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A Comparison of Bonding Parameter of Rare-Earth Complexes in Different Amino-acids

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***Abstract**- The absorption spectra of Neodymium and Erbium are recorded in visible region by taking Glycine and Arginine as primary ligand and Thiourea as a secondary ligand in the molar ratio1:2:1. In case of rare-earth complexes induced electric dipoles are responsible for the f-f transitions. Some transitions are arising due to electric as well as magnetic field. Energy levels corresponding to different peaks of Neodymium and Erbium can be expressed in terms of Slater-Condon's and Lande's parameters. In Neodymium complexes ten peaks and in Erbium complexes eight peaks are observed in visible region. After complexation values of Slater-Condon's and Lande's parameters decrease as there is expansion of central metal ion on complexation. By using Taylor's series expansion these parameters are calculated. Bonding parameter corresponding to these complexes also depends on Slater-Condon's and Lande's Parameters. In case of Neodymium: Glycine: thiourea bonding parameter is 0.1269707 but in Arginine it is 0.10997. In Arginine complex with Neodymium bonding parameter is less which indicates less involvement of 4f orbital. In Neodymium complexes bonding parameter is not real therefore all complexes of this rare-earth show ionic bonding. In case of Erbium: Glycine: thiourea bonding parameter is 0.6959 but in Arginine it is 0.712. In Arginine complex with Erbium bonding parameter is real for all complexes of this rare-earth and hence shows covalent bonding.*

***Key-words*: Neodymium, Erbium, Glycine, Arginine, bonding parameter**

Introduction

In free ion states, magnetic transitions are responsible and on complexation there exists induced electric dipole transitions which are responsible for the spectral lines of these complexes. The Judd-Ofelt theory is mainly used to calculate intensity of 4f transitions in rare-earth complexes [1]. The values of various parameters like Slater-Condon's, Lande's and bonding parameters are computed by using partial regression method. Due to narrow line width and weak interaction of ion with surrounding ligands make the rare-earth complexes as a useful lasing materials [2]. Various Co-workers studied f-f transitions in rare-earth complexes [3-7]. By observing the spectra of these complexes, position of different peaks can be calculated. Energy corresponding to these peaks can be expressed in terms of Slater-Condon's and Lande's parameters Victory

Devi Ch. and Rajmuhon Singh N. (2014) studied the Binding Interaction of Nd(III) with D-proline and DL-Proline [8].

Objectives

- To Compare Nephelauxetic ratio of Neodymium and Erbium complexes.
- To express the relation of energy levels of different complexes and Slater – Condon parameters F2, F4, F6 and Lande's parameter ξ4f.
- To compare the bonding parameters and hence to find nature of bonding for different complexes.

Hypothesis

Expansion of 4f orbital's (after Complexation) can be expressed in terms of Nephelauxetic Ratio (β). Nephelauxetic Ratio $\beta = F^c{}_k / F^f{}_k$

$F^c{}_k$ = Complex state, Slater-Condon Parameters, $F^f{}_k$=free ion state, Parameters

Relation between Bonding parameter and Nephelauxetic Ratio is $b^{1/2} = [(1-\beta)/2]^{1/2}$

If β>1 Then Complex is Ionic If β<1 Then Complex is Covalent

METHODS and PROCEDURE

Complexes of Neodymium and Erbium are prepared in Glycine and Arginine as primary ligand and thiourea as a secondary ligand in the molar ratio 1:2:1 in water and ethanol as solvents. Spectra of these complexes are recorded by the spectrophotometer. Working of spectrophotometer is based upon Beer Lamberts Law which relates absorbance and concentration of complexes. Source of light, Monochromator, sample, cells, detector and photoelectric unit are the major components of spectrophotometer. Absorption peaks for Neodymium and Erbium are recorded in visible region.

Results

In case of Neodymium Complexes ten peaks and for erbium eight peaks are observed in visible region by using Labinda Spectrophotometer. Bands of Neodymium are observed as

$4F_{3/2}$	$4F_{5/2}$	$4F_{7/2}$	$4F_{9/2}$	$4G_{5/2}$	$4G_{7/2}$	$4G_{9/2}$	$2G_{9/2}$	$4G_{11/2}$	$2P_{1/2}$

Erbium, ground state is $4I_{15/2}$. Eight bands of Erbium are designated as.

