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A Comparative Study of Parameters of Neodymium in Threonine and with Urea and Thiourea

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Abstract: Among metals, the rare-earth elements form an outstanding and unique group. The Configuration of rare-earths ion is given by $(1s^2 2s^2 2p^6 3s^2 3p^6 3d^{10} 4s^2 4p^6 4d^{10} 5s^2 5p^6) 4f^n 5d^1 6s^2$ and value of n varies from one to fourteen. These fourteen elements form 4f inner transition series. f-f transitions of rare-earth complexes lie in UV-visible region. 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.

These parameters changes due to change in ligands and also change in solvents. Electronic transitions take place due to Electric dipole, Magnetic dipole and Electric Quadrupole transitions.

Keywords: Rare-earth, Electrostatic-Magnetic Interactions, Lande's Parameter and f-f Transitions.

I. INTRODUCTION

In rare earth complexes, observed intensities of spectral lines are very large. This cannot be explained on the basis of magnetic dipole and electric quadrupole interactions. Induced electric dipole transitions are mainly responsible for the occurrence of these lines. Induced electric dipole transition is strongest in three. Oscillator strength corresponding to these transitions can be expressed in terms of three T_λ parameters. According to Judd, T_λ parameters have contribution due to two parts, radial as well as perturbing configurations. The electronic and spin orbit interactions yield energy level parameters that deviates much from the observed energy levels. In case of Lanthanides, metals become ionized by successive removal of electrons. When all electrons of 6s and 5d are removed then this is known as third stage ionization.

Magnetic interactions can also be expressed in terms of product of radial and integral part. F_4 and F_6 can be expressed in terms of F_2 alone. Hence in this way the number of parameters reduced to two instead of four.

In rare-earths, f-f transitions are forbidden by parity and spin conservation rules and due to this, there is a very small area of absorption cross-section of rare-earth. When there is formation of ternary complexes of rare-earths, two ligands are always preferred, one ligand absorbs energy and transfer to the lanthanide, known as antenna effect and second ligand removes the remaining water molecule in the co-ordination sphere to avoid radiation less transition.

After complexation, a decrease in value of Lande's parameter is large as compare to Slater-Condon parameter. It means ligands effect is more at spin-orbit coupling than the electronic repulsion. Judd-Ofelt parameters that is T_λ parameters if it changes it means there is change in environment around the metal. Judd used odd parity terms of ligands and applied second order perturbation theory to explain the intensities of different peaks of rare-earths.

II. PREPARATION OF SAMPLE

Solutions of Neodymium in Threonine as a primary ligand and Urea and Thiourea as secondary ligands are prepared in ethyl alcohol. Their ternary complexes are studied in solvent form. The calculated energy levels corresponding to different peaks of Neodymium are compared with the experimentally observed values.

The energy level values changes due to change in ligands or change in solvents. All reagents are taken of standard purity. All chemicals are from C.D.H Company.

The complexes are prepared by taking amino-acid that is Threonine as primary ligand and Urea or Thiourea as secondary Ligand mixed in 1:1:2 molar ratios. The solution is stirred for half an hour. Magnetic stirrer method is used for uniform heating. The absorption spectra of the complexes are recorded with UV-VIS Spectrophotometer LABINDA 3000⁺ in visible range.

A. Formula Used For Various Parameters

Judd-Ofelt theory explains the coupling of 4f states to the surrounding orbitals. This theory is quite useful for intensity measurements of lanthanide's ternary complexes. Intensity of various transitions is expressed in terms of T_λ and $(\Omega)_\lambda$ parameters. For solids and liquids Judd and Ofelt theory describes transitions (4f-4f) for rare-earth ions. With the help of this theory, theoretical value of line strength can be calculated.

$$S_{ED} = e^2 \sum_{t=2,4,6} \Omega_t |\langle f^n [SL] J || U^t || f^n [S^1 L^1] J^1 \rangle|^2$$

Judd-Ofelt theory is used to find a set of omega parameters ($\Omega_2, \Omega_4, \Omega_6$) by fitting the experimental data on absorption or emission measurements. For rare-earth host

$$f \left[\left| \langle [SL] J \rangle, \langle [S^1, L^1] J^1 \rangle \right| = \frac{mc}{\pi n^2 N} \right] \alpha(\nu) d\nu$$

Where, S =spin quantum number

Theoretical value of oscillator strength is given by

$$P_{ed} = \sum T_\lambda \nu < f^n \psi_j || U^\lambda || f^n \psi_j >^2$$

The bonding in rare-earth complexes is weaker than 3d orbital's. Bonding in rare-earth complexes is considered to be ionic because of their inert gas electronic configuration. 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). This reduction is expressed in terms of a ratio known as Nephelauxetic ratio.

$$\beta = F_k^c / F_k^f, \quad \text{Bonding parameter is } b^{1/2} = [(1 - \beta) / 2]^{1/2}$$

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

The value of β depends on the ligands and varies along the nephelauxetic series.

