Variation in Spectral Parameter of Gd (III) ion with Bioactive N, O-Containing -Heterocyclic Aromatic Ligand

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Abstract: **The importance and versatility of derivatives of quinolines is well established in many forms of drugs, potential use of lanthanide complexes as diagnostic molecule have also been reported in literature but studies on biological aspects of complexes of lanthanides related with bioactive species are lesser. The constructions and characterizations of lanthanide complexes are currently of great interest because of their unique physico-chemical properties and various applications in medical field. The present work describes the synthesis, spectral and biological investigations on the complexes of quinoline derivatives with Gd (III) ions in agreement to Green chemistry approach. The magnetic moment of Gd (III) complexes showed slightly higher-values which originated due to low J-J separation leading to thermal population of next higher energy J levels and susceptibility due to first order Zeeman Effect. For various peaks of Gd (III) Intensity (Judd Oflet T_2, T_4, T_6 and oscillator strength $P_{obs} \times 10^{6)}$, Bonding $b^{1/2}$, Symmetry (T_4/T_6) and Cordination (T_4/T_2) RMS deviation σ parameters have been computed using partial and multiple regression methods. In this research investigations on micellar doped Gd(III) systems have been reported first time. Antimicrobial activities of compounds have also been determined.**

Keywords: **Quinoline, Gd (III), Antimicrobial activity, bonding parameters.**

1. INTRODUCTION

Very Interesting part of lanthanide chemistry is that the efficient shielding of the 4f shells by closed $5s^2$ and $5p^6$ shells leads the trivalent lanthanide ions to exhibit unique spectroscopic properties. Since the 4f lie deep in the nucleus core, the ligand environment only weakly affects the lanthanide electron cloud which is small in magnitude. The line width of the 4f-4f bands is considerably smaller than that observed for transition metal ions and the peak position of the spectral band reveals a part of $4f^n$ configuration.(1-4) In the present study, the properties of lanthanides are mainly focused on the comparative absorption spectrometry(5) and the corresponding changes in oscillator strength of different 4f-4f transition spectra as probe(6-7) in understanding the characteristics of Gadolium(III) and Gadolium(III) with 2Hydroxy qinoline in alcoholic (Et-OH) and Micellar medium (viz: TX-100, HTAB and SDS) also Antimicrobial activities of Gd (III)-2HQ in alcoholic medium have been determined.

2. MATERIAL AND METHOD

Gadolium chloride of 99.9% was purchased from Ms. Indian Earth limited and ligand was synthesized in our laboratory. The solvents used in doped system are Ethyl Alcohol (AR 99.9%, Jiangsu-Hliaxi International Trade Co. Ltd., Made in China) and Triton-X-100, HTAB and SDS , (Loba Chemia Pvt.Ltd., Mumbai, India).The saturated solution of ligand and metals Gd(III) ion 0.05 M were prepared in different solvents (Triton X-100 of 100 CMC (1.8×10^{-2} M, Sodium Dodecyl sulphate, (SDS) of 75 CMC (0.05 M), and Hexadecyl Trimethyl Ammonium Bromide, (HTAB) of 100 CMC (9.2×10^{-2} M) is used for preparing saturated solution of ligand and metal. Absorption spectra of each solution at room temperature in 1:3 ratio (Metal: Ligand) were recorded on UV Visible Double Beam Spectrophotometer (UV-5704-SS) upgraded with resolution and expansion of scale in the region 190 nm to 1100 nm at Green chemistry research center (GCRC).