$4I_{9/2}$	$4S_{3/2}$	$2H_{11/2}$	$4F_{7/2}$	$4F_{5/2}$	$4F_{3/2}$	$2H_{9/2}$	$4G_{11/2}$

Position of Energy levels can be expressed in terms of Taylor-series expansion

$E_j(F_k, \xi_{4f}) = Eoj\ (F_k^o, \xi_{4f}^o) + \sum \partial E_j/\partial F_k\, \Delta F_k + \partial E_j/\partial \xi_{4f}\, \Delta \xi_{4f}$ Where, k = 2, 4, 6

Observed energy value relates with Slater-Condon parameters by the Judd-Ofelt Relation

$E_1 = 14.6818 \times F_2$, $E_2 = 0.0768 \times F_4$, $E_3 = 1.4844 \times F_6$

Bond strength of complexes can be represented by bonding parameters $b^{1/2}$

Fig-1 represents curve between absorbance and wavelength for Neodymium: Glycine: Thiourea in the molar ratio 1:2:1

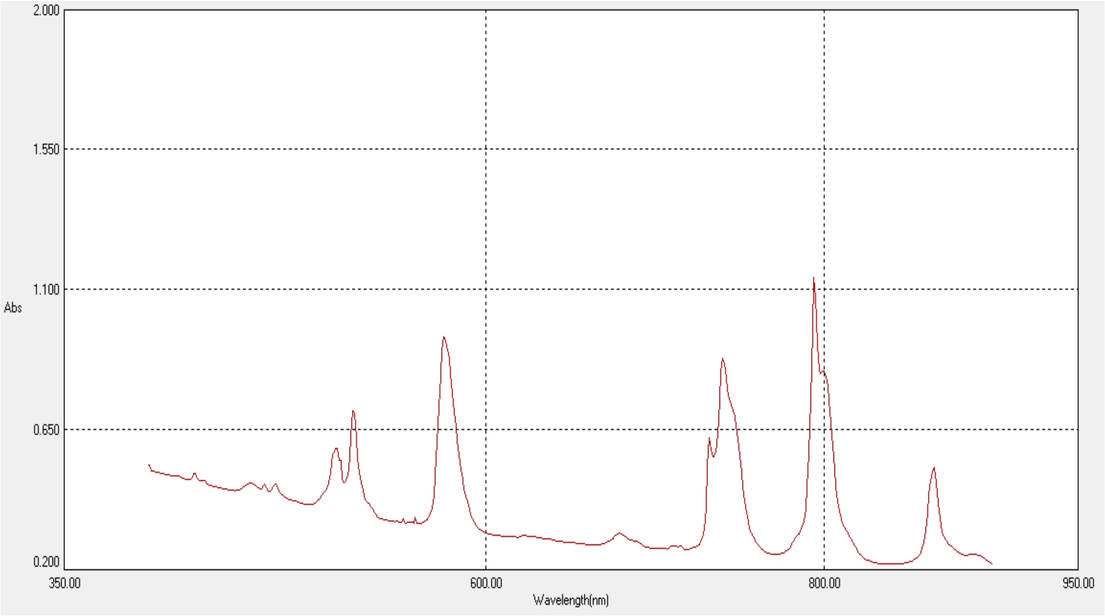

Fig-2 represents curve between absorbance and wavelength for Erbium: Glycine: Thiourea in the molar ratio 1:2:1

