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A Comparative Study of Bonding Parameter of Neodymium and Erbium in Alanine and in ThioUrea

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Abstract: Neodymium and Erbium both belong to Rare-earth series-4f. Absorption spectra of Neodymium and Erbium with Alanine as primary ligand and ThioUrea as secondary ligand have been observed. Spectra is recorded in the visible range by using UV Spectrophotometer. Various parameters Racah Parameter, Slater-Condon Parameters, Lande's Parameter and bonding parameters are calculated. Rare-earth ion shows its absorbtion spectra in near infrared, visible, and ultraviolet region. They undergo modifications when the rare earth ions are placed in different lattice sites in crystals or different environments.

Keywords-Neodymium, Erbium, Thiourea, UV-VS spectrophotometer and Nephelauxetic Ratio

I. INTRODUCTION

Neodymium is mainly used in lasers, ceramic glasses and ceramic capacitors. In case of ternary complexes of Neodymium, the colour of it is reddish purple because of Nd^{+3}. Erbium III ion plays an important application in biological sciences.

In this work, ternary complexes of Neodymium (III) chloride hexahydrate (99.9% pure) and Erbium (III) chloride hexahydrate (99.99% pure) are prepared. Their solutions are prepared in amino acid Alanine, as primary ligand and Thiourea as secondary Ligand. For finding the natural frequency of lanthanides, absorption and luminescence spectroscopy are useful, either in solution or in glasses form, rare-earth complexes show lines. These bands are due to incomplete 4f shell, electronic to electronic transitions. In free ion, only magnetic transitions are allowed but on complexation, electric dipole transitions are induced as Ligand field mixes odd parity configuration to the rare-earth configuration. Racah introduced a much simpler method based on Taylor series expansion to solve these energy levels. On complexation, the repulsion decreases, causing a red shift of bands as compared to the bands of free ions. This phenomenon is known as Nephelauxetic effect. f-f transitions of rare-earth complexes in visible region are studied by various co-workers [1-15]. In the present study, solution spectra of rare-earths Neodymium and Erbium are studied. Due to electrostatic and magnetic interactions, there exist energy levels associated with rare-earth elements. The energy levels of these elements can be expressed in terms of four parameters (F_2, F_4, F_6) and Lande's parameter. Ten peaks are observed for Neodymium and eight peaks are observed for Erbium in visible region. Due to complexation, some of the absorption bands are modified and become more intense. These bands are due to hypersensitive transitions known as hypersensitive bands In the present study, Slater-Condon parameters, Lande's parameter are calculated for each ternary complex of Neodymium and Erbium. Their calculated values are compared with observed ones. Nephelauxetic Ratio determined bond strength and type of bonding in both complexes.

A. Preparation of Sample

Neodymium and Erbium are taken and are of standard purity. Their solutions are prepared in Alanine as primary ligand and Urea and Thiourea as secondary ligands. Their ternary complexes are studied in solvent form. The calculated energy levels corresponding to different peaks of Neodymium and Erbium Complexes are compared with the experimentally observed values. The energy level value changes due to change in ligands or change in solvents

B. Parameters

Change in environment of rare-earth ions sometimes doesn't change the position of energy levels too much. This causes only a slight change in various parameters [2]. It is very difficult to solve these parameters using method of diagnolisation because in some cases number of levels are higher than number of parameters**.** Various parameters like Slater-Condon, Lande's and Racah (Energy level parameter) on complexation as compared to free ion reveals, that on complexation there is change in symmetry around the metal ion, types of bonding between metal and ligands etc. Bonding parameter $b^{1/2}$ expresses bond strength of rare-earth complexes.

