ( $\sim 10^{-6}$ ).

Oscillator strength for transition of energy can be calculated by using Judd-Ofelt parameters ( $T_2$ ,  $T_4$  and  $T_6$ ) with the help of formula-

$$P_{\text{cal}} = T_2 \nu [U^{(2)}]^2 + T_4 \nu [U^{(4)}]^2 + T_6 \nu [U^{(6)}]^2 \dots \dots \dots \text{eq.2}$$

Where  $[U^{(2)}]^2$ ,  $[U^{(4)}]^2$ ,  $[U^{(6)}]^2$  are matrix elements<sup>(5)</sup>.

Partial and multiple regression method has been used to calculate  $T_\lambda$  parameter<sup>(6-9)</sup>. This can be shown as follows-

$$Y = a + b_1 X_1 + b_2 X_2 + b_3 X_3 + \dots \dots \dots + b_p X_p$$

Where:-  $a=0$

$$X_1 = [U^{(2)}]^2, X_2 = [U^{(4)}]^2, X_3 = [U^{(6)}]^2$$

$X_1$ ,  $X_2$  and  $X_3$  for each band are measured separately from matrix element.

$$b_1 = T_2 = C_{11} \sum X_1 Y + C_{12} \sum X_2 Y + C_{13} \sum X_3 Y \dots \dots \dots \text{eq.3}$$

$$b_2 = T_4 = C_{12} \sum X_1 Y + C_{22} \sum X_2 Y + C_{23} \sum X_3 Y \dots \dots \dots \text{eq.4}$$

$$b_3 = T_6 = C_{13} \sum X_1 Y + C_{23} \sum X_2 Y + C_{33} \sum X_3 Y \dots \dots \dots \text{eq.5}$$

$b_1$ ,  $b_2$  and  $b_3$  values are equal to  $T_2$ ,  $T_4$  and  $T_6$  respectively. For measurement of  $b_1$ ,  $b_2$  and  $b_3$  values, it is required to measure  $\sum X_1 Y$ ,  $\sum X_2 Y$  and  $\sum X_3 Y$ .

Where-

$$\sum X_1 Y = \frac{\sum X_1 Y - \sum X_1 \sum Y}{N} \dots \dots \dots \text{eq.6}$$

$$\frac{\sum x_2 y - \sum X_2 \sum Y}{N} \dots\dots\dots \text{eq.7}$$

$$\frac{\sum x_3 y - \sum X_3 \sum Y}{N} \dots\dots\dots \text{eq.8}$$

Where:-

$$Y = P_{\text{obs}} / v \dots\dots\dots \text{eq.9}$$

$$N = 4 \text{ (for Tm) \& } N = 8 \text{ (for Er) } \dots\dots\dots \text{eq.10}$$

For calculating C<sub>11</sub>, C<sub>12</sub>....., few steps are employed by utilizing matrix elements of the table 1

**Table 1. Matrix For Calculating C<sub>11</sub>, C<sub>12</sub> ..... Etc. From The Values Of A<sub>11</sub>, A<sub>22</sub> ..... Etc.**

Line	Abbreviated Solution					
1	a <sub>11</sub>	a <sub>21</sub>	a <sub>31</sub>	1.0	0	0
2	-	a <sub>22</sub>	a <sub>32</sub>	0	1.0	0
3	-	-	a <sub>33</sub>	0	0	1.0
4	a <sub>11</sub>	a <sub>21</sub>	a <sub>31</sub>	d <sub>11</sub> (=1)	0	0
5	1	b <sub>21</sub>	b <sub>31</sub>	e <sub>11</sub>	0	0
6	-	a <sub>22.1</sub>	a <sub>32.1</sub>	d <sub>11.1</sub>	d <sub>12.1</sub>	0
7	-	1	b <sub>32.1</sub>	e <sub>11.1</sub>	e <sub>12.1</sub>	0
8	-	-	a <sub>33.12</sub>	d <sub>11.12</sub>	d <sub>12.12</sub>	d <sub>13.12</sub>
9	-	-	1	e <sub>11.12</sub>	e <sub>12.12</sub>	e <sub>13.12</sub>
10	-	-	-	C <sub>11</sub>	C <sub>12</sub>	C <sub>13</sub>
11	-	-	-	-	C <sub>22</sub>	C <sub>23</sub>
12	-	-	-	-	-	C <sub>33</sub>

