A study of covalency of Erbium and Neodymium ternary complexes in Alanine and Urea

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Abstract: The element of the first series that is from Cerium to Lutetium (Ce to Lu), which form a part of the sixth period are called lanthanides. These fourteen elements form 4f inner transition series. They are heavy metals. Their Laser properties were demonstrated in early sixties by Whan and Crossby. In this study two rare-earth Neodymium and Erbium have been taken. Due to electrostatic and magnetic interactions, there exist energy levels associated with rare-earth element. The energy levels of these elements can be expressed in terms of four parameters (F₂, F₄, F₆) and Landes parameter. By taking their spectra, we know position of energy levels. Both Neodymium and Erbium complexes are studied in solvent form. 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. Occurrence of these bands is explained by Judd.

Key-Words: Neodymium, Erbium, Alanine, Urea and hypersensitive transitions

I. INTRODUCTION

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. These energy states are calculated by the diagonalization of complete matrices developed by Slater and Condon. But calculation is done by this method is applicable only for the configuration not more than f². Racah introduced a simpler method based on Taylor series expansion to solve these energy levels.

All f-f transitions of rare-earth complexes in visible region are studied by various coworkers [1-19]. The solution spectra of rare-earth Neodymium and Erbium have been studied. In case of rare-earth complexes, electric field which is produced by the distortion of the tri-positive ions by the surrounding atmosphere is weak as compare to rigid crystals.

The different modes by which electronic transitions are

In case of rare earth complexes observed intensities of spectral lines are too large and 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 Tₜ parameters. According to Judd, Tₜ parameters have contribution due to both parts, radial as well as perturbing configurations. The electronic and spin orbit interactions yield energy levels parameters that deviate much from the observed energy levels.

Experimental
Two Rare-earth Neodymium and Erbium are taken. Their solutions are prepared by taking Alanine, as primary ligand and Urea as secondary ligand. 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. These energy level values change due to either change in ligands or change in solvents.
All reagents used in this study are taken of standard purity. In this work all chemicals are taken from C.D.H Company. The complexes are synthesized by taking Amino-acid that is Alanine as primary ligand and Urea as secondary Ligand, mixed in 1:1:2 molar ratio. The solution is stirred for half an hour with magnetic stirrer method. The formation of complex is also checked by infrared spectra in Chemistry lab of S.P.C Government College, Ajmer. The absorption spectra of the complexes are recorded with UV-VIS Spectrophotometer LABINDA 3000°. Peaks of these absorption spectra are recorded in between 400nm to 800nm.

**SPECTRA OF NEODYMIUM, ALANINE AND UREA (AS OBSERVED WITH UV-SPECTROPHOTOMETER LABINDA 3000°)**

**SPECTRA OF ERBIUM, ALANINE AND UREA (AS OBSERVED WITH UV-SPECTROPHOTOMETER LABINDA 3000°)**

**Parameters**

Some parameters are calculated after taking its absorption spectra. These parameters are, Slater-Condon Parameters, Lande parameter, Bonding parameter, Oscillator Strength, Judd-Ofelt parameters and Omega parameters.

The electronic transitions within f⁶ configuration will arise due to

1) Electric –dipole  
2) Magnetic- dipole  
3) Electric quadrupole

Formula for calculation of Oscillator Strength is

\[ P = 4.6 \times 10^{-9} \times \epsilon_{\text{max}} \times \Delta \nu_{1/2} \]

Where \( \epsilon_{\text{max}} = \) Molar Extinction Coefficient \( \Delta \nu_{1/2} = \) Half Band Width

From the Spectrum, Half Band Width

\[ \epsilon_{\text{max}} = \frac{1}{C \times L} \times \frac{\text{Log } I_0}{I} = \frac{1}{C \times L} \times \text{Optical Density} \]

C= Concentration of the Solution. \( L = \) Thickness of Cell in cm
The values of reduced matrix elements are collected from W.T. Carnall [19]. The parameter $b^{1/2}$ is measurements of types of bonding is calculated by the given formula

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

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 inter-electronic repulsion parameters. This effect is known as Nephelauxetic effect [17]. This effect is usually expressed in term of $\beta$ 

$$\beta = F_k^c / F_k^f$$

Where $c$=complex state 

$ f$ =free ion state

1) If $\delta$ is positive then there is covalent bonding between metal and ligands.
2) If $\delta$ is negative then there is ionic bonding between metal and ligands.

