An absorption electronic spectral study for the interaction of Er(III) ion systems involving some biologically important ligands in DMF stereo medium

Samata Jain*, Sushma Jain and Ramesh Dedar

* Department of Chemistry. Government Dungar PG College, Bikaner 334001 (India)

Email: jainche23@gmail.com

_____

ABSTRACT

The electronic spectral parameters viz. Oscillator strength (P) , Judd-Ofelt (T_λ) , Racah parameter (E^k), Slater - Condon parameter (F_k) , Bonding parameters ($b_{1/2}$), Nephelauxetic ratio (β) , Percent covalency (δ) and rms deviation (σ) have been evaluated for some (eight) biological important ligands (N,O,S) with Er(III) in DMF solvent. The change in symmetry (stereo environment) around the doped Er (III) ion has been studied with respect to f-f transition involved in the system. A constant amount of $Er(NO_3)_3.6H_2O$ salt (0.0443 gm) has been added to DMF solvent at 298 K. Er (III) spectra is measured in 350-700 nm region and it gives ten bands in visible region. The study infers the change in symmetry around doped Er (III) ion_4 F^{11} and M-L interaction. The greater change in symmetry is observed when Er (III) biotin system has taken in this investigation.

Keywords: Doped system, electronic spectra, nephelauxetic effects, symmetry change.
_____

INTRODUCTION

The lanthanide materials are of interest due to their numerous applications such as laser materials[1,2] , phosphors for florescent, semiconductors[3], MRI contrast agent[4], shift reagent for NMR spectroscopy[5-7]. It is also used as chemo sensors for medical purpose. The many medicines produced for the treatment of tuberculosis[8] , cancer[9], hepatitis , leprosy, eczema and rheumatism contain lanthanide ion. Lanthanides are used as hosts for optical devices. Rare earth doped heavy metal fluoride glasses[10] are transparent from UV to IR [10-12] and they are stable against atmosphere and moisture. So they are used for laser action and amplifier[13-17]. Recently it has been investigated that lanthanum is a substitute of action of Ca^{+2} in biological system[4]. The use of lanthanides as probes in the exploration of the structure and function of bimolecular reaction[18]. Er (III) ion plays a very important role in many electronic systems. Therefore organometallic rare earth (III) complexes are used in biological/ pharmaceutical applications due to their antimicrobial, antitumor, antituberculostatic and anticancer action[19-24].

The optical absorption spectra of the lanthanide complexes give very narrow and line like 4f-4f transitions[1,19] which are very unique from other metal complexes and molecular species. The 4f shell is efficiently shielded by the close 5s and 5p shell, the ligand environment has only a weak influence on the electronic cloud of the lanthanide ion. Therefore some transitions of the lanthanides are very sensitive to the change in the coordination sphere and symmetry around the metal ion[1-3] . These are termed as hypersensitive transition. In the present investigation eight ligands (Ascorbic acid (As A), Biotin (B), Gibberalic acid (GA), Indole acetic acid (IAA), Indole -3-butyric acid (IBA) , Niacin (Ni) , Pyridoxine (Py) , 4-Chlorophenoxyacetic acid (4-ClPh A) have been used. On examining electronic spectral parameters of the systems under study the covalency is inferred to some extent to metal-ligand bonding. The study also provides some useful information regarding validity of Judd-Ofelt equation, interelectronic repulsion, spin orbit interaction and symmetry changes around Er (III) ion .

