Spectral Study of Some Rare-Earth complexes in Urea and in Thiourea

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Abstract

Rare-Earth Elements show quite unique and interesting properties. Neodymium belongs to Lanthanide and its configuration is $4f^4 5d^0 6s^2$. Equal volume of neodymium and Glycine (primary Ligand) and Urea and thiourea as secondary ligand are mixed, their solution are prepared in 1:2:1 molar ratio. Their absorption spectra of complexes is recorded by UV-VIS spectrometer .The value of different parameters F_2, F_4, F_6, Lande's parameter, Intensity parameters T_2, T_4, T_6 have been reported. The effect of Glycine on the position and intensity has been discussed in terms of bonding parameter. Optical density is calculated by the standard formula and from wavelength curve, their optical strength can be calculated. On the basic of deviation, Covalency is calculated.

Key words- Labinda, Neodymium, Glycine, Urea, , Slater Condon and Covlancey.

INTRODUCTION

The rare earth elements form an outstanding and unique group among metals. They may be ionised by successive removal of electrons. The tripositive rare earth ions have attracted the attention of a number of workers with the recent surge of interest in the optical properties of rare earth ions in crystals. The electronic spectra of rare earths, both in natural and free ion states consists of closely spaced group ($\approx 10^2$-10^3 cm^{-1}) of sharp lines in the near infrared, visible, and ultraviolet region. The matrix elements of electrostatic interactions corresponding to H_e can be written as

$$E_e = \sum_{K=0}^{6} f_K \, F^K \qquad \ldots\ldots\ldots(1)$$

Where f_k represents angular part of the interaction and value of K is even. F^k are Slater-Condon parameters.

$$F_K = \frac{F^K}{D_K}$$

F_k= It is a reduced Slater radial integral

Value of D_k is given by Condon and Shortely.

$$F_K = \frac{1}{D_K} \int_0^\infty \int_0^\infty \frac{r_<^K}{r_>^{K+1}} R_i^2(r_i) R_j^2(r_j) r_i^2 \, r_j^2 \, dr_i \, dr_j \quad \ldots\ldots (2)$$

R= 4f radial wave function

$R_<$ = Radius of electron near to the nucleus

$R_>$ = Radius of next electron under consideration

Where i^{th} and j^{th} represent corresponding electrons.

They undergo modifications when the rare earth ions are placed in different lattice sites in crystals or different environments. Rare-earth complex usually do not form good single crystals and also decomposes in glassy matrix. They can be studied either in powder form by diffuse reflectance or in solution spectra, offers the possibility to study the solvent effect

RESULTS and DISCUSSION

The effect of complexation on the free ions is the red shift of electronic transitions. The red shift is due to the expansion of metal orbital radius, resulting in the decrease of the interelectronic repulsions parameters. This effect is known as Nephelauxetic effect. This effect is usually expressed in term of β

$$\beta = F^c_k \nearrow F^f_k$$

Where c=complex state,f =free ion state

δ =(1-β) / β, Where δ is a bonding parameter.

If δ is positive then there is covalent bonding between metal and ligand.

If δ is negative then there is ionic bonding between metal and ligand.

By calculating Slater-Condon parameter F_2,Racah Parameter can be calculated

$$E^1=14.6818F_2\,, \quad E^2=0.0768F_2\,, \quad E^3=1.4844F_2$$

Oscillator Strength corresponding to different peaks of Neodymium and Erbium are calculated from the formula for Oscillator Strength. It is given by

