Absorption Spectra of Neodymium (Rare-Earth) in Different Ternary Complexes in Visible Region and Determination of Different Parameters

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Abstract

Neodymium an element of inner transition series(4f).The optical absorption spectra of Neodymium with different Ligands, aminoacid that is Glycine as primary ligand and Urea orThiourea as **secondary** ligand have been studied.There spectra is recorded in the visible range of 380nm to 900nm.This spectra is recorded by UV-VS spectrometer 3000^+.Different parameters Slater-Condon parameters, Omega Parameters, Lande's Parameter and optical density are calculated and compared with standard one.By knowledge of rmsdeviation, nature of complex formation is determined. Strength of bonding helps to tell about the type of bonding between metal and ligands.

Keywords: Neodymium, Aminoacid (Glycine), Urea, Thiourea UV-VS Spectrometer and Ligands, Judd-Ofelt Parameters.

Introduction

In the last sixty years, Lanthanides have gained much importance and have drawn the attention of researchers in Physical and chemical sciences [1-18]. Absorption spectra of Neodymium have been studied in its ternary complexes [2, 11, 13, 19]. Much work has been done on rare-earth with oxygen and carboxylic acids. Different ternary complexes of Neodymium with amino acid as primary ligand and urea or thiourea as secondary ligands are prepared in alcohol.With the help of energy parameters, Judd-Oflet parameters Structure and bonding of complexes have been studied. 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. 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. A general theory of the solvent effect on the intensities of f-f transitions of lanthanide complexes [9] based on the static and dynamics coupling between metal ion ligand and solvent molecules will be discussed.

Review of Literature

The electronic spectrum of rare-earths, both in neutral and free ion states, consists of closely spaced group of sharp lines in the near infrared, visible and ultraviolet regions. They undergo modification when the rare-earth ions are placed in different lattice sites in crystals or in different environments. These electronics spectra have been extensively studied in the last 60 years [1-19]. Judd and Wybourne have given a vivid description of the theory of their origin.

Until 1962, the emphasis was laid mainly upon the calculation of energy levels and interactions parameters only [10] when Judd and Ofelt independently presented a theory for oscillator's strength (P) of the absorption lines of rare-earth ions in the solution in visible and near infrared regions, resulting from the transitions within the 4f^n configurations. Judd has expressed the oscillator strength of these induced transitions in terms of three $T_\Lambda$parameters.Tandon, Gokhroo, Surana, Bhutra and Tendon (1992) studied diffused reflectance spectra of twenty four Pr^{+3} and Nd^{+3} ternary amino acid complexes. Preliminary work by the researchers [3,7,9,11,12,13,17,19] suggests that structural differences have a greater effect on the detail of the absorption spectrum than do minor differences in composition. N.Guskos and Majsczyk (2010) studied f-f transitions of Erbium.

Devi and Singh (2011) observed that there is red shift as Uracil is added to Pr(III). The positive value of $b^{1/2}$ parameter indicates that some covalent character in metal-ligand bond.

Gupta and Ujjwal (2013) studies optical absorption spectra of Neodymium in different solvent. The value of energies and intensities of various transitions have been calculated using Judd and Ofelt relation is in good agreement with experimental result. The complex studied is found to be ionic in nature [7]. S.L Meena(2017) studied properties of rare-earth doped in Zinc Lithium Bismuth Borate Glasses.

Aim of The Study

To study different parameters, Energy levels, Slater-Condon and Omega parameters. Optical strength of each peak has been studied. Finally type of bonding of complex of Neodymium is calculated.

Expermental Details

For the present research work, the rare earth metals of 99.9% purity has taken from C.D.H company. All other Chemicalsaminoacids, Urea, Thiourea and alcohol are of standard purity will be taken. The complex will be synthesized with Gycine as primary ligand and Urea or Thiourea as secondary ligand in1:1:2 molarratios [7]. The absorption spectra of the complexes will be recorded with UV-VIS Spectrophotometer LABINDA 3000$^+$. These absorption spectra will be recorded in between 190nm to 1100nm.The formation of complex is also checked by infrared spectra in Chemistry lab.