MATERIALS AND METHODS

Standard grade chemicals $Er(NO_3)_3.6H_2O$ (99.9% purity) (procured from Indian rare earths) and biologically important compounds Ascorbic acid (As A), Biotin (B), Gibberalic acid (GA), Indole acetic acid (IAA), Indole -3-butyric acid (IBA), Niacin (Ni), Pyridoxine(Py)), 4-Chlorophenoxyacetic acid (4-ClPh A) (SD fine) were used . Saturated solutions of ligands were prepared in DMF and 0.0443 gm of Er $(NO_3)_3.6H_2O$ was added to saturated solution of ligand ($10cm^3$). Spectra of these solutions were recorded by using standard spectrophotometer (S L 164 double beam UV visible) at 298 K in 350-700 nm range. Ten peaks have been obtained for Er (III) ion system which is clear from Figure.
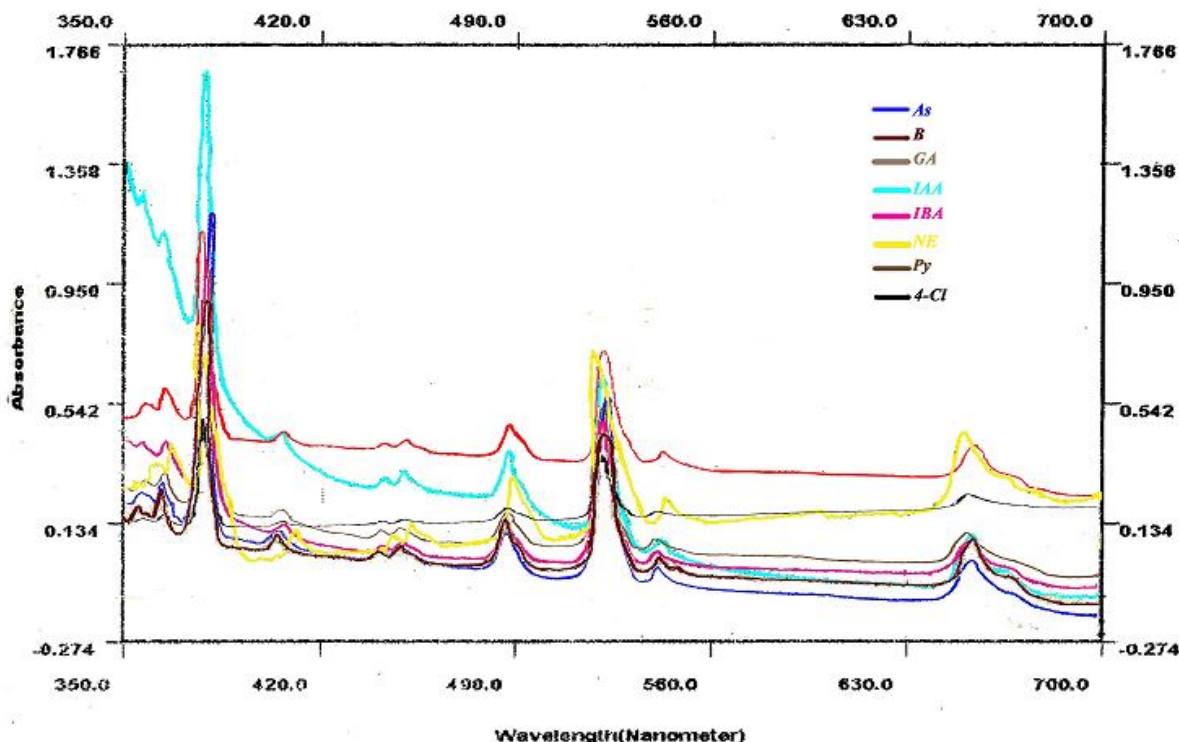
Er(III) + Some Biological Ligand In DMF Solvent Concentration of Er(III) 0.01M

RESULTS AND DISCUSSION

In the present study the f-f transitions result from spin orbit interaction in Er (III) ion and ligands. The decrease in E^k, F_k and $\zeta 4F$ parameters from free ion indicate decrease in interelectronic repulsion and spin orbit interaction which suggest expansion of the central metal ion on complexation. The values of Judd-Ofelt parameters (T_4, T_6) can also be used to indicate a linear relationship between oscillator strength (P) and νT_4 or νT_6 at least with reference to hypersensitive band $_4G^{11/2}$. The deep lying 4f sub shell experiencing intense shielding make these orbitals less available for bonding thereby leading to lesser degree of metal-ligand interaction. The present study shows that the f-f transitions result from spin orbit interaction in metal and ligands. Evaluated values of P, T_λ (T_2, T_4, T_6), E^k (E^1, E^2, E^3), F_k (F_2, F_4, F_6), $\zeta 4F$, $b_{1/2}$, β, δ % and rms deviation (σ) are tabulated. The calculations of these parameters have been computed by the programme developed by earlier workers.