The bonding in rare-earth complexes is weaker than 3d orbital's.When rare-earth ternary complexes are formed the electronic repulsion becomes weaker as compared to free ions. This is due to delocalization of molecular orbitals over the ligands and away from the metal. The chemical bond for rare-earth complex is considered to be ionic because of their inert gas electronic configuration. It is due to well shielding of 4f orbitals. But experimentally, covalency is also observed for some rare-earth complexes. On complexation, there is expansion of 4f orbital's which can be expressed in terms of Nephelauxetic Ratio (β)[16-20]. Delocalization of molecular orbitals increases separation between electrons and reduces repulsion between electrons. This reduction is expressed in terms of a ratio known as Nephelauxetic ratio. ng.

$$\beta = F^{c}_{k} \; / \; F^{f}_{k}$$

Where, c = complex state f = free ion state

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

$$\delta = (1-\beta) / \beta$$

Fig.1 : Absorption Spectra of Neodymium:Alanine:Thiourea in the molar Ratio 1:1:2

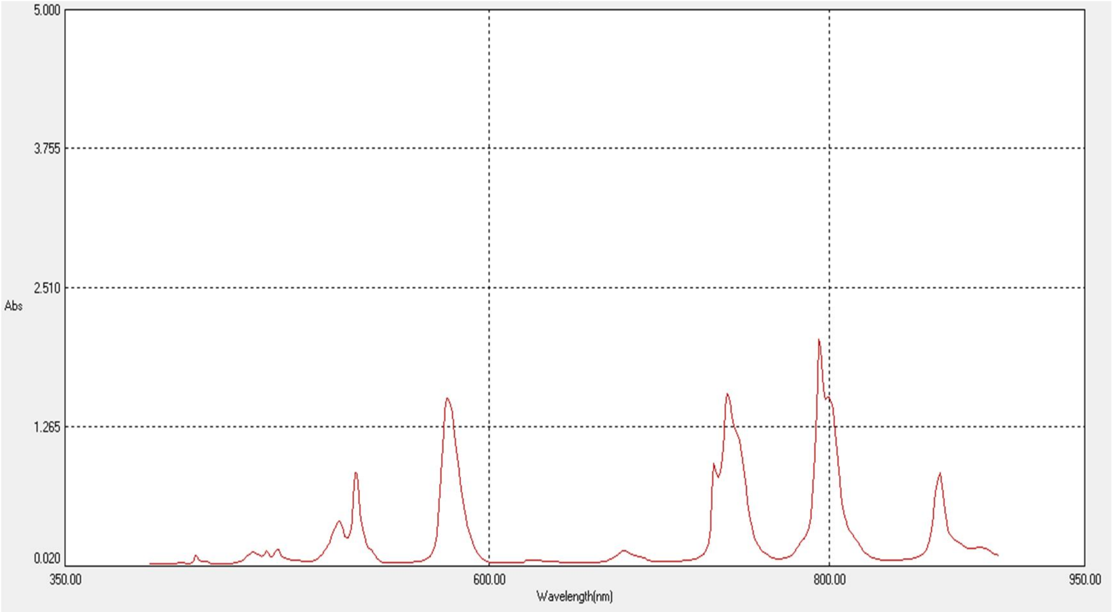
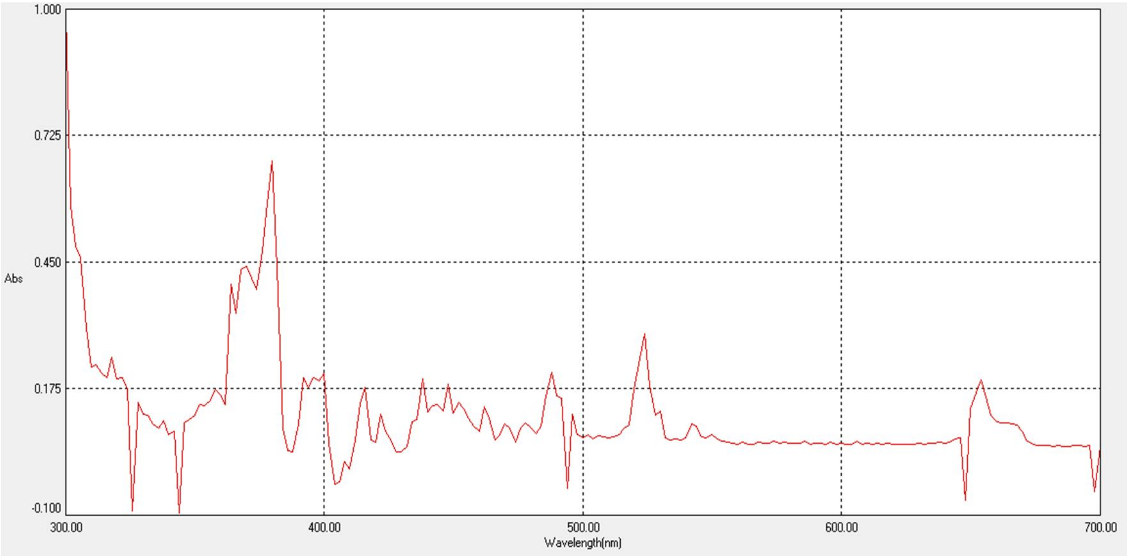