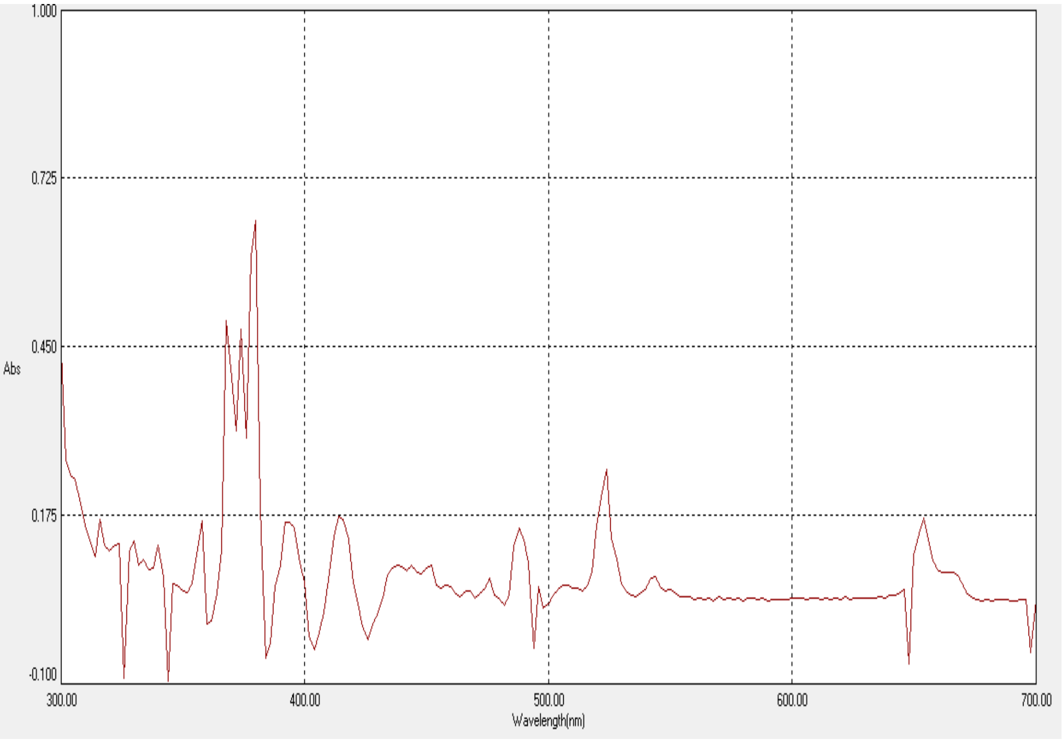

Fig-3 represents curve between absorbance and wavelength for Neodymium: Arginine: Thiourea in the molar ratio 1:2:1

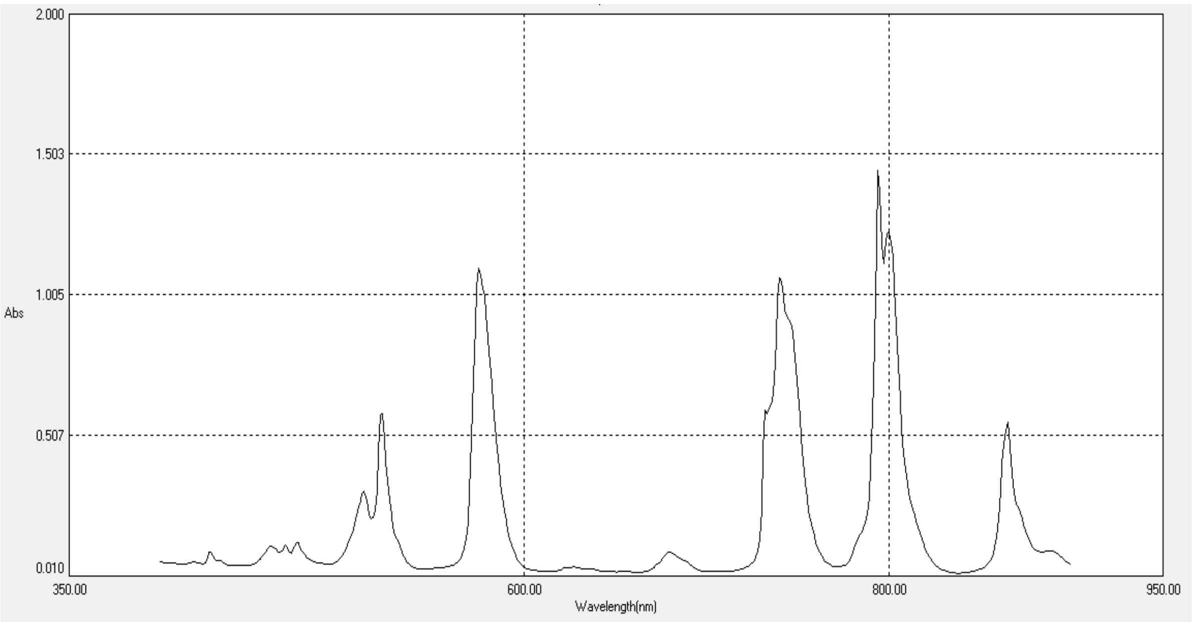

Fig-4 represents curve between absorbance and wavelength for Erbium: Arginine: Thiourea in the molar ratio 1:2:1

