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Spectroscopic studies of Nd(III) with Hexafluoroacetylacetone and their complexes

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ABSTRACT

Studying the absorption difference and comparative 4f-4f transition spectra of Nd(III) with hexafluoroacetylacetone[$C_5H_2O_2F_6$] and their complexes with o-phenanthroline and bipyridyl using comparative absorption spectroscopy involving 4f-4f transitions in various solvents like methanol acetonitrile and dimethylformamide, the change in coordination sphere in various solvent medium is observed. The 4f-4f transition spectra yield sharp bands which were analyzed individually by Gaussian curve analysis, the energy interaction parameters ($F_2, F_4, F_{6\&}, E^1, E^2, E^3$)Lande spin orbit coupling (ξ_{4f}), nephelauxetic ratio (β), bonding parameter ($b^{1/2}$), percent covalency (δ), oscillator strength (P) were calculated and Judd Oflet intensity parameters have been computed on computer using partial multiple regression analysis.

Key words: Electronicspectra, hexafluoroacetylacetone

INTRODUCTION

The Ln(III) prasedonium and neodymium can be utilized as absorption spectral probe to investigate the interaction of biomolecule like calcium in vitra. The lanthanide complexes used as an anticancer material. The lanthanide chelate of ligand possessing oxygen and nitrogen donor atoms finds applications as fungicide and bactericides. Some complexes of lanthanide are used in radiological analysis in human body system[1]. The use of lanthanides as absorption spectral probe in several biochemical reactions involving Ca^{+2} and Mg^{+2} has open up a new dimension for the fast developing field of optical spectroscopy[2].

Khan et al[3] study the complexes of o-phenanthroline, bipyridine and pyridine, they are concluded that bipyridine is a weaker ligand than o-phenanthroline, pyridine has been found most effective in promoting 4f- 4f transitions intensity and increase in oscillator strength in this solvents due to dynamic ligand polarization mechanism.

Misra et al [4, 5] studies the solid complexes of Pr(III) and Nd(III) with adenine, adenosine, adenosine 5 monophosphateadenosine 5 diphosphate, adenosine 5 triphosphate were dissolved in organic solvents and their spectra were recorded. Their results suggest that these complexes, when dissolved in the solvents, retained their nonacoordinated stereochemistry possesses in their crystalline state. The silent changes in the oscillator strength of 4f-4f bands as well as the changes in magnitude of Judd Ofelt intensity parameters has led to an upsurge in the quantitative analysis of spectral behavior of Pr(III) and Nd(III) in crystalline as well as in solution state. This change depends on the nature of solvents mixture and varying affinities of ligands [6-8].

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The present study deals with comparative absorption spectral studies of Nd(III) with hexafluoroacetylacetone and their adducts with o-phenanthroline and bipyridyl. The 4f-4f absorption spectra of Nd(III) have been interpreted in terms of various parameters namely Salter-Condon (F_K), Lande spin orbit coupling (ξ_{4f}), Racah (E^K), nephelauxetic ratio (β), bonding parameter ($b^{1/2}$), percent covalency (δ), oscillator strength were calculated and intensity parameters have been computed on computer using partial multiple regression analysis, which gives information about the nature of bonding between Nd(III) metal and ligand complexes.

MATERIALS AND METHODS

Nd(III) chloride heptahydrated of 99.9% purity from M/s Indian Rare Earths Ltd., hexafluoroacetylacetone of AR grade from Aldrich USA, nitrogen donor ligands o-phenanthroline and bipyridine were from Sisco Chemical Laboratory. The CH₃OH, DMFand CH₃CN solvents used for recording the spectra. They were of AR grade from E. Merck. They are distilled before use. The elemental analysis was carried out on Carlo-Erba Strumentatzione StradaRivoltand 200 9D Rodono Italy, at CSMCRI Bhavnagar. Nd (III) contents were determined gravimetrically as Oxalateusing 8-hydroxyquinoline. All the spectra were recorded on Perkin Elmer Lambda-2 UV-Visible spectrophotometer in the range 400-900 nm, in the concentration of Nd(III) complexes in10⁻² M.