### Table 1 - Showing Observed and Calculated Energy Levels of Nd:Al:U

<table>
<thead>
<tr>
<th>Levels</th>
<th>$\psi_{5/2}$</th>
<th>$\psi_{3/2}$</th>
<th>$\psi_{7/2}$</th>
<th>$\psi_{9/2}$</th>
<th>$\psi_{11/2}$</th>
<th>$\psi_{13/2}$</th>
<th>$\psi_{15/2}$</th>
<th>$\psi_{17/2}$</th>
</tr>
</thead>
<tbody>
<tr>
<td>Observed energy</td>
<td>11560.7</td>
<td>2594.7</td>
<td>13513.51</td>
<td>14727.54</td>
<td>17361.11</td>
<td>19157.08</td>
<td>19531.25</td>
<td>21052.63</td>
</tr>
<tr>
<td>Calculate energy</td>
<td>11561.76</td>
<td>12574.59</td>
<td>14795.81</td>
<td>17396.22</td>
<td>19190.08</td>
<td>19579.04</td>
<td>21021.22</td>
<td>21676.69</td>
</tr>
<tr>
<td>Change in levels</td>
<td>1.06347</td>
<td>19.860</td>
<td>102.6</td>
<td>-68.26</td>
<td>-35.11</td>
<td>-33.01</td>
<td>-47.7</td>
<td>31.4</td>
</tr>
</tbody>
</table>

### 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 |

### Table 2 - Showing Observed and Calculated Oscillator Strength (OS) of Nd:Al:U ( x10^6)

<table>
<thead>
<tr>
<th>Levels</th>
<th>$\psi_{3/2}$</th>
<th>$\psi_{5/2}$</th>
<th>$\psi_{7/2}$</th>
<th>$\psi_{9/2}$</th>
<th>$\psi_{11/2}$</th>
<th>$\psi_{13/2}$</th>
<th>$\psi_{15/2}$</th>
<th>$\psi_{17/2}$</th>
</tr>
</thead>
<tbody>
<tr>
<td>Observed OS</td>
<td>1.346</td>
<td>2.3</td>
<td>1.78</td>
<td>0.106</td>
<td>3.38</td>
<td>1.94</td>
<td>0.51</td>
<td>0.341</td>
</tr>
<tr>
<td>Calculated OS</td>
<td>1.310</td>
<td>2.40</td>
<td>1.66</td>
<td>0.197</td>
<td>3.374</td>
<td>1.439</td>
<td>0.747</td>
<td>0.367</td>
</tr>
<tr>
<td>Change in OS</td>
<td>0.035</td>
<td>-0.10</td>
<td>0.118</td>
<td>-0.09</td>
<td>0.006</td>
<td>0.500</td>
<td>-0.23</td>
<td>-0.026</td>
</tr>
</tbody>
</table>

### INTENSITY PARAMETERS

| T2 | -9.448552E-05 | T4 | 4.570911E-04 | T6 | 1.554134E-04 |
| T4 / T6 | 2.941131 |
| rms Deviation | .2224793 |
| Refractive Index | 1.37 |

### OMEGA PARAMETERS

| OMEGA2 | -7.14518E-15 | OMEGA4 | 3.45661E-14 | OMEGA6 | 1.17526E-14 |

### Table 3 - Showing Observed and Calculated Energy Levels of Er:Al:U

<table>
<thead>
<tr>
<th>Levels</th>
<th>$\psi_{5/2}$</th>
<th>$\psi_{3/2}$</th>
<th>$\psi_{7/2}$</th>
<th>$\psi_{9/2}$</th>
<th>$\psi_{11/2}$</th>
<th>$\psi_{13/2}$</th>
<th>$\psi_{15/2}$</th>
</tr>
</thead>
<tbody>
<tr>
<td>Observed energy</td>
<td>15290.52</td>
<td>18416.20</td>
<td>19083.96</td>
<td>20491.18</td>
<td>22123.80</td>
<td>22522.52</td>
<td>24691.13</td>
</tr>
<tr>
<td>Calculated energy</td>
<td>15319.54</td>
<td>18280.7</td>
<td>19410.02</td>
<td>20550.49</td>
<td>22095.45</td>
<td>22482.27</td>
<td>24632.4</td>
</tr>
<tr>
<td>Change in energy</td>
<td>-29.023</td>
<td>135.50</td>
<td>-56.054</td>
<td>-59.30</td>
<td>28.34</td>
<td>40.25</td>
<td>58.72</td>
</tr>
</tbody>
</table>