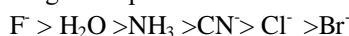


Fig. 1: Absorption Spectra of Neodymium:Threonine:Urea in the molar ratio 1:1:2

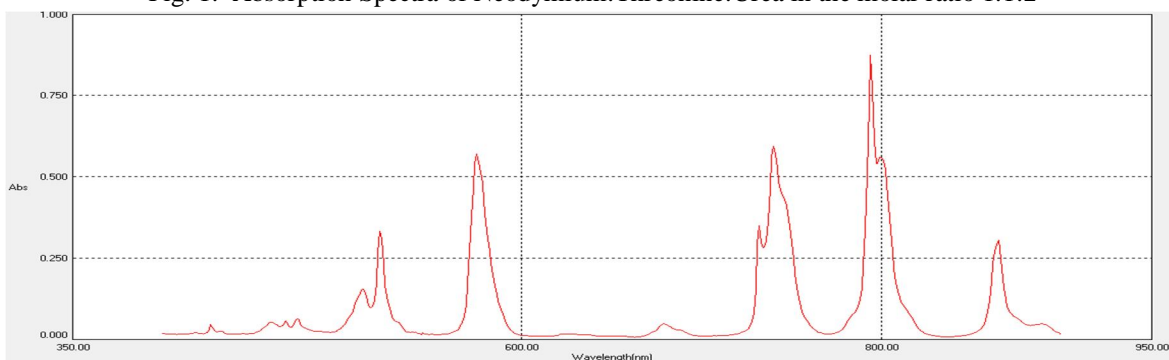


Fig. 2 : Absorption Spectra of Neodymium: Threonine: Thiourea in the molar ratio 1:1:2

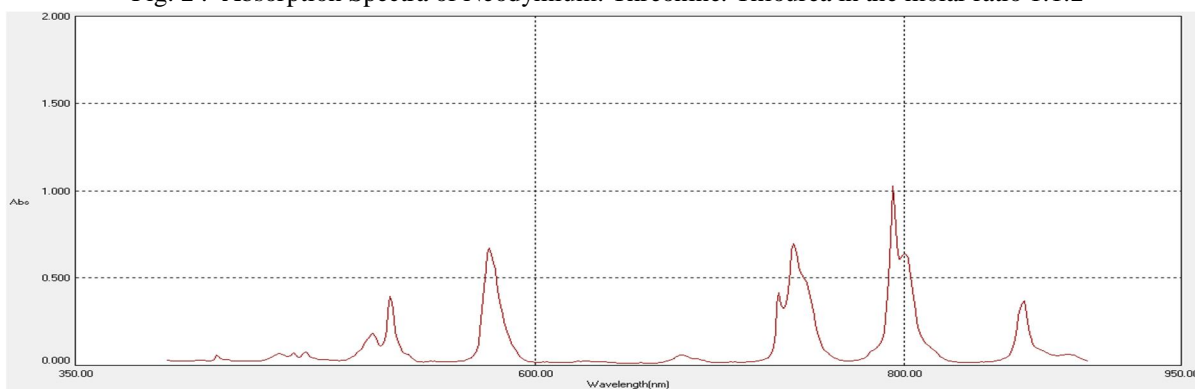


Table-1
Energy Levels of Neodymium: Threonine: Urea in the Molar Ratio 1:1:2

Levels	⁴ F _{3/2}	⁴ F _{5/2}	⁴ F _{7/2}	⁴ F _{9/2}	⁴ G _{5/2}	⁴ G _{7/2}	⁴ G _{9/2}	² G _{9/2}	⁴ G _{11/2}	² P _{1/2}
Observed energy	11560.70	12594.46	13495.28	14727.54	17391.30	19157.08	19531.12	21052.63	21691.97	23201.18
Calculated energy	11553.32	12577.16	13405.88	14780.26	17402.89	19198.21	19595.77	21019.08	21684.93	23203.23
Change in energy	7.38	17.29	89.40	-52.71	-11.58	-41.12	-64.65	33.55	7.04	-2.05

RMS Deviation : 42.79149, Nephelauxetic Ratio : 1.016285 , Bonding Parameter : 9.023465E-02

Table-2
Energy Levels of Neodymium: Threonine: Thio Urea in the Molar Ratio 1:1:2