3. METHODS

1. Experimental oscillator strength:

The strength of electronic transition is generally expressed in terms of a quantity called "Oscillator Strength" represented by 'P'. It is defined as the ratio of the experimental transition probability to that of the ideal case of a harmonic oscillator that is P_{obs}. For a one-electron transition, the ideal value of unity is obtained when all the molecules are transformed to the higher energy state i.e. when the transition probability is unity. The oscillator strength (8-9) can also be expressed.

$$P = 4.315 \times 10^{-9} \int \varepsilon \, d\nu \text{ --------------------------------------- (1)}$$

Where, ε = Molar Absorptivity or molar extinction Coefficient = OD / CL

ν = Frequency in wave number (cm-1)

The equation may be expressed in terms half band width

$$P_{obs} \approx 4.6 \times 10\text{-}9 \times \varepsilon_{max} \, \Delta\nu^{1/2} \text{ -------------------------------- (2)}$$

$\Delta\nu^{1/2}$ = Half Band Width

2. juddoffelt perameter

$$P_{cal} = T_2 \, \nu \, [U^{(2)}]^2 + T^4 \, \nu \, [U^{(4)}]^2 + T_6 \, \nu \, [U^{(6)}]^2 \text{ ---------------------(3)}$$

For comparison between the calculated (P_{cal}) and the observed (P_{obs}) values of oscillator strengths, the values of r.m.s. deviation have been computed from the relation

$$\sigma_{r.m.s.} = \left[\frac{\sum(P_{cal} - P_{obs})^2}{N} \right]^{\frac{1}{2}} \text{ ……………………… (4)}$$

Where N is the number of levels fitted.

Where $[U^{(2)}]^2$, $[U^{(4)}]^2$, $[U^{(6)}]^2$ are matrix elements

$$Y = a + b_1X_1 + b_2X_2 + b_3X_3 \text{--------------------------------------- (5)}$$

Where, $a = 0$

$X_1 = [U^{(2)}]^2$, $X_2 = [U^{(4)}]^2$, $X_3 = [U^{(6)}]^2$

The values of matrix elements $[U^{(2)}]^2$, $[U^{(4)}]^2$ and $[U^{(6)}]^2$ taken from Carnall et al (10).

$$b_1 = T_2 = C_{11}\sum x_1y + C_{12}\sum x_2y + C_{13}\sum x_3y \text{--------------------------(6)}$$

$$b_2 = T_4 = C_{12}\sum x_1y + C_{22}\sum x_2y + C_{23}\sum x_3y \text{--------------------------(7)}$$

$$b_3 = T_6 = C_{13}\sum x_1y + C_{23}\sum x_2y + C_{33}\sum x_3y \text{--------------------------(8)}$$

b_1, b_2 and b_3 values are equal to T_2, T_4 and T_6 respectively.

For measurement of b_1, b_2 and b_3 values, it is required to measure $\sum x_1y$, $\sum x_2y$ and $\sum x_3y$.

3. Nephelauxetic Ratio (β), Sinha's Covalency Parameters (δ%) and Bonding parameter ($b^{1/2}$) :

The effect of complexation on the free ion is the red shift of the electronic transition. This red shift of the bands is due to the expansion of the radius of central metal orbital. This phenomenon is called Nephelauxetic effect (β) as

$$\beta = \nu_c / \nu_f \text{ ---------------------------------------(9)}$$

Where, vc and vf are wave numbers of f-f transition for spectra of complex and free ion respectively.The Nephelauxetic ratio value can be used to calculate the bonding parameter, from the relation given as -

$b^{1/2} = [\frac{1}{2} (1-\beta)]^{1/2}$ ----------------------------------(10)

Positive value of bonding parameter ($b^{1/2}$) indicates covalent character in metal-ligand bond while negative value shows ionic character in metal-ligand interaction.Percentage covalent character in metal ligand bond can be expressed by Sinha's covalency parameter (δ%).

$\delta \% = [1-\beta/\beta] \times 100$------------------------------- (11)

Covalency angular overlap parameter (η) represents extent of overlapping (11- 15)

Between metal ion orbital and ligand orbital.