Parameters

Various Intensity parameters such as Judd Ofeltparameters(T_2, T_4, T_6), the bonding parameter $b^{1/2}$, the Slater – Condon parameters (F_2, F_4, F_6), Lande parameter (ξ_{4f}) and oscillator strength (P) , the covalency of the complex will be calculated[9]. The calculated energy levels parameters will be compared with the experimentally observed energy levels in different environments.The electronic transitions within f^n configuration will arise due to electric –dipole, magnetic- dipole and electric quadrupole [15].

Therefore $P = P_{ed} + P_{md} + P_{eq}$

The induced electric dipole transitions can occur due to the interaction of the central ion with the surrounding ligands. The oscillator strength is given by [18]

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

Where λ =2, 4, 6 .

Where U^λ = It is a tensor operator of rank λ, calculated by Carnall.

The energy levels of various transitions will be taken experimentally as well as theoretically by using Taylor Series expansion in first order approximation [7].

$E_j(F_k, \xi_{4f}) = Eoj (F_k^o , \xi_{4f}^o) + \sum \partial E_j/\partial F_k \Delta F_k + \partial E_j/\partial \xi_{4f} \Delta \xi_{4f}$

Where k = 2, 4, 6

The values of F_2, F_4, and F_6 parameters will be computed using Judd-Ofelt relation and will be arranged in Tabulated form. The values of reduced matrix elements will be collected from W.T. Carnall. The parameter $b^{1/2}$ is a measurements of types of bonding will be calculated by the given formula

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

Table1 Observed and Calculated Values of Energy Levels for Neodymium Complexes

Levels	Neodymium: Glycine: Urea (1:1:2)			Neodymium: Glycine: ThioUrea (1:1:2)		
	Obs.cm^{-1}	Cal.cm^{-1}	Delta E	Obs.cm^{-1}	Cal.cm^{-1}	Delta E
$^4F_{3/2}$	11560.70	11537.65	23.046	11560.7	11554.81	5.891
$^4F_{5/2}$	12578.61	12579.31	-0.698	12594.45	12583.55	10.901
$^4F_{7/2}$	13513.51	13410.11	103.401	13513.51	13407.99	105.519
$^4F_{9/2}$	14749.26	14789.17	-39.90	14727.54	14775.63	-48.088
$^4G_{5/2}$	17361.11	17383.33	-22.22	17415.84	17415.84	-24.710
$^4G_{7/2}$	19157.08	19188.27	-31.19	19210.09	19210.09	-16.238
$^4G_{9/2}$	19531.25	19603.25	-72.16	19611.28	19611.28	-80.031
$^2G_{9/2}$	21052.63	21021.75	30.88	21023.06	21023.06	29.572
$^4G_{11/2}$	21691.97	21708.01	-16.04	21691.79	21695.79	-3.814
$^2P_{1/2}$	23094.68	23101.43	-6.74	23098.70	23098.70	-4.019
rms deviation			45.54791			46.674

Table2 Calculated Value of Different Parameters-Slater Condon, Landes, Nephelauxetic Ratio and Bonding Parameter

	Neodymium: Glycine: Urea (1:1:2)	Neodymium: Glycine:Thio Urea (1:1:2)
F_2 (cm^{-1})	334.307	333.935
F_4 cm	48.179	48.744
F_6	5.207	5.17818
Zeta 4F	881.05	871.75
E^1	4995.222	5000.239
E^2	25.135	24.8831
E^3	495.567	496.97
F_4/F_2	.14411	.14597
F_6/F_2	1.5577E-02	1.55065-02
E^1/E^3	10.0798	10.061
E^2/E^3	5.0721-02	5.0069-2
Beta	1.009503	1.0083
$b^{1/2}$	6.89311-02	6.4728-02

Table-3 Observed and Calculated Value of Oscillator Strength for Neodymium Complexes

Neodymium: Glycine:Urea (1:1:2)   Neodymium:Glycine: thioUrea (1:1:2)

