

To Find Root Mean Square Deviation in Neodymium Complexes

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Abstract - Rare-earth element of the first series that is from Cerium to Lutetium, form a part of the sixth period are called lanthanides. These materials have different and unique properties. Ternary complexes of Neodymium with amino acids that is Arginine, and Theronine as primary ligand and Thiourea as secondary ligand are prepared in 1:2:1 ratio. Spectra of these complexes are recorded by UV-VIS spectrometer, LABINDIA 3000⁺. The value of different Slater-Condon parameters F_2, F_4, F_6 and Lande's parameter are calculated. The effect of various amino acids on the position and intensity has been discussed in terms of bonding parameter. After calculation of these Slater-Condon parameters, Nephelauxetic Ratio is calculated which is directly related to types of bonding. R.M.S deviation is calculated by Nephelauxetic ratio. 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. Hypersensitive transitions obey the selection rule of quadrupole transitions and therefore known as Pseudo-quadrupole transitions.

Key words- Arginine, Thiourea, Hypersensitive transitions, Neodymium, Slater Condon parameters, RMS deviation and UV Spectrophotometer.

I. INTRODUCTION

In case of ternary complexes of Neodymium, the colour is reddish purple because of Nd^{+3} . It can easily oxidise in air and it is one of the most reactive element. In pure form of Neodymium that is in free state its spectra lies in infrared red, visible and ultraviolet region. Neodymium spectra consists of ten peaks, some peaks will be displaced from its original positions during formation of Neodymium complexes. Some bands have maximum displacement and highest intensity known as Hypersensitive bands[7,8]. 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[5,6,16]. But according to Choppin, hypersensitivity is due to inclusion of Covalency within the framework of a vibronic mechanism. The different modes by which electronic transitions take place are Electric dipole, Magnetic dipole and Electric Quadrupole.

When there is formation of ternary complexes of Neodymium with amino-acids then red shift occurs. On complexation, there is very small change in F parameters and Lande's parameter. After formation of complex these

two parameters decrease slightly. The decrease in value of Lande's parameter is more than Slater-Condon parameters. This signifies that ligands affect the 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.

II. EXPERIMENTAL DETAILS

In the present study, one Rare-earth metal Neodymium is taken. Solutions of Neodymium are prepared in amino-acids that is Arginine, and Theronine as primary ligands and Thiourea as secondary ligand. Their ternary complexes are studied in solvent form. The calculated energy levels corresponding to different peaks of Neodymium Complexes are compared with the experimentally observed values. The energy level values changes due to change in ligands or change in solvents. All reagents used in this study are taken of standard purity. The complexes are prepared in the molar ratio 1:1:2. 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 (Visible Range).

III. 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. It is very difficult to solve these parameters using method of diagonalisation 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[11-16].

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. The energy levels of various transitions are experimentally as well as theoretically calculated by using Taylor Series expansion. 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 orbital's 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 orbital. 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)[1-4].
 $\beta = F_k^c / F_k^f$,
 Bonding parameter is $b^{1/2} = [(1 - \beta) / 2]^{1/2}$,
 $\delta = (1 - \beta) / \beta$

IV. OBSERVATION TABLES

Table-1 – It Represents Observed and Calculated Energy Levels of Neodymium Complex (ND:ARG:Thiourea) 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	11210.7	12562.28	13513.51	14727.00	17361.11	19083.96	19569.47	21052.63	21691.97	23310.02
Calculated energy	11445.47	12518.95	13377.46	14825.02	17203.9	19089.5	19531.16	21042.2	21679.23	23278.84
Change in energy	-234.76	43.32	1336.04	-98.01	157.21	-5.537	38.31	10.42	12.73	31.17

Table-2 – It Represents Observed and Calculated Energy Levels of Neodymium Complex (ND:Threonine:Thiourea) 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	21052.00	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	-0.15	-2.97

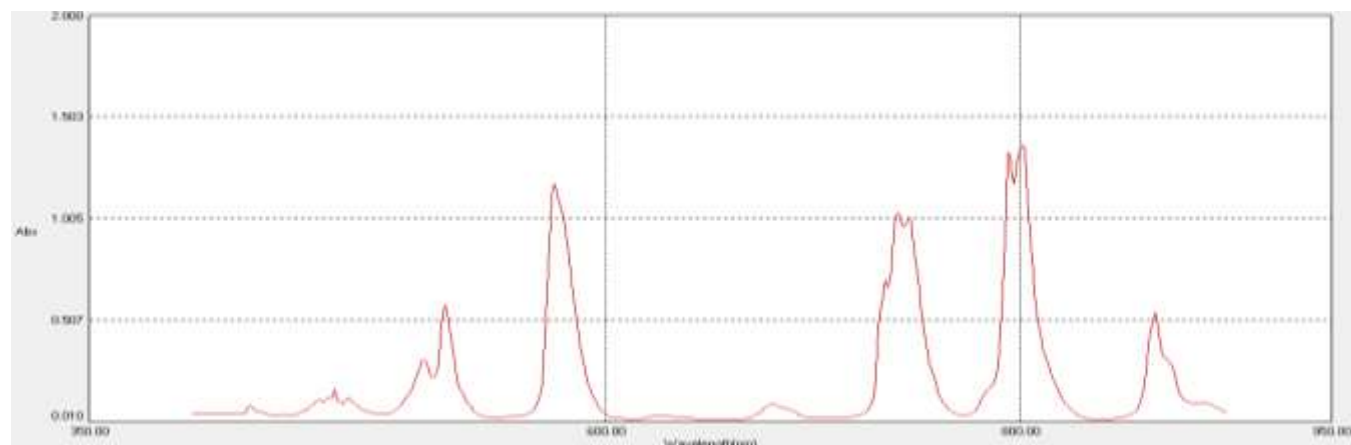
Table-4 ENERGY PARAMETERS and F PARAMETERS

