Characterization of Some Er (III) Systems In Terms of Electronic-Spectral Parameters

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Abstract

Er(III) systems with ligands Viz. Urea, Thiourea, Dimethylglyoxime, Semicarbazide , Thiosemicarbazide, Acetaldehyde-Semi-carbazone, N,N-Diphenylthiourea and Diphenylglyoxime were prepared on doped model pattern in DMSO solvent and examined for Metal-Ligand interaction on the basis of different parameters(suggested by theories of Lande,Carnall & Judd-Ofelt) such as Intensity Parameters (Oscillator Strength-P, Judd-Ofelt Parameters- T_2, T_4, & T_6, r.m.s. deviation- σ), Bonding Parameters(Nephlauxtic ratio- β, bonding parameter- $b^{1/2}$, symmetry parameters T_4/T_6). The validity of theories were established on the basis of low value of r.m.s. deviation.

Key words: Erbium(III),f-f transition,electronic spectral parameters, Ligands having N,S&O as donor atoms.

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.

The complexes of lanthanide (III) metal ions with organic reagents are significant because of their application in visible-ultraviolet (VUV) lasers, luminescent chemosensors for medical diagnosis, Schift reagent for NMR spectroscopy, as scintillators, in industries and biological systems[1-6]

The tri positive rare earth metal ions show comparatively little tendencies to form complexes with a variety of normally powerful coordinating agents due to their peculiar electronic configurations. However, certain chelating groups notably the β-Diketones[7-8], 8-Quinolinols[9-10], Oximes[11], Hetrocyclic compounds[12-13], Schiff's bases[14-17], Ald-imines, Keto-imines[18] and Coumarins[19-22] *etc*. are capable of overcoming this difficulty through the formation of the complex compounds.

In the present study, electronic-spectral characterization of various Er(III) systems in

DMSO medium involving ligands having "O", "N" and "S" donor atoms like Urea (L_1), Thiourea (L_2), Dimethylglyoxime (L_3), Semicarbazide (L_4), Thiosemicarbazide(L_5), Acetaldehyde Semi-carbazone (L_6), N,N-Diphenylthiourea (L_7), and Diphenylglyoxime (L_8) will be examined on the basis of theories given by Lande, Carnall & Judd-Ofelt[23-25]. On examining electronic-spectral parameters of the systems under study, the interaction in metal and ligands will be inferred.

Owing to the poor thermodynamic stability of lanthanide complexes, a doped model technique will be taken as system in the present electronic-spectral study. 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. deviate on-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_2, will be examined. Computerized method, developed by earlier workers was used for determination of above parameters[26].
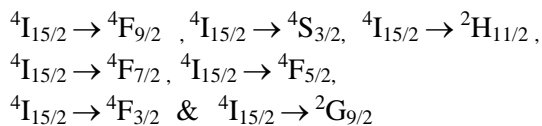
The study will also provide some useful information regarding inter-electronic repulsions, spin-orbit interaction and symmetry changes around lanthanide ion.

Experimental

Er(III) ion complexes were characterized through various electronic spectral parameters like Judd-Ofelt parameters ($T\lambda = T_2$, T_4, T_6, T_4/T_6 and T_4/T_2), Oscillator strength (P),

Nephelauxetic ratio (β), bonding parameter (b1/2), Sinha covalency parameter ($\delta\%$) and covalency angular overlap parameter (η), to have a comparative study of complexation with different ligands.

In the present investigation of Er (III) complexes, the solution spectra yields eight bands viz.
$^4I_{15/2} \rightarrow {}^4F_{9/2}$, $^4I_{15/2} \rightarrow {}^4S_{3/2}$, $^4I_{15/2} \rightarrow {}^2H_{11/2}$,
$^4I_{15/2} \rightarrow {}^4F_{7/2}$, $^4I_{15/2} \rightarrow {}^4F_{5/2}$,
$^4I_{15/2} \rightarrow {}^4F_{3/2}$ & $^4I_{15/2} \rightarrow {}^2G_{9/2}$

The bands having oscillator strength $\sim 10^{-5}$ and found much sensitive to the ligands & solvents are called hypersensitive transitions. Oscillator strength of the hypersensitive transitions exhibits greater variation than the oscillator strength of non hypersensitive transitions

For Er(III) : $^4I_{15/2} - {}^4G_{11/2}$ and $^4I_{15/2} - {}^2H_{11/2}$
are hypersensitive transitions among eight bands.