Levels	ObservedX10^6	Calculatedx10^6	Delta px10^6	Observedx10^6	Calculatedx10^6	Delta Px10^6
$^4F_{3/2}$	1.46	1.18	0..270	1.97	1.29	0.678
$^4F_{5/2}$	1.73	1.80	-7.98E-2	1.47	1.84	-0.37
$^4F_{7/2}$	1.288	0.947	0.340	1.54	0.83	0.709
$^4F_{9/2}$	.237	0.133	0.1038	0.224	0.128	9.52E-2
$^4G_{5/2}$	2.89	2.69	0.197	4.13	3.82	0.304
$^4G_{7/2}$	1.86	1.26	0.599	2.135	1.41	0.717
$^4G_{9/2}$	.78	.627	0.152	0.698	0.668	2.9E-2
$^2G_{9/2}$	.417	.325	0.091	0.522	0.351	0.170
$^4G_{11/2}$	.472	6.28E-2	0.409	0.508	6.49E-2	0.443
$^2P_{1/2}$	.36	0.371	-1.137E-2	0.57	0.405	0.164
rms deviation			0.2836			0.4440

Table -3 Variation of Intensity Parameters

Intensity parameters	ND:G:U	ND:G:TU
T_2	- 1.101	- 6.828
T_4	4.303	4.72
T_6	7.71	6.10
T_4/T_6	0.558	0.773

Refractive Index of Water: 1.37

Table-4 Variation of Omega Parameters

OmegaParameters	ND:G:U	ND:G:TU
Ω_2	8.33	5.16
Ω_4	3.25	3.57
Ω_6	5.83	4.61

Spectra of ND:G:U 1:1:2
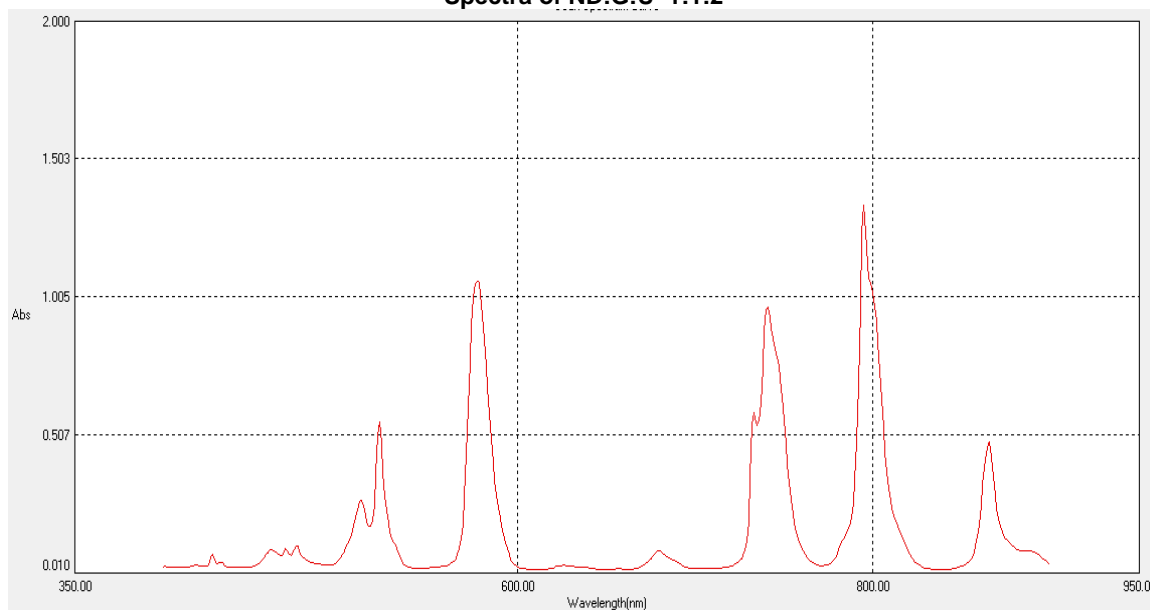
Spectra of ND:G:TU   1:2:1
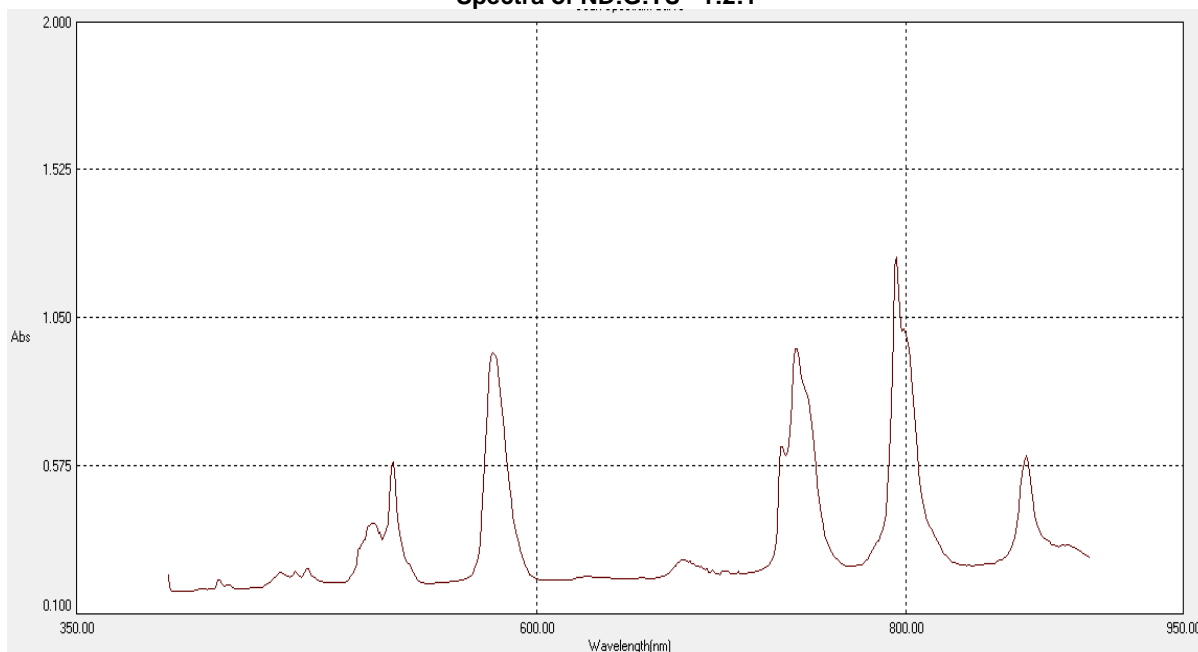
Results and Discussion