Synthesis of [Nd (Hfaa)₃(H₂O)₂]

Nd(III) chloride heptahydrate3.858gm was dissolved in distilled water, the methanolic solution ofhexafluoroacetylacetone6.24gm (4.25ml) was added very slowly with constant stirring on magnetic stirrer which resulted in isolation of yellow crystalline solid. After neutralizing the contents with ammonia the product was filtered, washed thoroughly with methanol and was recrystallized by methanol.

Synthesis of [NdHfaa)₃ (ph)]

The [Nd (hfaa)₃ (H₂O)₂]of 4.35gm added into methanolic solution of 0.992gmof o- phenanthroline and put it for constant stirring. Yield yellow precipitated the amount of precipitated increased tremendously on addition of ammonia solution drop wise. The yellow microcrystalline solid obtained was purified by recrystallization form methanol, the bipyridyl complexes have also been synthesized by similar procedure. These adducts have been synthesized and characterized by elemental analysis and molecular weight determination carried out at CSMCRI, Bhavnagar. Molecular weight and analytical data are shown in Table 1 and Table2. MetalNd(III) was estimated first by decomposing the chelate by concentrated nitric acid and evaporating it to dryness. The dried mass was extracted with dilute HCl and the metal was precipitated as Oxalate by using 8-hydroxy quinoline method.

The energy of $4f^n$ configuration consists of two major components, columbic and spin orbit interaction, between 4f electrons,

$\mathbf{E} = \mathbf{f}^{\mathbf{k}} \cdot \mathbf{F}_{\mathbf{k}} + \mathbf{A}_{\mathbf{so}} \cdot \boldsymbol{\xi}_{\mathbf{4f}}$

Where f^k and A_{so} are angular part and F_k and ξ_{4f} are the radial parts of columbic and spin orbit interactions.(Only terms with k = 2,4,6 are significant for configurations with equivalent electrons). The Columbic and magnetic interaction between $4f^n$ electrons leads to energy level of $4f^n$ configuration and these interaction can be expressed in terms of the electronic repulsion parameters Salter-Condon (F₂, F₄, F₆), G. Racah [9, 10]. (E¹, E², E³) and spin orbit interaction parameter, Lande spin orbit coupling (ξ_{4f}) as a first approximation. The energy E_j of the jth level is given by the following equation,

$$\begin{split} E_{j}(F_{k},\xi_{4f}) &= E_{oj}(F_{k}^{0},\xi_{4f}) + \sum (\delta E_{j}/\delta F_{k}) \ \Delta F_{k} + (\delta E_{j}/\delta \xi_{4f}) \ \Delta \xi_{4f} \\ & k = 2,4,6 \end{split}$$

Where, E_{oj} is the zero order energy of the jth level is given by Wong [11, 12]. The zero order energy values are E_{oj} , partial derivative ($\delta E_j/\delta F_k$) and ($\delta E_j/\delta \xi_{4f}$), for different levels were known. The nephelauxetic effects measures the change in F_k with respect to free ion and expressed by nephelauxetic ratio(β), which is defined as,

$$\beta = \mathbf{F}^{\mathbf{c}}_{\mathbf{k}} / \mathbf{F}^{\mathbf{r}}_{\mathbf{k}}$$

Where, c and f referred to complex and free ion. In our studiesinvolvingPr(III) and Nd(III) with widevariety of ligands, we have observed good linear relationship between bonding parameter,

(b^{1/2}) which is derived from the nephelaxetic effect (1- β), The oscillator strength of hypersensitive transition showed gradual increase with the increased nephelauxetic effect (1- β) and bonding parameter; $\mathbf{b}^{1/2} = [1 - \beta/2]^{1/2}$

S. P. Sinha [20-22] introduced another parameter, percentage covalency parameter (δ)as, $\delta = [1 - \beta / \beta] \times 100$

The experimental value of oscillator strength (P_{obs}) of absorption bands were calculated by performing Gaussian curve analysis using the following relationship,

$$p = 4.31 \times 10^{-9} \times \left[\frac{9n}{(n^2+2)^2}\right] \varepsilon_m(\bar{v}) \, d\bar{v}$$

Also the observed value of oscillator strength (p) for all peaks in complex has been computed using the following relationship.

$$p=4.\,60 imes10^{-9} imesarepsilon_m imes\Delta v_2^{\perp}$$

Where \mathcal{E}_{m} is the molar extinction coefficient corresponding to energy $(\overline{\boldsymbol{v}})$, n is the refractive index of the medium.