Fig. 2 : Absorption Spectra of Erbium : Alanine: Thiourea in molar ratio 1:1:2



C. *Observation Tables*

Table1 Observed and calculated values of energy levels for Neodymium and Erbium Complexes

Neodymium: Alanine: ThioUrea (1:1:2) Erbium:Alanine:ThioUrea (1:1:2)

Levels	Obs.cm^{-1}	Cal.cm^{-1}	Delta E	Levels	Obs.cm^{-1}	Cal.cm^{-1}	Delta E
$^4F_{3/2}$	11560.69	11567.20	-6.511	$^4I_{9/2}$	15290.52	15266.38	24.138
$^4F_{5/2}$	12594.44	12572.91	21.5	$^4S_{3/2}$	18867.92	18645.34	222.58
$^4F_{7/2}$	13513.51	13406.59	106.91	$^2H_{11/2}$	19230.76	19299.9	-69.13
$^4F_{9/2}$	14727.54	14781.23	-53.69	$^4F_{7/2}$	20491.8	20549.65	-57.85
$^4G_{5/2}$	17331.02	17405.33	-74.31	$^4F_{5/2}$	22123.89	22088.74	35.15
$^4G_{7/2}$	19193.85	19181.13	12.72	$^4F_{3/2}$	22522.52	22546.08	-23.55
$^4G_{9/2}$	19531.25	19566.56	-35.30	$^2H_{9/2}$	24691.13	24616.7	74.56
$^2G_{9/2}$	21008.40	20992.67	15.72	$^4G_{11/2}$	26315.78	26734.33	-418.54
$^4G_{11/2}$	21645.02	21662.20	-17.17	$^4G_{9/2}$	22932.83	27710.77	222.05
$^2P_{1/2}$	23419.2	23417.86	1.3				
rms deviation			47.21				179.53

Table2 Calculated value of different parameters-slater Condon ,Landes, Nephelauxetic ratio and bonding parameter.

Neodymium: Alanine: ThioUrea (1:1:2) Erbium:Alanine:ThioUrea (1:1:2)

F_2 (cm^{-1})	342.28	1.28
F_4 cm	47.48	2.90
F_6	5.56	6.79
Zeta 4F	869.75	147.8
E^1	5119.76	1576.49
E^2	26.53	4.17
E^3	496.51	202.47
F_4/F_2	0.138	2.2
F_6/F_2	0.0162	5.3
E^1/E^3	10.31	7.7
E^2/E^3	0.053	0.02061
Beta	1.0335	-0.00289
$b^{1/2}$	0.129	0.708