Table -1. Computerised values of oscillator strength, T_λ etc., for Er (III) system.

S.N	System	$P_{cal.}10^5$ ($^4G_{11/2}$)	$P_{obs.}10^5$ ($^4G_{11/2}$)	$T_\lambda \times 10^8$			T_4/T_6	rms σ $\times 10^8$
				T_2	T_4	T_6		
1	Er+DMF+As A	0.136	0.149	0.7890	0.214	0.466	0.4283	9.06
2	Er+DMF+B	0.275	0.284	1.0000	0.493	0.961	0.5134	13.1
3	Er+DMF+GA	*0.041*	0.043	0.5660	0.046	0.161	0.2839	1.38
4	Er+DMF+IAA	0.097	0.077	0.7890	0.134	0.369	0.3627	9.88
5	Er+DMF+IBA	0.102	0.0130	0.5920	0.245	0.317	0.7715	13.0
6	Er+DMF+Ni	0.176	0.181	0.3480	0.291	0.628	0.5212	5.29
7	Er+DMF+Py	0.097	0.049	0.8950	0.176	0.338	0.5212	18.3
8	Er+DMF+4-ClPh A	0.099	0.097	0.7130	0.204	0.334	0.6117	2.16

Table -2. Computerised values of various parameters for Er (III) system

SN	System	F_2	F_4	F_6	%rF_2	$\zeta 4F$	E^1	E^2	E^3	B	$b^{1/2}$	rms	δ%
1	Er free ion	441.680	68.327	7.490	-	2369.40	6855.00	32.126	645.57	-	-	-	-
2	Er+DMF+As A	433.04	67.95	7.01	0.1377	2461.71	6673.38	30.920	644.76	0.9986	0.0262	161.24	0.140
3	Er+DMF+B	432.92	67.96	7.02	1.5140	2433.59	6673.40	30.900	644.48	0.9983	0.0287	36.99	0.170
4	Er+DMF+GA	433.18	68.16	7.05	0.5780	2456.72	6688.27	30.901	644.27	0.9989	0.0220	69.02	0.110
5	Er+DMF+IAA	433.18	68.16	7.05	0.5780	2456.72	6688.27	30.902	644.27	0.9990	0.0230	69.02	0.100
6	Er+DMF+IBA	433.18	68.16	7.05	0.5780	2456.72	6688.27	30.901	644.27	0.9990	0.0230	69.02	0.100
7	Er+DMF+Ni	432.95	68.02	7.02	0.6500	2424.83	6676.42	30.902	645.45	0.9984	0.0281	122.20	0.160
8	Er+DMF+Py	433.18	67.93	7.02	1.1400	2456.01	6674.70	30.950	644.83	0.9989	0.0230	119.86	0.110

378

9	Er+DMF+ 4-ClPh A	433.2 4	68.1 2	7.01	0.51 35	2458. 31	6697. 79	30.9 51	642. 93	0.99 00	0.02 12	72.8 9	0.10 0

The energy of 4f-4f transition consists of two major components. Columbic represented by Slater Condon parameters (F_K) and spin orbit interaction represented by Lande $\zeta 4F$ between 4f electrons. While f^K and A_{SO} are the angular components spin orbit columbic interaction as given by the following relation[25,26].