	E ₁	E ₂	E ₃	F ₂	F ₄	F ₆
Nd:Arg:Thiourea	5050.31	26.47	488.61	338.37	46.27	5.53
Nd:Threo:Thiourea	5019.79	25.11	496.98	335.20	48.60	5.23

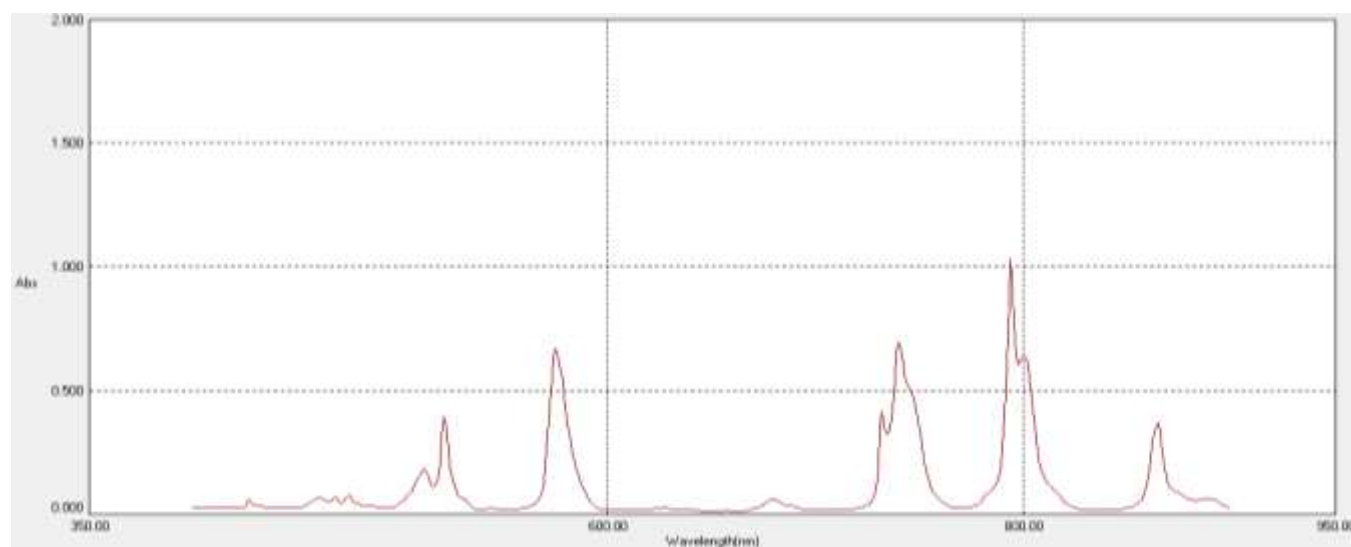
Table-4

	ND:ARG:ThioUrea	ND:THREO:ThioUrea
RMS Deviation	106.097	45.996
Nephelauxetic Ratio	1.021	1.0122
Bonding Parameter	0.104	0.0781

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



Absorption Spectra of Neodymium:Threonine:ThioUrea in the molar ratio 1:1:2



V. RESULTS AND DISCUSSION

By change in environment by changing different amino-acids small change in peaks of Neodymium. Bands of Neodymium are intense as compared to their neighboring metals. As atomic number is even, Oddo-Harkins rules states that their bands are more intense as compared to odd atomic number nuclei. Forbidden Transitions are responsible for the Visible and near Infra-red spectra of Neodymium ternary complexes. There are some bands which are more intensified by magnitude as compared to others, known as hypersensitive bands. In case of 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. Even minor co-ordination changes around the $Nd(III)$, change the intensity too much. Some other bands also show large change in intensity but they do not obey normal selection rules. These transitions are known as Pseudo-hypersensitive transitions. 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. 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. The ratio of F_4/F_2 is nearly ten times as compared to F_6/F_2 . On complexation there is expansion of 4f orbital's which can be expressed in terms of Nephelauxetic Ratio (β).

Because of electron-electron repulsion and spin orbit interaction, Nephelauxetic ratio decreases and covalency increases. Due to shortening of metal-Ligand distance, Nephelauxetic ratio increases and hence Nephelauxetic ratio effects coordination number and overall geometry of complex. 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.

VI. CONCLUSION

For Neodymium, it is ionic in nature. For Neodymium – Nephelauxetic, Ratio, $\beta > 1$. Therefore, $b^{1/2}$ is not real and $\delta = (1-\beta)/\beta$ is negative in this present work. Hence all ternary complexes of Neodymium make Ionic bonding with different amino-acids and with Thiourea. B for Nd:Arg:TU is 1.021 and for Nd:Threo:TU is 1.012. Hence with Arginine band is more ionic than Threonine.

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