A Comparison of Lande's Factor in Different Amino acids in Neodymium Complexes

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ABSTRACT

Red shift occurs when there is formation of ternary complexes of Neodymium and Erbium with amino-acids. Slater-Condon parameters (F) and Lande's parameter changes slightly after formation of complexes. These two parameters decrease slightly. There is large decrease in Lande's parameter as compare to Slater-Condon parameters. This signifies that ligands affect spin-orbit coupling more than the electrostatic repulsion. Columbic and spin-orbit parameter decreases and there is expansion of the central metal ion on complexation, Nephelauxetic ratio increases. Repulsion of electron-electron within 4f orbital is the largest and it is in the order of 10^4/cm. The order of splitting due to spin–orbit coupling is 10^3/cm. Lanthanide complexes have high coordination numbers. Bonding in rare-earth complexes is weaker than in the 3d complexes. Bonding parameter $b^{1/2}$ expresses bond 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.

Keywords– Lande's Parameter, Spin-orbit coupling, Nephelauxetic ratio,4f Orbitals and red-shift.

INTRODUCTION

To calculate the natural frequency of lanthanides, absorption and luminescence spectroscopy are useful, either in solution or in glasses form, rare-earth complexes show lines. Bands are due to incomplete 4f shell, electronic to electronic transitions[1-10]. 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. Different Energy states are calculated by the diagonalization of complete matrices developed by Slater and Condon. This method is applicable only for the configuration not more than f^2.

Due to electrostatic and magnetic interactions, there exist energy levels associated with rare-earth elements. Energy levels of these elements can be expressed in terms of four parameters (F_2,F_4,F_6) and Lande's parameter. Knowledge of their spectra, position of energy levels are measured.Spectra of Neodymium complexes are studied in solvent form. Ten peaks are observed for Neodymium in visible region[13-14]. 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. These bands are very sensitive to the change in environments. Different researchers gave different explanations of these bands. According to Judd, these bands are due to spherical Harmonics. Induced electric dipole transitions are mainly responsible for the occurrence of these lines. 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 transition is strongest in three.

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. According to Judd, the theory of splitting of levels by crystalline field is developed by Stevens (1952). Valuable information is got from fluorescence and absorption spectra of crystals like various energy levels, their locations and effect of crystal field on them. In rare-earths, f-f transitions 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. The energy levels of various transitions are experimentally as well as theoretically calculated by using 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

The values of F_2, F_4 and F_6 parameters are computed using Judd-Ofelt relation. Least square fit or partial regression method yields values of ΔF_k and ξ_{4f}. Only f^n interactions are considered and all spin-orbit interactions are to be neglected. In case of Neodymium Complexes $E_1 > E_3 > E_2$.

Method of preparation of Complexes

Three amino –acids are taken and Rare-earth metal is Neodymium ,their solutions are prepared in three amino-acids that is Glycine, Alanine, Arginine, as primary ligands and Urea as secondary ligands. 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. The complexes are prepared by taking one of the Amino-acid that is Glycine, Alanine, Arginine, as primary ligand and Urea as secondary Ligand mixed in 1:1:2 molar ratios. The solution is stirred for half an hour with magnetic stirrer method. 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 (Visible Range).