$$E = f^K F_K + A_{SO} \zeta 4F$$

The observed band energies as E_{obs} and the zero point energy E_{oj} and partial derivatives of Er (III) are used. The correction factors ΔE^K and $\Delta \zeta 4F$ have been calculated by the least squares fit method. The calculated correction factors are then added to the zero order parameters to obtain the Racah parameter (E^K) and the spin orbit interaction parameters $\zeta 4F$. The Slater integrals (F_K) have been evaluated from Racah parameters using relevant expressions. The rms deviations between the energies $E_{(cal)}$ calculated using these parameters and the observed energies E_{obs} are in experimental limits . The value of oscillator strengths of the complex are found to be higher as compared to free ion which shows higher complexation . Hence it may be concluded that higher magnitude of oscillator strength indicates inner sphere complexation[27]. The values of Slater Condon (F_K) , Racah parameter (E^K) have been given in table 1 and 2 .The relation among different F^K parameters is found to be $F_2 > F_4 > F_6$ and E^k parameters is $E^1 > E^3 > E^2$. From the observations and calculations the following points may be concluded-

1) Very much variation in the intensities of the oscillator strength P (obs.) and P(cal.) have been found in the present study. From the result it has been found that Er (III) biotin system shows the best inner sphere complexation among all the systems under study.

2)The value of nephelauxetic ratio β has been found less than one in all the systems and the value of $b^{1/2}$ is positive, indicating covalent characters[28-31]. From the result it has been found that Er (III) biotin system shows lowest value of β and highest value of $b^{1/2}$. The highest value of Sinha's covalency parameter $\delta\%$ shows highest covalent character. Therefore from the result it has been found that Er (III) biotin system has highest covalent character among all systems.

3) The Lande parameter ($\zeta 4F$) indicates decrease in spin orbit interaction. The value of $\zeta 4F$ for all systems has been found to be very low . The greater decrease $\zeta 4F$ value indicates decrease in interelectronic repulsion and spin orbit interaction, which suggests expansion of the central metal ion orbits on complexation[32].

4) The F_2 parameter indicates decrease in interelectronic repulsion and may be attributed to chelation of metal ion with ligand present in surrounding environment[32]. From the results very much decrease in F_2 parameter has been found in Er (III) biotin system.

5) Very much variation in Judd-Ofelt parameters (T_2 , T_4 , T_6) is observed which lies in the ordered $T_2 > T_6 > T_4$ .These data is good agreement with the Er (III) ion characterization. Judd-Ofelt intensity Parameter T_λ have also been computed from Judd-Ofelt expression by using partial and multiple regression method. The T_2 , T_4 and T_6 values are very high in Er(III) biotin system. So Er (III) biotin system shows better inter ligand interaction and greater change in symmetry. The ratio of T_4 / T_6 indicates symmetry around cation .The ratio of T_4 / T_6 values indicate remarkable changes in symmetry around Er (III) ion in all systems.

6) Small values of rms deviation for P(obs) and P(cal) for all bands in Er (III) systems proved the validity of Judd-Ofelt equation. From the results Er (III) biotin system shows highest rms deviation.

7) Validity of Slater Condon and Lande theory has been proved by the rms deviation (rms σ) values of energies among all the system. From the result Er (III) biotin system shows lowest rms deviation (σ) .

APPLICATION.

The examination of electronic spectral parameters of the systems, the covalency is inferred to some extent to metal-ligand bonding. The study also provides some useful information regarding validity of Judd-Ofelt equation, interelectronic repulsion, spin orbit interaction and symmetry changes around Er (III) ion .

379

ACKNOWLEDGEMENT

REFERENCES

[1]   T.Katsugama , H. Mastumura , *J Appl. Phys*. **1994** , 75 ,   2743-2748.

[2]   J.S.Sangara , L.E. Busse , I.D. Aggarwal *, J. Appl. Phys.* **1994** , 75, 4885-4891.

[3]   H. J.Lozy Kowsk, A.K Alshawa , I. Brown , *J. Appl. Phys.* **1994,** 76 ,   4836-4846 .

[4]   B.Kalagouda Gudasi, C. Vidyadhar , A. Havanur,P. Siddappa, R. Basavaraj Patil , Hindawi Publishing Corporation, Metal Based Drugs article ID 37348 , 2**007,** 7

[5]   E.Robert , Sievers Rogar E Rondeau ; *J. Am. Chem. Soc*, **1971,** 6 , 1522-1524 .