Levels	⁴ F _{3/2}	⁴ F _{5/2}	⁴ F _{7/2}	⁴ F _{9/2}	⁴ G _{5/2}	⁴ G _{7/2}	⁴ G _{9/2}	² G _{9/2}	⁴ G _{11/2}	² P _{1/2}
Observed energy	11560.70	12594.46	13513.51	14727.54	17391.30	19193.85	19531.25	21052.63	21691.97	23148.15
Calculated energy	11558.05	12582.94	13408.71	14777.96	17416.45	19209.34	19607.23	21023.05	21692.13	23151.13
Change in energy	2.64	11.52	104.79	-50.41	-25.15	-15.48	-75.97	28.94	-0.1562	-2.97

RMS Deviation : 45.99605 , Nephelauxetic Ratio : 1.012217, Bonding Parameter : 7.815589E-02

Table-3 Oscillator Srength
Neodymium: Threonine: Urea (1:1:2) Neodymium: Threonine: ThioUrea (1:1:2)

Energy levels	Observed Value(10 ⁶)	Calculated Value	Difference	Energy levels	Observed Value(10 ⁶)	Calculated Value	Difference
⁴ F _{3/2}	0.602	1.076	-0.474	⁴ F _{3/2}	0.705	1.59	-0.89
⁴ F _{5/2}	2.68	2.47	0.0209	⁴ F _{5/2}	3.57	3.08	0.487
⁴ F _{7/2}	1.68	2.12	-0.443	⁴ F _{7/2}	1.385	2.27	-0.890
⁴ F _{9/2}	0.056	0.225	-0.169	⁴ F _{9/2}	0.0635	0.261	-0.197
⁴ G _{5/2}	2.62	2.84	-0.226	⁴ G _{5/2}	2.56	2.96	-0.402
⁴ G _{7/2}	1.08	1.22	-0.140	⁴ G _{7/2}	1.205	1.69	-0.49
⁴ G _{9/2}	0.306	0.681	-0.375	⁴ G _{9/2}	0.255	0.926	-0.671
² G _{9/2}	0.145	0.313	-0.168.	² G _{9/2}	0.144	0.450	-0.306
⁴ G _{11/2}	0.132	0.078	0.0539	⁴ G _{11/2}	0.154	0.101	0.052
² P _{1/2}	00.064	0.314	-0.250	² P _{1/2}	0.15	0.480	-0.330

B. Parameters: ND: ARG: U

1) Intensity Parameters

T2: -6.969522E-05

T4: 3.54792E-04

T6: 2.144349E-04

T4 / T6: 1.654545

rms Deviation : .2827713, Refractive Index : 1.37

2) *Omega Parameters*

OMEGA2: -5.270496E-15

OMEGA4: 2.68301E-14

OMEGA6: 1.6216E-14

C. *Parameters: ND: ARG: TU*1) *Intensity Parameters*

T2: -1.817966E-04

T4: 5.503827E-04

T6: 2.180566E-04

T4 / T6: 2.524035

rms Deviation : .5411221

2) *Omega Parameters*

OMEGA2: -1.374783E-14

OMEGA4: 4.162107E-14

OMEGA6: 1.648989E-14

III. RESULTS AND DISCUSSIONS

Judd-Ofelt Theory is useful for intensity measurements of lanthanide's ternary complexes. Intensity of various transitions is expressed in terms of T_λ and Ω_λ parameters.

This theory is most suitable to characterize the intensities of forced electric dipole transitions between the 4f states of rare-earth (III) ions. Since the absorption and emission probabilities for an ion matrix combination are expressed as set of three Judd-Ofelt parameters. The Judd-Ofelt intensity parameters are calculated by knowing the oscillator strength of various peaks. T_2 parameter is function of ligand concentration only.

It changes with the change in concentration. With organic solvents parameter T_2 changes significantly because these solvents have high coordinating power in comparison to water. T_4/T_6 refers to symmetry around the metal ion.

The electronic transitions within f^n configuration will arise due to electric-dipole, magnetic-dipole and electric-quadrupole transitions. Nephelauxetic Ratio of Neodmium: Threonine: Urea is 1.016285. But for Neodmium: Threonine: ThioUrea it is 1.012217. In case of urea it is negligible higher as compared thiourea.

IV. CONCLUSION

Bonding in rare-earth complexes is weaker than in the 3d complexes. Bonding parameter $b^{1/2}$ expresses bonding strength of rare-earth complexes. In case of rare-earth complexes value of $b^{1/2}$ is small as compared to 3d complexes. This suggests that 4f orbitals are slightly involved in bonding for the rare-earth complexes.

For Neodymium, Nephelauxetic Ratio, $\beta > 1$. Therefore, $b^{1/2}$ is not real and $\delta = (1-\beta) / \beta$ is negative in this work. Hence all ternary complexes of Neodymium make Ionic bonding with threonine and with urea and thiourea.

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