RESULTS AND DISCUSSION

The Fig. 1 shows comparative absorption spectra of Nd(III) complexes in methonal. There is marginal red shift observed in 4f-4f transition bands of [Nd(hfaa)₃ (H₂O)₂] and blue shift observed in o-phenanthroline. The enhancement is more in case bipyridyl indicating that bipyridyl is a better ligand than o-phenanthroline when recorded in methanol. The intensity order of Nd(III) complexes is ${}^{4}F_{5/2} > {}^{4}G_{5/2} > {}^{4}F_{7/2} > {}^{3}F_{3/2} > {}^{4}G_{7/2}$ [23-28]. Table 1shows the observed and calculated values of molecular weight of Nd(III) complexes. These are characterized by elemental analysis and molecular weight determination carried out at CSMCRI, Bhavnagar. Molecular weight and analytical data are shown in Table 1 and Table2.



Fig. 1 Comparative absorption spectra of 1)[Nd(hfaa)₃(H₂O)₂]2)[Nd(hfaa)₃(oph)] 3)[Nd(hfaa)₃(bipy)] complexes in methanol.

Table 1 shows the observed and calculated values of molecular weight ofNd(III) complexes.

Complexes	Cal. MW	Obs. MW
Nd (hfaa) ₃ (H ₂ O) ₂	832.90	831.50
Nd (hfaa) ₃ (oph)	1011.70	1009.64
Nd (hfaa) ₃ (bipy)	1070.78	1069.89

Table 2 shows the observed and calculated values of analytical data of Nd(III) complexes.

Complexes	% metal		%Ca	rbon	% Hyc	lrogen	% Nitrogen		
	Obs	Cal	Obs	Cal	Obs	Cal	Obs	Cal	
Nd (hfaa) ₃ (H ₂ O) ₂	16.60	16.28	20.16	21.71	1.11	1.21	-	-	
Nd (hfaa) ₃ (oph)	13.38	13.78	31.38	32.16	2.65	2.87	2.48	2.57	
Nd(hfaa) ₃ (bipy) ₂	13.86	13.31	30.35	30.37	2.69	2.53	2.32	2.62	

Table 2 shows the observed and calculated values of analytical data

Table 3 Experimental and Computed energies values in (cm⁻¹) of Nd(III) complexes in CH₃OH, DMF and CH₃CN solvents

Complexes	${}^{4}G_{7/2}$		⁴ G _{5/2}		⁴ F _{7/2}		⁴ F _{5/2}		⁴ F _{3/2}		rme
Complexes	obscal		obscal		obscal		obscal		obscal		1.111.5.
Solvent MeoH											
Nd(hfaa) ₃ (H ₂ 0) ₂	19100	19165	17230	17296	13361	13370	12498	12536	11542	11479	51.61
Nd(hfaa) ₃ (phen)	19165	19166	17272	17290	13370	13371	12504	12527	11546	11476	36.21
Nd(hfaa) ₃ (bipy)	19122	19166	17194	17282	13368	13355	12500	12522	11544	11467	56.66
Solvent DMF											
Nd(hfaa) ₃ (H ₂ 0) ₂	19081	19119	17171	17235	13354	13318	12483	12486	11518	11433	52.88
Nd(hfaa) ₃ (phen)	19091	19115	17233	17351	13352	13318	12488	12486	11519	11432	51.13
Nd(hfaa) ₃ (bipy)	19104	19065	17191	17235	13365	13325	12498	12494	11534	11402	62.12
Solvent CH ₃ CN											
Nd(hfaa) ₃ (H ₂ 0) ₂	19147	19200	17264	17313	13377	13391	12501	12551	11540	11399	45.52
Nd(hfaa) ₃ (phen)	19180	19192	17269	17309	13409	13310	12506	12552	11550	11492	36.56
Nd(hfaa) ₃ (bipy)	19152	19169	17194	17279	13381	13373	12500	12535	11538	11468	45.66

Table 3 shows experimental and computed energies of Nd(III) complexes in CH₃OH, DMF and CH₃CN solvents. The r.m.s. deviation σ are varies from 36.21 to 62.12, clearly shows that accuration of various energy interaction parameters.