### ENERGY PARAMETERS

| E1 | 1419.283 | E2 | 4.829614 | E3 | -222.057 |
| E1 / E3 | -6.391528 | E2 / E3 | -2.174944E-02 |

### F PARAMETERS

| F2 | -7.921631 | F4 | -1.25707 | F6 | 6.802421 |

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Zeta4F : -3.613403
F4 / F2 : .1586883
F6 / F2 : -.8587147
rms Deviation : 142.1014
Nephelauxetic Ratio : -1.793523E-02
Bonding Parameter : .7134197

Table-4: Showing Observed and Calculated Oscillator Strength (OS) of Er:Al:U ( x10^6)

<table>
<thead>
<tr>
<th>Levels</th>
<th>4I02</th>
<th>5S02</th>
<th>4I02</th>
<th>4F02</th>
<th>5P02</th>
<th>4F02</th>
<th>4H02</th>
<th>4G02</th>
</tr>
</thead>
<tbody>
<tr>
<td>Observed OS</td>
<td>1.027</td>
<td>0.586</td>
<td>1.94</td>
<td>1.42</td>
<td>0.431</td>
<td>0.382</td>
<td>0.844</td>
<td>6.374</td>
</tr>
<tr>
<td>Calculated OS</td>
<td>1.135</td>
<td>0.524</td>
<td>2.34</td>
<td>1.748</td>
<td>0.666</td>
<td>0.410</td>
<td>0.770</td>
<td>6.25</td>
</tr>
</tbody>
</table>

INTENSITY PARAMETERS
T2 : 1.572679E-04  T4 : 1.814551E-05  T6 : 1.338741E-04
T4 / T6 : .1355416
rms Deviation : .2121908
OMEGA PARAMETERS
OMEGA2 : 1.181157E-14  OMEGA4 : 1.362815E-15  OMEGA6 : 1.005459E-14

II. Results and Discussion

Forbidden Transitions are responsible for the Visible and near Infra-red spectra of Neodymium and Erbium ternary complexes. Neodymium and Erbium belongs to lanthanides series.

Ternary complexes of Neodymium and Erbium with Alanine act as primary ligands and Urea as secondary ligands are studied in the molar ratio 1:1:2. Their spectra are studied in solution form by the UV – Spectrophotometer Labinda 3000°.

Slater-Condon parameters and Landes parameter are specified by the electronic energy levels. Observed energy levels corresponding to different peaks of Neodymium and Erbium complexes are nearly same as calculated value. Hence R.M.S deviation is small which confirms the formation of complex. On complexation the value of Slater-Condon and Lande’s parameters decreases. The ratio of F4/F2 for Neodymium complexes is 0.139 and for Erbium complexes is 0.158.

Bonding in rare-earth complexes is weaker than in the 3d complexes. Bonding parameter b1/2 expresses bonding strength of rare-earth complexes. In case of rare-earth complexes value of b1/2 is small as compared to 3d complexes. This suggests that 4f orbitals are slightly involved in bonding for the rare-earth complexes.

It has been observed from the calculation that bond strength for Neodymium is less than that of Erbium complexes. According to this, as atomic number of metal ion increases, contraction of 4f orbitals increases. By knowing the value of F3, Nephelauxetic ratio and bonding parameters are calculated. It has been observed that if ligands are same and solvent is same then as atomic number increases, covalency increases. It also increases with increase in number of amino-acids for same rare-earth.

Hypersensitivity is not described by T4 parameter alone but it is expressed in ratio of T4/T2 and T6/T2. Oscillator strength of different peaks can be expressed in terms of T2, T4, T6 parameters. For Neodymium ratio of T6/T2 is 2.45 and for Erbium ratio of T6/T2 is 0.135.

III. Conclusion

In case of Nd(III) bonding parameter is not real therefore its ternary complexes will make ionic bonding with other ligands. But for Erbium bonding parameter is positive and high which indicates strong covalency. On complexation intensity of peaks are not changes too much but their absorbance changes.

References


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