II. RESULT AND DISCUSSION

In case of Neodymium with other ligands, only ten peaks are observed in the visible region (380nm to900nm).Figure-1 represents various peaks of Neodymium and in case of Erbium only eight peaks are visible. Figure-2 represents various peaks of Erbium.For Neodymium, ground state of Nd^{+3} is $4I_{9/2.}$ Ten bands of Neodymium are designated as $4F_{3/2}$, $4F_{5/2}$, $4F_{7/2}$, $4F_{9/2}$, $4G_{5/2}$, $4G_{7/2}$, $4G_{9/2}$, $2G_{9/2}$, $4G_{11/2}$ and $2P_{1/2}$. In Nd^{+3}, transition $4I_{9/2}$ to $4G_{5/2}$ is hypersensitive transition. For Erbium, ground state is $4I_{15/2}$. Eight bands of Erbium are designated as $4I_{9/2}$, $4S_{3/2}$, $2H_{11/2}$, $4F_{7/2}$, $4F_{5/2}$, $4F_{3/2}$, $2H_{9/2}$, and $4G_{11/2}$. In case of Erbium(III), transitions $2H_{11/2}$ and $4G_{11/2}$ are hypersensitive transitions.

In Table1- first column shows calculated value and second column represents observed energy corresponding to ten peaks for Neodymium in Alanine and ThioUrea in the molar ratio 1:1:2.It also represents for Erbium metal too. For these complexes the R.M.S deviation is very small.

With the help of GW BASIC software calculated different parameters, Slater-Condon parameters F_2 ,F_4 and $F_{6,}$ Lande`s parameter, Nephelauxetic ratio and bonding parameter.

R.M.S deviation is small which confirms the formation of complex. In some cases value of T_2 is Negative which makes r.m.s deviation is very small.

The bonding in rare-earth complexes is weaker than 3d orbital's. The chemical bond for rare-earth complex is considered to be ionic because of their inert gas electronic configuration. It is due to well shielding of 4f orbitals. But experimentally covalency is observed for some rare-earth complexes. It has been observed from the calculations that bond strength for Neodymium is less than that of Erbium complexes.

According to this result, as the atomic number of rare-earth metal increases, contraction of 4f orbitals increases. By knowing the value of Nephelauxetic ratio, bonding parameter is calculated. It has been observed that if ligands are the same and the solvent is the same then as atomic number increases, covalency increases. Hence bonds formation in Erbium complexes are Covalent in nature but for Neodymium, it is ionic in nature.

For Neodymium - $\beta > 1$. Therefore, $b^{1/2}$ is not real and $\delta = (1-\beta)/\beta$ is negative. Hence Neodymium make Ionic bonding with amino-acid and with thiourea. For Erbium-Nephelauxetic Ratio, $\beta < 1$, therefore $b^{1/2}$ is real and $\delta = (1-\beta)/\beta$ is positive. Hence Erbium make Covalent bonding with amino-acid and thiourea. Atomic number of Erbium is greater than Neodymium. This indicates that as atomic number increases covalency also increases.

III. CONCLUSION

A. R.M.S deviation is small. It means there is prefect formation of complex.

B. For Neodymium, Nephelauxetic ratio is greater than one it means bonding between metal and ligand is ionic in nature. Due to strong affinity of complex formation of neodymium it finds wide variety of application in synthesis of proteins with different type of amino acids. The rare-earth polymers are also used in wave-guide and in polymers.

C. For Erbium, Nephelauxetic ratio is less than one it means bonding between metal and ligand is covalent in nature.

REFERENCES

[1] Shelby, J.E., Ruller, J.,(1987). Properties of Barium Gallium Germanate Glasses. Physics and Chemistry of Glasses, 28, 262-265.

[2] Arya, A., &Verma, R. S., (2018). Effect of PH variation on intensity parameters of Er (III)- Atropine doped systems having different metal-Ligand ratios. IJCRT, 6(1march 2018), 52-58.

[3] Arya, A., & Verma, R. S., (2018). Electronic spectral intensities of trivalent Neodymium-Brucine doped systems in Ethanol medium at PH 2 to 6 with different metal-ligand concentration. IJCRT, 6 (2 April 2018),198-210.

[4] Jain, S., & Verma, R.S.,(2002). Electronic characterization of Pr^{+3} system involving some analytically important reagents at PH 5 in ethanol medium. Oriental Journal of Chemistry, 18(3), 517-520.