Table 4 shows energy interaction parameters Slator Condon (F_k), Lande spin orbit interaction (ξ_{4f}), nephelauxetic ratio (β), bonding parameters ($b^{1/2}$) and covalency (δ) for Nd(III) complexes in CH₃OH, DMF and CH₃CN solvents. It shows that the values of nephelauxetic effect (β) in Nd(III) complexes werevaries from 0.975 to 0.991 which is less than unity. The value of bonding parameters ($b^{1/2}$) were varies from 0.104to 0.108 and which is positive indicate covalent bonding between Nd(III) and ligand. Misra et al [29-33] observed decrease in the values of (F_k , E^k) and ξ_{4f} parameters as compared to corresponding parameters of aqueous ion. They also observed that Nd(III) complexes with β -diketones and nitrogen donor ligands. These⁴F_{5/2}, ⁴G_{5/2}, ⁴F_{7/2}, ³F_{3/2}, ⁴G_{7/2} transitions are not hypersensitive in orthodox sense,

 $Table \ 4 \ Computed \ values \ of \ energy \ interaction \ parameters \ Slator \ Condon \ (F_k), \ Lande \ spin \ orbit \ coupling \ (\xi_{4f}), \ nephelauxetic \ ratio \ (\beta), \ bonding \ parameters \ (b^{1/2}) \ and \ covalency \ parameter \ (\delta) \ for \ Pr(III) \ complexes \ in \ CH_3OH, \ DMF \ and \ CH_3CN \ solvents$

Complexes	F ₂	F ₄	F ₆	(ξ_{4f})	E^1	E^2	E^3	β	b ^{1/2}	(δ)
Solvent MeoH										
Nd(hfaa) ₃ (H ₂ 0) ₂	330.66	47.77	5.15	886.13	4971.12	24.44	490.22	0.975	0.104	2.244
Nd(hfaa) ₃ (phen)	331.20	47.98	5.16	884.88	4972.54	24.56	491.89	0.977	0.106	2.321
Nd(hfaa) ₃ (bipy)	330.98	48.22	5.16	894.21	4976.22	24.34	492.31	0.990	0.106	2.256
Solvent DMF										
$Nd(hfaa)_3(H_20)_2$	330.98	48.70	5.16	884.68	4953.66	24.46	493.78	0.981	0.107	2.781
Nd(hfaa) ₃ (phen)	330.85	47.87	5.15	883.89	4972.12	24.45	491.45	0.984	0.108	2.331
Nd(hfaa) ₃ (bipy)	331.21	46.98	5.16	884.12	4972.12	24.41	491.41	0.985	0.107	2.321
				Solvent	CH ₃ CN					
Nd(hfaa) ₃ (H ₂ 0) ₂	331.12	47.96	5.15	895.44	4974.62	24.23	492.12	0.991	0.104	2.146
Nd(hfaa) ₃ (phen)	330.25	48.63	5.15	895.46	4974.69	24.36	492.33	0.988	0.105	2.221
Nd(hfaa) ₃ (bipy)	330.56	48.80	5.15	895.98	4974.88	24.27	492.23	0.991	0.104	2.234

All these fivetransitions⁴F_{5/2}, ⁴G_{5/2}, ⁴F_{7/2}, ³F_{3/2}, ⁴G_{7/2}ofNd(III)are showing substantial variation of oscillator strength which conform the ligand mediated pseudohypersensitivity of these pseudohypersensitive transitions. Karaker shows that the shape, energy and oscillator strength of hypersensitive and pseudohypersensitive transition can be correlated with coordination number [34-36]. Table 5 shows experimental and computed values of Oscillator strength the (σ) r. m. s. deviation varies from 2.146 to 2.781.In neodymium (III)complexes also we have observed high sensitivity of $^{4}I_{9/2} \rightarrow ^{4}G_{7/2}$, $^{4}F_{7/2}$, $^{4}F_{5/2}$, $^{3}F_{3/2}$ transitions addition to the known hypersentitive, $^{4}I_{9/2} \rightarrow ^{4}G_{7/2}$ transition. Our studies involving about three hundred spectra of Pr(III)&Nd(III),have clearly indicated hypersensitive cannot be restricted to hypersensitive transitions only but the nature, coordinating ability, chelating power, normalized bite

conformation of ligand and nature of complex species may induce hypersensitivity to non hypersensitive transition we would like to back call transitions as pseudo hypersensitive transitions.