**STEPS**

Line	Instruction
1, 2, 3	Enter sums of squares and products $a_{11} = \sum x_1^2 = \sum X_1^2 - (\sum X_1)^2 / N$ $a_{22} = \sum x_2^2 = \sum X_2^2 - (\sum X_2)^2 / N$ $a_{33} = \sum x_3^2 = \sum X_3^2 - (\sum X_3)^2 / N$ $a_{21} = \sum x_2 x_1 = \sum X_2 X_1 - (\sum X_2 \sum X_1) / N$ $a_{31} = \sum x_3 x_1 = \sum X_3 X_1 - (\sum X_3 \sum X_1) / N$ $a_{32} = \sum x_3 x_2 = \sum X_3 X_2 - (\sum X_3 \sum X_2) / N$
4	Copy line 1

- 5 Divide each entry in line 4 by  $a_{11}$
- 6  $a_{22.1} = a_{22} - a_{21} b_{21}$   
 $a_{32.1} = a_{32} - a_{31} b_{21}$   
 $d_{11.1} = 0 - d_{11} b_{21}$   
 $d_{12.1} = 1 - 0x b_{21}$
- 7 Divide each entry in line 6 by  $a_{22.1}$
- 8  $a_{33.12} = a_{33} - a_{31} b_{31} - a_{32.1} b_{32.1}$   
 $d_{11.12} = 0 - d_{11} b_{31} - d_{11.1} b_{32.1}$   
 $d_{12.12} = 0 - d_{12.1} b_{32.1}$   
 $d_{13.12} = 1.0$
- 9 Divide each entry in line 8 by  $a_{33.12}$
- 10, 11, 12  $C_{11} = d_{11} e_{11} + d_{11.1} e_{11.1} + d_{11.12} e_{11.12}$   
 $C_{12} = d_{11.1} e_{12.1} + d_{11.12} e_{12.12}$   
 $C_{13} = d_{11.12} e_{13.12}$   
 $C_{22} = d_{12.1} e_{12.1} + d_{12.12} e_{12.12}$   
 $C_{23} = d_{12.12} e_{13.12}$   
 $C_{33} = d_{13.12} e_{13.12}$

The following relation is used to check the results obtained-

$$C_{11}Xa_{11} + C_{12}Xa_{21} + C_{13}Xa_{31} = 1.0$$

**(b) Judd-Ofelt parameters- $T_2, T_4$  and  $T_6$ :**

The interaction between lanthanide ion and ligand are predominantly measured by three main parameter known as Judd-Ofelt parameters<sup>(6-7)</sup> ( $T_2, T_4$  and  $T_6$ ).

These 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 ( $T_6$ ). These parameters are measured by partial and multiple regression method.

**(c) r.m.s deviation ( $\sigma$ ):**

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

(By putting the values of  $P_{cal}$  and  $P_{obs}$  from eq.1 and eq.2)

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

Higher value of rms deviation ( $\sigma$ ) shows a larger magnetic dipole interaction whereas low value of r.m.s deviation prove Judd Ofelt Theory.

## **Experiment & observation**

This chapter covers experimental & observation part, it includes preparation of Tm(III) systems with sulphonanilides. Along with various observations & absorption spectra related to various parameters.

Six systems were prepared by using standard grade chemicals TmCl<sub>3</sub>.6H<sub>2</sub>O & ligands L<sub>1</sub> to L<sub>6</sub> in DMF medium by using standard method. Solution spectra have been taken for Tm(III) systems by standard spectrophotometer (systronic 106) in the range 400-820 nm.

Six sulphonanilides taken as ligands were synthesized by employing two steps, as mentioned in literature

### ***Experimental method for determination of formation constant of the complex:***

Various methods are used for determination of stability of complexes viz;

Potentiometric,

pH titration technique,

Solvent Extraction,

Calorimetric method,

Polorographic method etc.

Jobs method is a variation of spectrophotometric method, which is used to determine the composition of a complex and mainly used for solutions where only one complex is formed.

This method is based on the fact that most of the complexes absorb light differently than the metal ions from which they are formed. The relationship between the absorbance or optical density at particular wavelength and concentration is expressed by Beer's law.

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