It is difficult to explore the spectra of Ln ions in different systems, particularly in hypersensitive region. In order to get better spectra, one should go for better legating system or for dilution. In the present work, former aspect has been taken into consideration by selecting various ligands having N, S&O donor atoms and doped model technique has been used. In this technique, a saturated solution of ligand is prepared in a suitable solvent and during solubilization phenomenon, stoichiometric amount of metal ion is added. In the present work, eight systems of Er(III) ion, doped in saturated solution of ligand have been prepared by adding 0.082 g. $ErCl_3.6H_2O$ (Supplied by Across Limited, USA) per 25 ml of ligand

solution. Thus for performing electronic spectral study, concentration of $ErCl_3.6H_2O$ (molecular weight-273.61) has been taken in 0.012M and ligand concentration has been taken in saturated amount.

The solution spectrum of each system has been recorded in the range 400-850 nm by using standard spectrophotometer. All the systems were characterized by various parameters.

Calculation :

Different parameters were calculated by using partial and multiple regression method by using following formulae-

(i) Intensity Parameters :

(a) Oscillator Strength (P):

$$P = 4.315 \times 10^{-9} \int \in d \; v$$

(where $\in$ = molar absorptivity (1)
v = frequency in wave number)

$$\approx 4.6 \times 10^{-9} \times \in_{max} \Delta \; v_{1/2}$$

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

$$P_{obs} = T_2 \; v[U^{(2)}]^2 + T_4 \; v[U^{(4)}]^2 + T_6 \; v[U^{(6)}]^2$$
(2)

(where $[U^{(2)}]^2$, $[U^{(4)}]^2$, $[U^{(6)}]^2$ are matrix elements

(c) R.M.S deviation (σ)

$$\sigma = [\sum(P_{cal} - P_{obs})^2 / N]^{1/2}$$
(3)

(where N = Number of levels taken)

(ii) Bonding Parameters:

(a) Nephelauxetic ratio (β)

$$\beta = v_c / v_f$$
(4)

(where v_c & v_f = wave numbers of f-f transition in spectra of metal complex and free metal ion in solvent)

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

$$b^{1/2} = [\tfrac{1}{2} (1-\beta)]^{1/2}$$
(5)

(c) Sinha's Covalency parameter ($\delta\%$) :

$$\delta = [1-\beta / \beta] \times 100$$
(6)

(d) Covalency angular overlap parameter (η):

$$\eta = [1 - \beta^{1/2} / \beta^{1/2}]$$
(7)

Metal-Ligand interaction was evaluated on the basis of these parameters.

Results and Discussion

The interaction between lanthanide ion and ligand can be predominantly measured by three main parameters known as Judd-Ofelt parameters[23-24] (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[27-28].

The values of various spectral parameters including oscillator strength (P), Nephelauxetic ratio (β), bonding parameter ($b^{1/2}$), Sinha covalency parameter ($\delta\%$) and Covalency angular overlap parameter (η) etc. have been reported in table 3.

The observed change in the various intensity parameters show that the f $\leftrightarrow$ f transition resulting from spin-orbit interaction in Er (III) ion is due to the interaction of f orbital with the ligand present in the saturated solution.

The calculation of various parameters involve Slater-Condon & Lande and Judd-

Table 1. Observed And Calculated Values Of Oscillator Strength (P) Of The Four Bands Recorded For Er (III)Ion Systems Involving Ligand Environment in DMSO Solvent.