Complexes	${}^{4}\mathrm{G}_{7/2}$		${}^{4}\mathrm{G}_{5/2}$		⁴ F _{7/2}		⁴ F _{5/2}		⁴ F _{3/2}		σ
complexes	obscal		obscal		obsCal		obscal		obscal		r.m.s.
Solvent MeoH											
Nd(hfaa) ₃ (H ₂ 0) ₂	9.702	8.774	32.97	32.55	13.87	13.98	14.96	16.55	5.122	5.641	0.884
Nd(hfaa) ₃ (phen)	12.54	12.98	40.36	39.98	17.33	18.66	19.99	21.98	7.446	7.841	1.121
Nd(hfaa) ₃ (bipy)	9.982	9.662	36.98	36.92	16.19	16.01	16.44	17.99	5.968	6.234	0.654
Solvent DMF											
Nd(hfaa) ₃ (H ₂ 0) ₂	11.32	11.12	37.77	38.87	20.98	19.52	18.68	20.45	6.566	7.654	1.238
Nd(hfaa) ₃ (phen)	13.12	12.95	43.89	43.78	20.96	20.45	21.12	22.11	8.123	8.654	1.325
Nd(hfaa) ₃ (bipy)	11.56	11.32	37.98	38.10	19.45	17.55	18.12	20.96	7.65	7.335	1.356
Solvent CH ₃ CN											
Nd(hfaa) ₃ (H ₂ 0) ₂	10.56	08.54	25.88	27.85	11.95	12.06	12.54	14.32	4.880	5.023	1.566
Nd(hfaa) ₃ (phen)	15.54	12.97	34.87	35.11	20.75	20.23	18.22	20.65	6.323	8.121	2.110
Nd(hfaa) ₃ (bipy)	14.78	11.22	32.02	34.12	17.22	16.56	16.49	16.12	4.612	6.855	2.322

Table 5 Experimental and computed values of Oscillator strength (Px10⁶) in CH3OH, DMF, CH3CN

Table 6 shows Judd Ofelt intensity parameters are derived from the observed oscillator strength and T_4/T_6 varies from 0.614 to 0.798 this shows the wide variation of oscillator strength of pseudo hypersensitive transitions. The variation of T_2 , T4,T6 parameters clearly shows that, the high sensitivity towards coordination and position of the substituent as well as the nature of solvent.

Table No- 6 Judd Oflet Intensity Parameters (Tx10¹⁰)for Nd(III) Complexes in different Solvents

Complexes	T ₂	T_4	T ₆	T_4/T_6
Solvent MeoH				
Nd(hfaa) ₃ (H ₂ 0) ₂	12.492	21.912	29.708	0.737
Nd(hfaa) ₃ (phen)	13.854	24.213	39.421	0.614
Nd(hfaa) ₃ (bipy)	16.985	22.445	29.661	0.767
Solvent DMF				
$Nd(hfaa)_3(H_20)_2$	16.321	24.545	29.458	0.830
Nd(hfaa) ₃ (phen)	14.584	23.988	35.122	0.683
Nd(hfaa) ₃ (bipy)	13.882	20.584	27.898	0.737
Solvent CH ₃ CN				
Nd(hfaa) ₃ (H ₂ 0) ₂	15.323	21.213	26.588	0.798
Nd(hfaa) ₃ (phen)	16.231	20.897	30.584	0.683
Nd(hfaa) ₂ (bipy)	13.211	20.514	26.985	0.760

CONCLUSION

The results of this study reveals that the Nd(III) complexes with hexafluoroacetylacetone and their adducts with phenanthroline and bipyridyl complexes creates high degree of intensification to of ${}^{4}I_{9/2} \rightarrow {}^{4}G_{5/2}$, ${}^{4}F_{5/2}$, pseudo hypersensitive transitions, in different immediate coordination environment around Pr(III) as a results of different functional groups of β -diketone and ligands. It is quite apparent the stereochemistry possible for octacoordination and are interconvertible. The change in the stereochemistry could change the distance between Nd(III) and ligands. Hence, this could change the extent of interactions between lanthanide and ligands.

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