$\eta = [1 - \beta^{1/2} / \beta^{1/2}]$-- (12)

TABLE. I: Computed values of judd Oflet Parameter (Tλ) , Symmetry Parameter (T4/T2), andCordination Parameter (T4/T6) of Gd(III)-2HQ Complex in alcoholic and micellar medium

S.N.	Parameter	Gd(III)-2HQ (Et-OH)	Gd(III)-2HQ (TX-100)	Gd(III)-2HQ (HTAB)	Gd(III)-2HQ (SDS)
1	$T_2 \times 10^9$	1447.554	979.506	627.139	202.478
2	$T_4 \times 10^9$	-78724.197	-50680.739	-29749.680	-3353.804
3	$T_6 \times 10^9$	24.409	18.469	21.649	13.639
4	T_4/T_6	-3225.199	-2744.140	-1374.182	-245.901
5	T_4/T_2	-54.384	-51.741	-47.437	-16.564

TABLE. II: Observed and calculated values of Oscillator strength ($P \times 10^6$) of various Absorption Transitions of Gd(III)-2HQ Complex in alcohilic and Micellar medium

COMPOUND		Gd(III)-2HQ (*EtOH*)		Gd(III)-2HQ (TX-100)		Gd(III)-2HQ (HTAB)		Gd(III)-2HQ (SDS)	
S.N.	Energy Levels	$P_{obs}\times10^6$	$P_{cal}\times10^6$	$P_{obs}\times10^6$	$P_{cal}\times10^6$	$P_{obs}\times10^6$	$P_{cal}\times10^6$	$P_{obs}\times10^6$	$P_{cal}\times10^6$
1	$^8S_{7/2} \rightarrow ^6D_{5/2}$	148.443	153.996	91.441	98.344	62.157	65.327	18.950	21.404
2	$^8S_{7/2} \rightarrow ^6D_{9/2}$	3.885	16.112	5.554	20.687	14.710	24.989	28.076	34.619
3	$^8S_{7/2} \rightarrow ^6I_{15/2}$	12.351	27.941	2.635	19.952	10.890	24.265	9.730	15.513
4	$^8S_{7/2} \rightarrow ^6I_{7/2}$	3.126	4.259	2.096	3.041	3.823	3.698	0.943	2.364
5	$^8S_{7/2} \rightarrow ^6P_{1/2}$	23.841	6.160	3.356	39.338	1.907	26.131	0.549	8.561
6	r.m.s.(σ)	19.237		19.350		13.277		5.450	

TABLE. III: Nephelauxetic Ratio (β), Sinha's Covalency Parameters (δ%) and Bonding parameter ($b^{1/2}$) of Gd (III)-2HQ complex in alcoholic and micellar medium

ALCOHOLIC MEDIUM

S.N.	Energy Levels	ν_c (cm^{-1}) Obs	β	$b^{1/2}$	δ%	η
1	$^6D_{5/2}$	42553.19	1.002	0.033	-0.212	-0.001
2	$^6D_{9/2}$	40485.83	1.024	0.110	-2.372	-0.012
3	$^6I_{15/2}$	37105.75	0.998	0.030	0.186	0.001
4	$^6I_{7/2}$	36036.04	1.002	0.030	-0.180	-0.001
5	$^6P_{1/2}$	30395.14	0.957	0.146	4.444	0.022