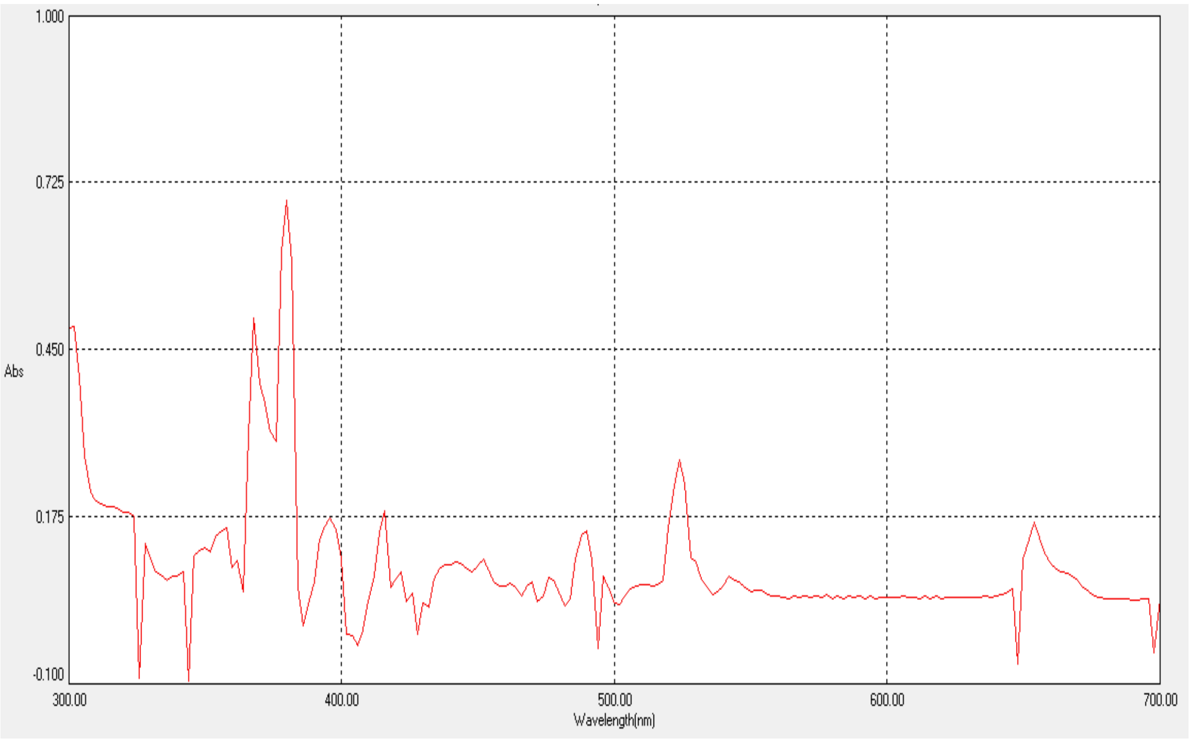

Table-1

Parameters	Neodymium:Giycine:ThioUrea	Erbium:Glycine:ThioUrea
E_1	5122.898	1580.586
E_2	26.35655	10.57
E_3	496.8451	228.34
E_1/E_3	10.31086	6.921
E_2/E_3	0.053047	4.630
F_2	341.8377	13.827
F_4	47.84321	9.185
F_6	5.557	7.681
$F_{4/}/F_2$	0.1399	0.664
$F_{6/}/F_2$	0.01625	0.555
Nephelauxetic Ratio	1.0322	0.0313
Bonding parameters	**0.12697**	**0.695**

Table-2

Parameters	Neodymium:Arginine:ThioUrea	Erbium:Arginine:ThioUrea
E_1	5078.081	1484.384
E_2	25.921	4.999
E_3	496.38	224.36
E_1/E_3	10.23	6.61
E_2/E_3	0.05	0.022
F_2	339.17	6.40
F_4	47.9	0.817
F_6	5.43	6.99
$F_{4/}/F_2$	0.141	0.1277
$F_{6/}/F_2$	0.016	1.09
Nephelauxetic Ratio	1.02	-0.01449
Bonding parameters	**0.109**	**0.7122**

Table-1 represents Comparison of Energy, Slater-Condon, Nephelauxetic Ratio and Bonding parameters between Neodymium and Erbium Complexes and Glycine as Primary Ligand. For Neodymium $\beta>1$ and bonding parameter is not real. For Erbium **β**<1 and bonding parameter is real. **Table-2** represents Comparison of Energy, Slater-Condon, Nephelauxetic Ratio & Bonding parameters between Neodymium and Erbium Complexes and Arginines Primary Ligand.

Conclusion

For rare-earth complex bonding is considered to be ionic because of their inert gas electronic configuration and well shielding of 4f orbitals. But experimentally covalency is observed for Erbium complexes. Electron–electron repulsion and spin orbit interaction, decreases

Nephelauxetic ratio but increases covalence. Nephelauxetic ratio increases because of shortening of metal–Ligand distance. Nephelauxetic ratio effects Coordination number and Geometry of complex.

Implication of Study:

Rare-earth complexes with amino-acids exhibit sharp bands in uv-visible region. This spectrum provides important information regarding outer and inner co-ordination sphere. Bonding Parameter of these complexes provides information about the nature of bonding ionic or covalent. Rare –earth incorporated with amino-acids has wide applications in the field of Medicine, Biology and Agriculture. Due to their narrow line width they are using as Lasing action (LASER)

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