

Comparative Absorption Spectral Studies of Pr (III) with Hexafluoroacetylaceton complexes in various solvents

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ABSTRACT

In the present study, the 4f-4f transitions of Pr(III) with hexafluoroacetylaceton $[CF_3COCH_2COCF_3]$ and their adducts with structurally related ligands o-phenanthroline $[C_{12}H_{12}N_2]$ and bipyridyl $[C_{10}H_8N_2]$ complexes in various solvents viz., methanol (CH_3OH), acetonitrile $[CH_3CN]$ and dimethyl formamide $[(CH_3)_2NCHO]$ have been successfully carried out. In the absorption difference and comparative absorption spectrophotometric study, the 4f-4f transition spectra yield sharp bands which were analyzed individually by Gaussian curve analysis, energy interaction parameters (F_K, E^K), Lande spin orbit coupling (ζ_{4f}), nephelauxetic ratio (β), bonding parameter ($b^{1/2}$), percentage covalency (δ) and intensity parameters. By using partial multiple regression analysis method, these parameters were computed on computer to determine the possible geometry of complexes in solution and nature of the bond between lanthanide metal and ligands.

Key words: Electronic spectra, hexafluoroacetylaceton, nephelauxetic effects

INTRODUCTION

In lanthanides the electrons are successively added to inner lying 4f sub-shell filled by strongly positive and large sized ions. These ions undergo shrinkage in ionic size known as lanthanide contraction. This shrinkage influences the coordination chemistry of lanthanide and affects both coordination number and coordination geometry [1-2]. The use of lanthanides as absorption spectral probe in several biochemical reactions involving Ca^{+2} and Mg^{+2} has opened up a new dimension for the fast developing field of optical spectroscopy [3].

Few researchers have been studied the solid complexes of Pr(III) and Nd(III) from mononucleotide and mononucleosides dissolved in organic solvents and their spectra were recorded. Their results reveal that these complexes, when dissolved in the solvents, retained their noncoordinated stereochemistry in their crystalline state [4-6]. The silent changes in the oscillator strength of 4f-4f bands as well as the change 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 solvent mixtures and varying affinities of ligands [7, 8].

In the present study, we have prepared $[Pr(hfaa)_3(H_2O)_2]$ complex and their adducts with structurally related nitrogen donor ligands viz., o-phenanthroline and bipyridyl. Absorption spectra of Pr(III) have been interpreted in terms of Salter-Condon (F_K), Lande spin orbit coupling (ζ_{4f}), Racah (E^K), nephelauxetic ratio (β), bonding

parameter ($b^{1/2}$), percentage covalency (δ), oscillator strength and intensity parameters. By using partial multiple regression analysis method, these parameters were computed on computer. The computed parameters give information about the nature of complexation.

MATERIAL AND METHODS

Pr(III) chloride heptahydrated of 99.9% purity from M/s Indian Rare Earths Ltd., Hexafluoroacetylacetone [$\text{CF}_3\text{COCH}_2\text{COCF}_3$] from Aldrich Chemicals USA, nitrogen donor ligands viz., o-phenanthroline and bipyridyl were obtained from Sisco Chemical Laboratory. The AR grade CH_3OH , DMF and CH_3CN solvents (E. Merck) were used for recording the spectra. The elemental analysis was carried out on Carlo-Erba Strumentazione Strada Rivoltand 200 9D Rodono Italy, at CSMCRI Bhavnagar. Pr(III) contents were determined gravimetrically as Oxinate using 8-hydroxyquinoline. All the spectra were recorded on Perkin Elmer Lambda-2 UV-Visible spectrophotometer in the range 380-620nm, in the concentration of Pr(III) complexes in 10^{-2} Molar.

Synthesis of $[\text{Pr}(\text{hfaa})_3(\text{H}_2\text{O})_2]$

The Pr(III) chloride heptahydrated 3.734 gm was dissolved in distilled water. The methanolic solution of hexafluoroacetylacetone 6.24gm 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 and recrystallized by methanol.

Synthesis of $[\text{Pr}(\text{hfaa})_3(\text{oph})]$

The $[\text{Pr}(\text{hfaa})_3(\text{H}_2\text{O})_2]$ of 4.15 gm added into methanolic solution of 0.992 gm of o-phenanthroline and put it for constant stirring. On addition of ammonia solution drop wise, the amount of yellow precipitated increased tremendously. The product was filtered, washed thoroughly and recrystallized by methanol. By using similar procedure, the bipyridyl complexes were synthesized. The synthesized adducts were characterized by using elemental analysis and molecular weight determination. These characterizations were carried out at CSMCRI, Bhavnagar, India.