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|	TX-100 MICELLARMEDIUM					
1	$^6D_{5/2}$	40160.64	0.946	0.165	5.732	0.028
2	$^6D_{9/2}$	38910.51	0.984	0.088	1.581	0.008
3	$^6I_{15/2}$	37453.18	1.007	0.061	-0.743	-0.004
4	$^6I_{7/2}$	36036.04	1.002	0.030	-0.180	-0.001
5	$^6P_{1/2}$	31695.72	1.002	0.028	-0.158	-0.001
	HTAB MICELLAR MEDIUM					
1	$^6D_{5/2}$	41666.67	0.998	0.032	0.209	0.001
2	$^6D_{9/2}$	38314.18	0.985	0.088	1.556	0.008
3	$^6I_{15/2}$	33112.58	0.925	0.193	8.050	0.039
4	$^6I_{7/2}$	31796.50	0.994	0.056	0.640	0.003
5	$^6P_{1/2}$	30721.97	1.012	0.078	-1.214	-0.006
	SDS MICELLAR MEDIUM					
1	$^6D_{5/2}$	42283.30	0.996	0.046	0.425	0.002
2	$^6D_{9/2}$	38759.69	0.983	0.093	1.775	0.009
3	$^6I_{15/2}$	37037.04	0.998	0.030	0.186	0.001
4	$^6I_{7/2}$	36429.87	1.015	0.085	-1.436	-0.007
5	$^6P_{1/2}$	31897.93	1.008	0.063	-0.791	-0.004
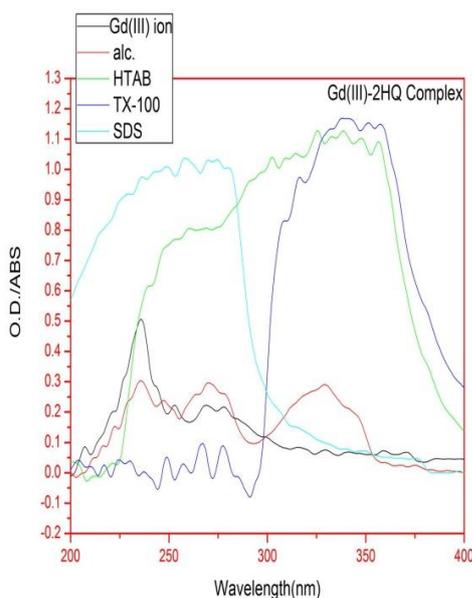
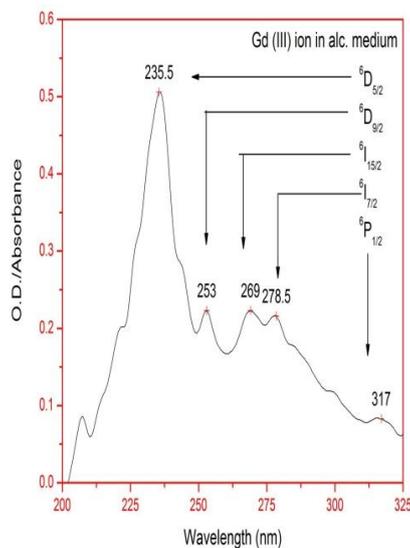**Fig.1 Variation of optical density with wavelength for Gd (III) complex in different solvent**

Fig.2 UV-visible spectra of Gd (III) ion

4. RESULT AND DISCUSSION

The absolute value of oscillator strength and T_2, T_4 and T_6 are determined under different experimental condition for Gd (III)-complexes (Table I, II and III). This clearly shows a significant change in the oscillator strength of f-f transition in Gd(III) ion. The values of various parameters such as nephelauxetic ratio (β), bonding parameter ($b^{1/2}$), Sinha's covalency parameter (δ%) and Covalency angular overlap parameter (η) reveals that the involvement of 4f-orbital has negligible for lanthanide complexe as compared to transition metals. This observation is in agreement with the fact that the interaction between lanthanide cation and neighbouring ligands contracts the 4f wave function of metal ion, which is expected to increase inter-electronic repulsion and spin-orbit interaction, leading to a decrease in covalent character in the complexes.

Comparative absorption spectra of Gd (III)-complexes in alcoholic and micellar medium (Fig-1-2) clearly show a significant enhancement in the oscillator strength and intensity parameter T_2, T_4 and T_6. The higher value of oscillator strength (P) shows lower symmetry in complexes .The T_2 and T_6 (Judd-Ofelt parameter) has been found to be positive for all systems which has significance while T_4 has been found to be negative which has no significance.

5. CONLUSION

From the above discussions through variation in the magnitude of oscillator strength and intensity Parameters (T_2, T_4 and T_6).The value of β if approaches to 1 in alcoholic medium, reflects decreasing covalent character of complex. We can suggest that minor coordination changes in the Gd (III)-2HQ complex are caused by the different coordinating sites of 2HQ, solvent nature and nature of Gd(III)-2HQ bond, which do induce significant variation in the intensity of f-f transitions.

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