S. N.	BANDS →Er (III) system	$^4I_{9/2}$ O.S[P] X 10^6 Exp.	$^4I_{9/2}$ Cal	$^4F_{9/2}$ O.S[P] X 10^6 Exp.	$^4F_{9/2}$ Cal	$^4S_{3/2}$ O.S[P] X 10^6 Exp.	$^4S_{3/2}$ Cal	$^2H_{11/2}$ O.S[P] X 10^6 Exp.	$^2H_{11/2}$ Cal	$^4F_{7/2}$ O.S[P] X 10^6 Exp.	$^4F_{7/2}$ Cal	$^4F_{5/2}$ O.S[P] X 10^6 Exp.	$^4F_{5/2}$ Cal	$^4F_{3/2}$ O.S[P] X 10^6 Exp.	$^4F_{3/2}$ Cal	$^2G_{9/2}$ O.S[P] X 10^6 Exp.	$^2G_{9/2}$ Cal
1	Er (III) + L$_1$	6.07	4.71	47.39	39.70	9.21	13.51	62.52	54.68	56.20	48.16	20.70	16.27	37.87	9.44	34.57	19.19
2	Er (III) + L$_2$	12.42	4.57	45.24	38.53	9.89	13.16	79.10	68.68	63.48	46.89	20.28	15.92	36.95	9.17	35.19	18.66
3	Er (III) + L$_3$	9.50	4.91	43.92	40.30	10.87	13.39	84.79	78.81	59.73	48.04	19.64	16.20	34.17	9.37	16.19	19.14
4	Er (III) + L$_4$	5.98	4.67	47.39	39.71	8.79	13.62	62.52	54.74	56.37	48.47	21.56	16.40	37.72	9.52	34.68	19.31
5	Er (III) + L$_5$	4.79	4.80	47.22	40.94	8.14	14.08	62.38	56.47	56.04	50.06	20.70	16.95	36.80	9.84	30.18	19.96
6	Er (III) + L$_6$	7.48	4.71	47.311	39.25	9.44	13.25	62.65	53.76	57.51	47.36	20.70	15.97	38.80	9.26	35.65	18.84
7	Er (III) + L$_7$	5.27	4.66	46.15	39.97	8.145	13.84	60.86	54.68	56.04	49.13	19.66	16.66	36.95	9.65	30.09	19.60
8	Er (III) + L$_8$	12.88	4.62	45.24	38.35	9.89	12.89	79.10	68.31	63.48	46.32	20.28	15.55	36.95	9.01	35.19	18.30

Table 2. Computed Values Of T_λ Parameters For Er (III) Systems Involving Ligand Environment in DMSO Solvent.

S.N.	Er (III) system	$T_2 \times 10^9$	$T_4 \times 10^9$	$T_6 \times 10^9$	T_4/T_6	r.m.s deviation $(\sigma)\pm 1.0 \times 10^{-9}$
1.	Er (III) + L$_1$	2.4363	2.0088	3.3150	0.6059	12.6002
2.	Er (III) + L$_2$	3.5197	1.9469	3.2293	0.6028	13.9828
3.	Er (III) + L$_3$	4.1623	2.1010	3.3029	0.6361	10.3003
4.	Er (III) + L$_4$	2.4514	1.9900	3.3433	0.5952	12.5734
5.	Er (III) + L$_5$	2.5377	2.0431	3.4564	0.5910	11.1269
6.	Er (III) + L$_6$	2.3763	2.0089	3.2521	0.6177	13.445
7.	Er (III) + L$_7$	3.3970	2.2278	3.0077	0.7407	12.4418
8.	Er (III) + L$_8$	3.4793	1.9722	3.1785	0.6204	14.2442

Table 3. Computed Values Of $b^{1/2}$, β, η & δ For Er (III) Systems.

S.N.	Er (III) system	β	$b^{1/2}$	δ	η
1.	Er (III) + L$_1$	0.9891	0.0735	1.094	0.0054
2.	Er (III) + L$_2$	0.9882	0.0766	1.1902	0.0059
3.	Er (III) + L$_3$	0.9891	0.0735	1.094	0.0054
4.	Er (III) + L$_4$	0.9882	0.0766	1.1902	0.0059
5.	Er (III) + L$_5$	0.9872	0.0796	1.2865	0.0064
6.	Er (III) + L$_6$	0.9891	0.0735	1.094	0.0054
7.	Er (III) + L$_7$	0.9872	0.0796	1.2865	0.0064
8.	Er (III) + L$_8$	0.9891	0.0735	1.094	0.0054

Ofelt theories as reported by earlier workers.[29-30] Red-shift has been observed in all energy bands as compared to the free ion, thereby, establishing the validity of Slater-Condon and Lande theory.

The R.M.S. deviation varies from 10.30. x 10^{-9} to 13.98 x 10^{-9} in all the systems. The R.M.S. deviation is very small, suggesting the validity of Judd-Ofelt theory for f-f transition.

The T_4/T_6 ratio varies 0.5910 to 0.7407, which indicates variation in symmetry around doped Er(III) ion in saturated ligand solution.

The values of Nephelauxetic ratio (β) and bonding parameter ($b^{1/2}$) as well as little variation in their values, suggest that the 4f orbitals are very slightly involved in the bonding in saturated solutions doped with Er (III) ion.

This study is useful to find out a comparative complexing tendency of various ligands when interacted with Er(III) ion

separately and will also be used to compare complexing tendency of Tm(III) ion & Er(III) ion with same ligands[31].

Acknowledgement

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