$$P=4.6 \times 10^{-9} \times \varepsilon_{max} \times \Delta\nu_{1/2}$$

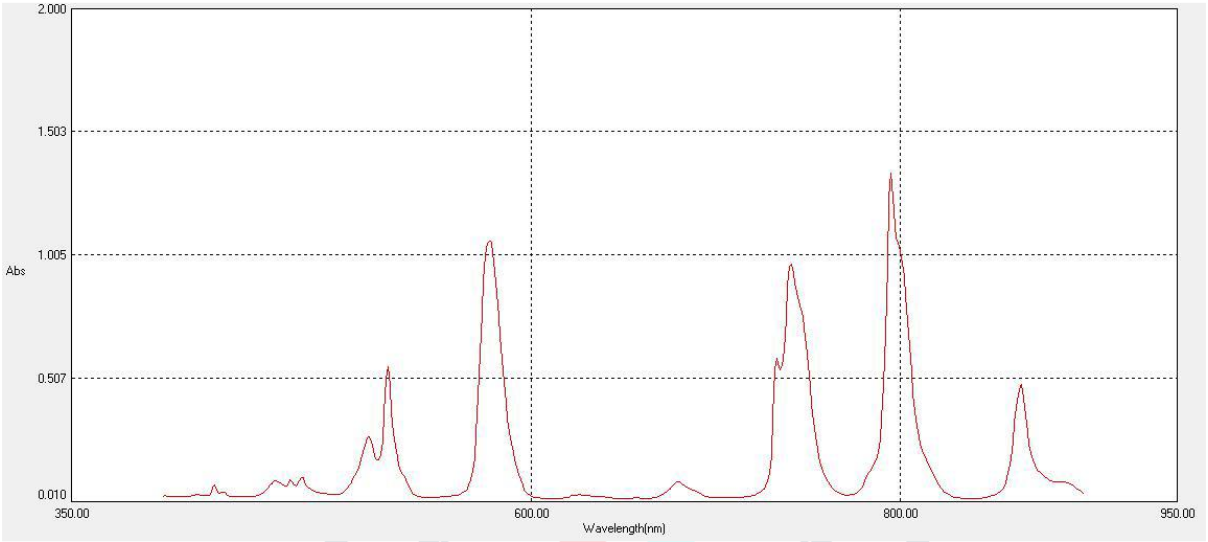
Where, ε_{max} = Molar Extinction Coefficient

$\Delta\nu_{1/2}$=Half Band Width

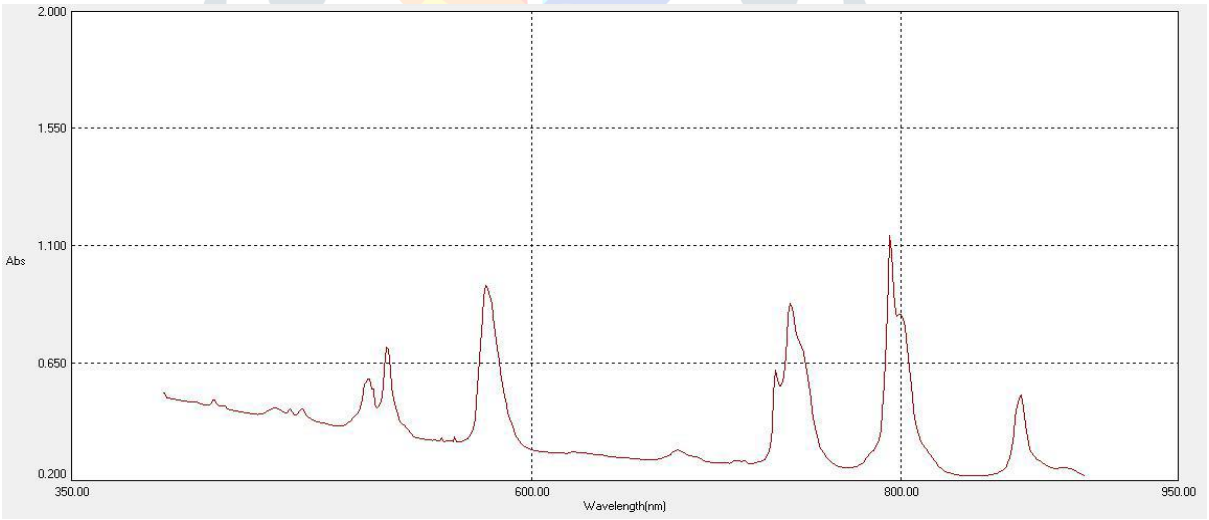
From the Spectrum, Half Band Width

ε_{max} = 1/ C x L (Log I_0/I) = 1/ C x L (Optical Density)