The Coulombic and magnetic interaction between $4f^n$ electrons leads to energy level of $4f^n$ configuration. These interactions could be expressed in terms of the electronic repulsion parameters, Salter-Condon (F_2, F_4, F_6), Racah (E^1, E^2, E^3), spin orbit interaction parameter and Lande spin orbit coupling (ξ_{4f}) as a first approximation [9, 10]. The energy E_{so} arising from the most important magnetic interaction which is spin orbit interactions, may be written as,

$$E_{so} = A_{so} \xi_{4f}$$

Where A_{so} is the angular part of spin-orbit interaction and ξ_{4f} is the radial integral and known as Lande's parameter. The energy E_j of the j^{th} level is given by the following equation,

$$E_j(\mathbf{F}_k, \xi_{4f}) = E_{oj}(\mathbf{F}_k, \xi_{4f}) + \sum_{k=2,4,6} (\delta E_j / \delta F_k) \Delta F_k + (\delta E_j / \delta \xi_{4f}) \Delta \xi_{4f}$$

Where, E_{oj} is the Zero order energy of the j^{th} level. It is given by Wong [11, 12]. The values of 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,

$$\beta = F_k^c / F_k^f$$

Where, c and f referred to complex and free ion. The amount of mixing of $4f$ orbital and ligand orbital can be measured by the bonding parameter ($b^{1/2}$) which is given by [13-17],

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

The percentage covalency parameter (δ) is given by [18],

$$\delta = [1 - \beta / \beta] \times 100$$

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

$$P_{\text{obs}} = 4.60 \times 10^{-9} \epsilon_m(\bar{\nu}) (d\bar{\nu})$$

Where ϵ_m is the molar extinction coefficient corresponding to energy ($\bar{\nu}$).

RESULTS AND DISCUSSION

The Fig. 1 shows comparative absorption spectra of Pr(III) complexes in methanol. There is marginal red shift of 4f-4f transition bands in $[\text{Pr}(\text{hfaa})_3(\text{H}_2\text{O})_2]$. The enhancement is more in case of o-phenanthroline indicates a better ligand than bipyridyl when recorded in methanol. The intensity of ${}^3\text{H}_4 \rightarrow {}^3\text{P}_2 > {}^3\text{H}_4 \rightarrow {}^3\text{P}_1 > {}^3\text{H}_4 \rightarrow {}^3\text{P}_0 > {}^3\text{H}_4 \rightarrow {}^1\text{D}_2$ [19, 20].

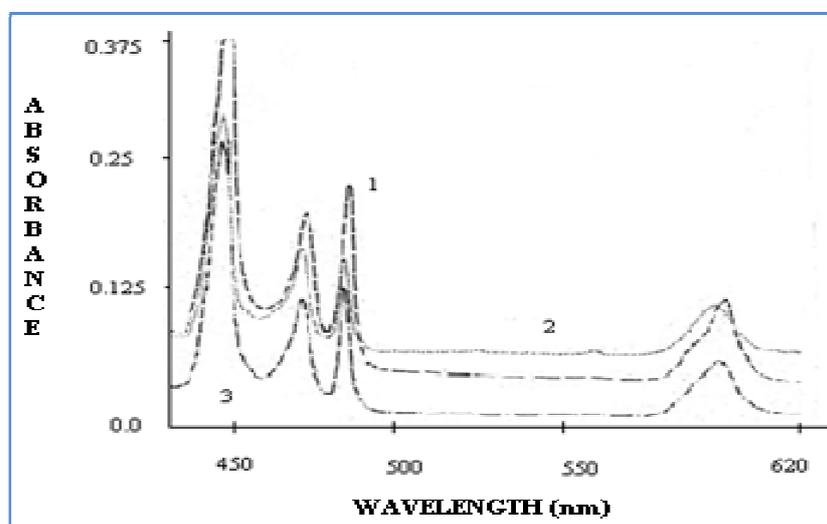


Fig. 1 Comparative absorption spectra of 1) $[\text{Pr}(\text{hfaa})_3(\text{oph})]$, 2) $[\text{Pr}(\text{hfaa})_3(\text{H}_2\text{O})_2]$, 3) $[\text{Pr}(\text{hfaa})_3(\text{bipy})]$ and complexes in methanol.

The molecular weights and analytical data are shown in Tables 1 and 2 respectively. The metal Pr(III) were estimated gravimetrically as oxinate by using 8-hydroxy quinoline method.

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

Complexes	Cal. MW	Obs. MW
$\text{Pr}(\text{hfaa})_3(\text{H}_2\text{O})_2$	829.40	828.20
$\text{Pr}(\text{hfaa})_3(\text{oph})$	991.67	990.40
$\text{Pr}(\text{hfaa})_3(\text{bipy})$	963.63	949.66

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

Complexes	% metal		% Carbon		% Hydrogen		% Nitrogen	
	Obs	Cal	Obs	Cal	Obs	Cal	Obs	Cal
$\text{Pr}(\text{hfaa})_3(\text{H}_2\text{O})_2$	16.96	16.20	20.08	21.71	1.08	1.21	-	-
$\text{Pr}(\text{hfaa})_3(\text{oph})$	14.18	14.10	31.25	32.68	1.58	1.61	2.52	2.82
$\text{Pr}(\text{hfaa})_3(\text{bipy})$	14.82	14.31	30.20	31.59	1.56	1.68	1.40	1.47

Table 3 shows experimental and computed values of Pr(III) complexes in CH_3OH , DMF and CH_3CN solvents. The r.m.s. deviation σ are varies from 109.70 to 170.80 shows that accuration of the various energy interaction parameters.