[5] Upase, A.B., & Kalbende, P.P.,(2011). Spectrophotometric micro determination of Thorium(IV) and Uranium(VI) Chrome Azurol-S in the Presence of Cationic surfactant. E-Journal of chemistry, 8(3), 1132- 1141.

[6] Guskos, N., Majszczyk, J., Typek, J., Zolnierkiewicz, G., Tomaszewicz E., & Aidinis, K., (2010). Relative Intensities of f-f Transitions of Erbium(III) ion studied by photoacoustic spectroscopy. Rev.Adv.Mater.Science, 23, 97-101.

[7] Laegsgaard, J., (2002). Dissolution of rare-earth Clusters in siO_2 by Aluminium Doping, A microscopic model. Physical Review B,65,174114

[8] Ofelt, G.S.,(1962). "Intensities of crystal spectra of rare-earth ions". J. Chem. Phys. 37, 511-520.

[9] Vasiliu, I.C., Constantinescu, C., Voicescu, M., & Emandi, A., (2011). Solvent effects on the absorption and fluorescence spectra of Er(III) Complexes: Determination of ground and excited state dipole moment. Digital Journal of Nanomaterials and Biostructures, 6, 603-608.

[10] Agarwal, M., Bhatia, B., & Gehlot, A., (2016). Ultraviolet and Visible Up conversion Luminescence and Spectroscopic properties in Neodymium doped soda lime Silicate glasses. IJIRSE, 3(4), 175-181.

[11] Bhatia, B., & Meena, S.L., (2016). The Fluroescence of Pr^{+3} in Zinc Lithium bismuth borate glasses with large stimulated emission cross-section. Scientific Research, 6(2), 9-17.

[12] Chavan, M.C., Vaidya, P.V., Lokhande, N.R., & Ghoshal, M.N., (2010). Bonding and Energy parameters for some Pr(III) mixed ligand complexes. Asian Journal of Chemistry, 22(4), 2575-257 Judd, B.R., (1961). Optical Absorption Intensities of Rare-Earth Ions. Physical Review, 127, 750-760.

[13] Kumar, P.A., & Rao, T.R., (1997). Studies on some Rare-Earth metal complexes: Ten and six-coordinated complexes of an unsymmetrical Aminoacid derivative. Indian Acad. Science, 109, 89-97.

[14] Narasimam, K.V., & Girja, M.,(1969). Visible Absorption Spectrum of Neodymium in Calcium Fluoride & Calcium Tungstate Lattices. Indian Journal of Pure and Applied Physics, 7, 427-430.

[15] Deepmala, Gokhroo, A.(2018).A study of covalency of Erbium and Neodymium ternary complexes in Alanine and Urea, IOSR Journal of Applied Physics ,10(6),12-16.

[16] Sengupta, D., & Artman, J.O., (1970). Energy–Level Scheme for Nd^{3+} in $LiYF_4$. Journal of Chemical Physics, 2, 1-9.

[17] Surana, S.S.L., Mathur, R.C., Mehta, P.C., & Tandon, S.P.,(1975). A Comparative Study of Strengths and Judd-Ofelt Intensity parameters of Various Nd^{3+} Complexes. Pure & Applied Physics, 6, 363-365.

[18] Tandon, S.P., & Gupta, J.P.,(1970). A Note on Kubelka-Munk Theory of Diffuse Reflectance. Indian Journal of pure & Applied Physics, 8, 231-232.

[19] Dimitrov, V., & Komatsu, T.,(2005). Classification of Oxide Glasses-A Polarizabilty Approach. Journal of Solid State Chemistry, 178, 831-846.

[20] Deepmala and Gokhroo,A.,(2018). Visible Absorption Spectra of Erbium and Neodymium in Arginine as a primary Ligand and Urea as a Secondary Ligands, Journal of Emerging Technologies and Innovative Research ,5(10),399-406.