[6]   Aryamitra Pandey , K.P. Soni and G.K. Joshi ; *Asian J of Chemistry*, **2000,** 12 (2) , 515-520

[7]   Gamal E. Khalil, Elizabeth K. Thompson, Martein Gauterman ; *Chemical Physics Letters*, **2007,** 435, 45-49

[8]   L. E. Walbum ; *Acta path micro Biol. Scand* , **1996,** 3 , 489 **.**

[9]   Ishiwara , *gaun* ,**1927,** 21 , 1 **.**

[10]   Iwako Kawabe and Akimasa Masuda , *Geochemical Journal* , **2001,** 35, 215-224 **.**

[11]   A. Florez , J.F.Martinez ,M. Florez ,P.Porcher , *J Non-Cryst. Solids*, **2001,** 284 , 261.

[12]   P.W.Ed Franch , Fluoride glasses for optical fibres ,Blackie, London **1990.**

[13]   M. Poulain , G.Maze ,*Chemtronics*, **1998,** 3, 77 **.**

[14]   J.Y. Allain , M.Moneri , H. Pogant , *Electron lett.* , **1990,** 26 , 166 .

[15]   Y. K. Sharma , S. P. Tandon , S. S. L. Surana , C. L. Can Gehlot , *J. Anal Sci Spectroscopy* , **2000,** 45 , 66 .

[16]   A.R. Devi , C.K Jayshankar , *Phys. And Chem. Glasses* , **1996,**36,37 **.**

[17]   Y. K. Sharma, R. P. Dubedi, V. Joshi, K. B. Karnataka , S. S. L. Surana , *Indian Journal of Engineering & Material Science*, **2005,** 12 , 65-74.

[18]   David Singh , CH Sumitra, N Rajmuhon Singh , Indra devi ; *J. chem. Sci.,* **2004,** 116 , 303-309.

[19]   Sujeet Jain , Ragini Singh , *J. Chem. Pharma Res.* , **2011,** 3 (1), 1-5.

[20]   N. Guskos, J. Majszezyk, J. Typek, G Zolnierkeiwicz, E Tomaszewicz , K Aidnis , *Adv. Mater. Sci.* , **2010,** 23 , 97-101.

[21]   J A Hutchinson and T H Allik ; *Appl. Phys. Lett.* , **1992**, 60, 1424.

[22]   S Jiang, M. Myers , N Peyghabarian, *J Non-cryst. Solids* , **1998,** 239, 143.

[23]   S Zhanga and D Sherrya ; *J. Solid State chem.* , **2003,** 171 , 38 **.**

[24]   B. Kaymakcioglou , S Rollas , *Farmaco* , **2002,** 57, 595.

[25]   E.Y Wong , *J Chem. Phys.* , **1961,** 35 , 544 .

[26]   E.Y Wong ; *J Chem. Phys.* , **1963,** 38 , 976 .

[27]   Y. K. Sharma , S. P. Tandon ,S.S.L. Surana , *Mater Sci Eng* ,**2000,** B77 , 167.

[28]   B. R. Arbad, S. R. Mirgane , V. N. Bhosale , *Int. J. Chem. Sci* , **2008,** 6 (1) , 285-290.

[29]   R. S. Verma, Sushma Jain ,G. K. Joshi, *Asian Journal of Chemistry*, **2001,** 13 (3) , 1067-1070.

[30]   R. S. Verma , G. K. Joshi, *Asian Journal of Chemistry*, **2001,** 13 (2).

[31]   Aryamitra Pandey , P.C. Tater , K. P. Soni , G. K. Joshi , *Asian Journal of Chemistry* , **2001,** 13 , 319-322 **.**

[32]   Jaishankar Acharya, R.S. Verma, R.P. Mathur, *J. Indian Chem. Soc.,* **2010,** 87, 465-470.

380