Observation Table

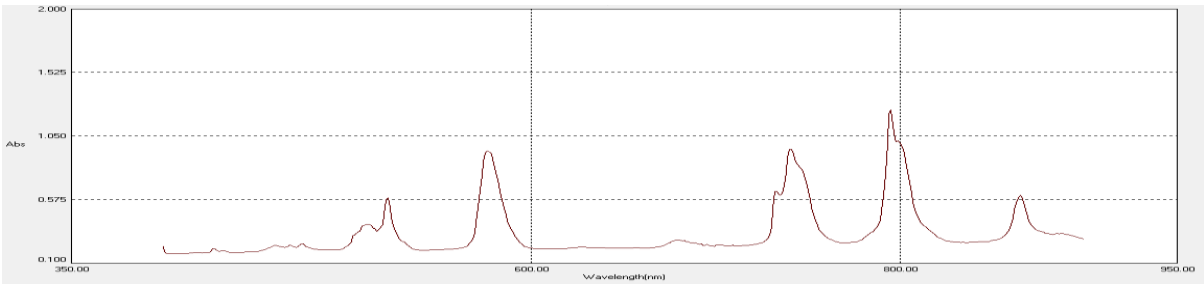
Energy Parameters and F Parameters

	ND:Gly:U	ND:Alan:U	ND:ARG:U
E_1	4995.222	5116.12	5019.81
E_2	25.13588	26.45	25.11
E_3	495.5675	496.07	496.98
E_1/E_3	10.07	10.31	10.100
E_2/E_3	0.0507	0.053	0.0505
F_2	334.307	341.80	335.19
F_4	48.17	47.54	48.60
F_6	5.207	5.56	5.23
Zeta 4F	881.05	873.99	871.22
F_4/F_2	0.144	0.13	0.145
F_6/F_2	0.015	0.016	0.01562

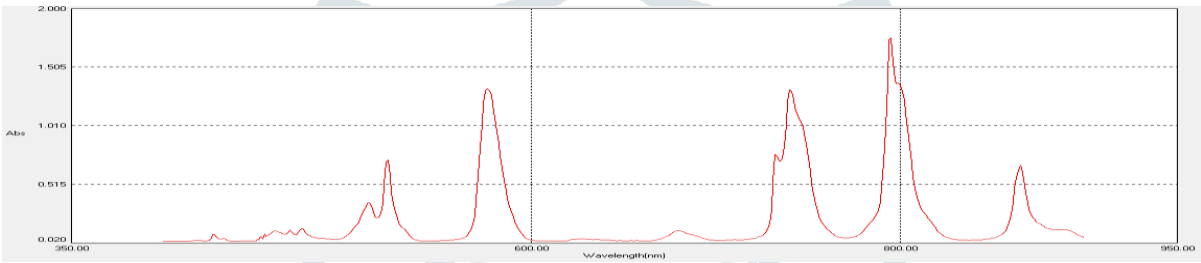
Results

Ten peaks are observed for Neodymium complexes.

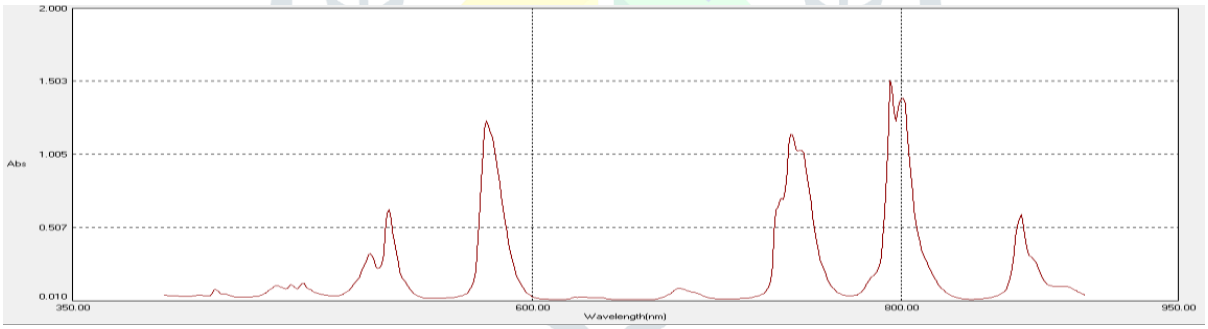
Absorption Spectra of Neodymium:Glycine:Urea in the molar ratio1:1:2



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



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



For all Neodymium complexes E_1/E_3 lies between 10.07and 10.31 and E_2/E_3 lies between 0.0505 and 0.0507. If we change the ligand then there is small change in this ratio. In all the ternary complexes $F_2>F_4> F_6$, value of F_2 is largest. On complexation values of Slater-Condon parameters, Lande's parameter and Racah parameters decrease. This indicates expansion of the central metal ion orbital which further decreases the inter-atomic repulsion and spin orbit interaction. Observed energy levels corresponding to different peaks of Neodymium complexes are nearly same as calculated values. Hence R.M.S. deviation is small, which confirms that the formation of complex is perfect. On complexation, the value of Slater- Condon parameters decreases. Value of Landes factor is minimum for Arginine i.e 871.22.For Alanine it is slightly higher and it is mximum for Glycine.

Conclusion

From observed and calculated value of oscillator strength by Judd-Ofelt relation, it is found that R.M.S. deviation is very small for all ternary complexes of Neodymium. Small R.M.S. deviation confirms applicability of Judd-Ofelt relation for these complexes

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