Absorption Spectra of Neodymium:Glycine:Urea in the molar ratio 1:2:1



absorption Spectra of Neodymium:Glycine:Thiourea in the molar ratio1:2:1



Observed and Calculated Energy levels parameters for Neodymium: Glycine : Urea in Molar Ratio 1:2:1

Levels	Observed	Calculated	Delta
4 F 3/2	11560.7	11536.07	24.6
4 F 5/2	12578.61	12569.45	9.15
4 F 7/2	13495.2	13399.84	95.32
4 F 9/2	14727	14781.15	-53.63
4 G 5/2	17331.00	17377.74	-46.72
4 G 7/2	19157.07	19186.25	-29.17
4 G 9/2	19.531.25	19591.68	-60.43
2 G 9/2	21052.63	21022.21	30.42
4 G 11/2 |	21691.97	21685.26	6.7
2 P ½	23148.15	23151.21	-3.05

ENERGY PARAMETERS
E1 : 5018.118
E2 : 25.25199
E3 : 495.5276
E1 / E3 : 10.12682
E2 / E3 : 5.095981E-02
F PARAMETERS
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F2 : 335.2371
F4 : 48.27884
F6 : 5.266763
Zeta4F : 877.5356
F4 / F2 : .144014
F6 / F2 : 1.571056E-02
rms Deviation : 45.09754
Nephelauxetic Ratio : 1.012311

Observed and Calculated Energy levels parameters for Neodymium: Glycine : ThioUrea in Molar Ratio 1:2:1

levels	Observed	Calculated	Delta
4 F 3/2	11560.7	11561.77	-1.06
4 F 5/2	12594.45	12574.59	19.865
4 F 7/2	13513.51	13410.89	102.61
4 F 9/2	14727.54	14795.81	-68.26
4 G 5/2	17361.11	17396.22	-35.11
4 G 7/2	19157.08	19190.08	-33.001
4 G 9/2	19531.25	19579.04	-47.78
2 G 9/2	21052.63	21021.22	31.41
4 G 11/2 |	21691.97	21676.60	15.28
2 P 1/2	23419.2	23417.24	1.9

ENERGY PARAMETERS
E1 : 5116.125
E2 : 26.45488
E3 : 496.0764
E1 / E3 : 10.31318
E2 / E3 : 5.332824E-02

F PARAMETERS
F2 : 341.8098
F4 : 47.5493
F6 : 5.561712
Zeta4F : 873.9931
F4 / F2 : .1391104
F6 / F2 : 1.627136E-02

rms Deviation : 46.27774

Nephelauxetic Ratio : 1.032159

Bonding Parameter : .1268051

CONCLUSION

In case of Neodymium ground state of Nd^{+3} is $4I_{9/2}$. Ten bands of Neodymium are observed and these bands are $4F_{3/2}$, $4F_{5/2}$, $4F_{7/2}$, $4F_{9/2}$, $4G_{5/2}$, $4G_{7/2}$, $4G_{9/2}$, $2G_{9/2}$, $4G_{11/2}$ and $2P_{1/2}$. In Nd^{+3}, transition $4I_{9/2}$ to $4G_{5/2}$ is hypersensitive transition. For Neodymium, Nephelauxetic Ratio, $\beta > 1$. Its value is higher when we add two moles of amino-acids. As amino-acid part increases value of β increases. Therefore, $b^{1/2}$ is not real and $\delta = (1-$
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β) / β is negative in this present work. Hence all ternary complexes of Neodymium make Ionic bonding with different amino-acids and with urea or thiourea.

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