Table-1 It shows variation of observed energy and calculated value of energy levels by converting into wavenumber .For Neodymium complexes it is observed that calculated value of energy level parameters matches the observed one. Small value of r.m.sdeviation shows that complex formation is perfect.Table2 represents Slater-Condon parameters F_2, F4 and F_6, Lande's parameter, Nephelauxetic ratio and bonding parameter. The observed value matches free ion value. Nephelauxetic ratio is greater than one which shows that bonding is ionic. In case of Urea bond is more ionicthanThiourea.table3represents oscillator Strength of different peaks of Neodymium complexes. Some peaks are more intense than others due to hypersensitive transition. Oncomplexation wave number of some peaks show large deviation than others.After formation of compex Value of F_2 decreases from free ion which indicates contraction of 4f orbital decreases. All parameters corresponding to $^4G_{5/2}$ are maximum because of Hypersensitive transition. From the observed oscillator strength its calculated values obtained by using Judd Ofeltrelation,ther.m.s deviation is small which confirms the formation of complex.In case of Thiourea value of oscillator is greater than Urea. Table 4 representscomparsionin intensity parameters of Neodymium complexes inUrea and Thiourea. The value of T_4 and T_6 increases and in some cases value of T_2 is Negative and therefore r.m.s deviation is very small.

Acknowledgement

Conclusion

There is very small RMS deviation between calculated and observed values which confirms the complex formationof Neodymium. The value of Nephelauxetic ratio for Neodymium complex is greater than one. Hence the complex is ionic in nature.In case of Complexation of Nd^+ with Urea, value of β is slightly greater than in comprasionwiththiourea.

Ten peaks are observed for Neodymium complexes in different enverionments. The values of all parameters for $^4G_{5/2}$ levels are maximum because of hypersensitive transition.In case of Neodymium complex T_4/T_6 is almost constant in all solvent.It is also very small.Value of RMS deviation is very small which confirms the formation of complexes.

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