Table 3 Observed and calculated energies (cm⁻¹) of Pr(III) complexes in CH₃OH, DMF and CH₃CN solvents.

Complexes and Solvents	³ P ₂		³ P ₁		³ P ₀		¹ D ₂		σ r.m.s.
	Obs	Cal	Obs	Cal	Obs	Cal	Obs	Cal	
CH₃OH									
Pr(hfaa) ₃ (H ₂ O) ₂	22538	22386	21360	21233	20777	20774	16930	17118	128'28
Pr(hfaa) ₃ (oph)	22530	22389	21359	21235	20778	20736	16942	17116	129.55
Pr(hfaa) ₃ (bipy)	22529	22375	21352	21121	20770	20768	16917	17003	109.70
DMF									
Pr(hfaa) ₃ (H ₂ O) ₂	22532	22382	21232	21351	20760	20756	16920	17110	133.28
Pr(hfaa) ₃ (oph)	22536	22372	21227	21360	20750	20752	16933	17109	135.80
Pr(hfaa) ₃ (bipy)	22522	22359	21197	21310	20746	20738	16861	17110	156.69
CH₃CN									
Pr(hfaa) ₃ (H ₂ O) ₂	22421	22446	21243	21116	20689	20681	16827	17110	170.80
Pr(hfaa) ₃ (oph)	22512	22369	21339	21212	20745	20748	16922	17105	128.90
Pr(hfaa) ₃ (bipy)	22514	22332	21331	21198	20731	20733	16901	17085	137.46

Table 4 shows energy interaction parameters, Slater Condon (F_k), Lande spin orbit interaction (ξ_{4f}), nephelauxetic ratio (β), bonding parameters (b^{1/2}) and percentage covalency (δ) for Pr(III) complexes in CH₃OH, DMF and CH₃CN solvents. It shows that the values of nephelauxetic effect (β) in Pr(III) complexes were varies from 0.921 to 0.929 which is less than unity. The value of bonding parameters (b^{1/2}) were varies from 0.127 to 0.132 and which is positive indicate covalent bonding between Pr(III) and ligand. Table 5 shows experimental and computed values of oscillator strength, the r.m.s. deviation σ varies from 0.68 to 2.98.

Table 4 Computed values of energy interaction parameters Slater Condon (F_k), Lande spin orbit coupling (ξ_{4f}), nephelauxetic ratio (β), bonding parameters (b^{1/2}) and covalency parameter (δ) for Pr(III) complexes in CH₃OH, DMF and CH₃CN solvents.

Complexes and Solvent	F ₂	F ₄	F ₆	(ξ _{4f})	β	(b ^{1/2})	(δ)
CH₃OH							
Pr(hfaa) ₃ (H ₂ O) ₂	311.63	42.98	4.70	672.75	0.923	0.131	3.621
Pr(hfaa) ₃ (oph)	311.60	43.02	4.72	676.24	0.929	0.132	3.510
Pr(hfaa) ₃ (bipy)	311.72	43.12	4.74	670.53	0.923	0.129	3.340
DMF							
Pr(hfaa) ₃ (H ₂ O) ₂	311.70	43.01	4.70	652.68	0.924	0.128	3.359
Pr(hfaa) ₃ (oph)	311.68	43.03	4.71	662.24	0.926	0.127	3.350
Pr(hfaa) ₃ (bipy)	311.75	43.10	4.72	571.37	0.921	0.130	3.527
CH₃CN							
Pr(hfaa) ₃ (H ₂ O) ₂	311.08	42.98	4.70	655.58	0.924	0.131	3.531
Pr(hfaa) ₃ (oph)	311.31	42.94	4.68	676.38	0.931	0.143	3.511
Pr(hfaa) ₃ (bipy)	311.33	42.95	4.69	670.60	0.934	0.137	3.519

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

Complexes and Solvents	³ P ₂		³ P ₁		³ P ₀		¹ D ₂		σ r.m.s.
	Obs	Cal	Obs	Cal	Obs	Cal	Obs	Cal	
CH₃OH									
Pr(hfaa) ₃ (H ₂ O) ₂	13.17	13.16	4.95	3.71	3.70	3.55	3.92	4.36	0.68
Pr(hfaa) ₃ (oph)	43.18	43.16	18.18	16.50	16.28	15.36	15.55	15.69	1.66
Pr(hfaa) ₃ (bipy)	30.35	31.40	11.97	9.80	9.05	8.66	13.04	12.54	1.44
DMF									
Pr(hfaa) ₃ (H ₂ O) ₂	26.56	27.44	10.66	9.01	8.11	7.99	10.22	10.12	1.30
Pr(hfaa) ₃ (oph)	35.04	34.88	13.76	8.21	8.10	8.01	10.71	11.11	2.98
Pr(hfaa) ₃ (bipy)	18.55	17.92	7.51	4.88	4.56	4.54	6.45	6.40	1.30
CH₃CN									
Pr(hfaa) ₃ (H ₂ O) ₂	10.98	11.44	4.55	3.51	3.22	3.56	3.57	3.88	0.78
Pr(hfaa) ₃ (oph)	34.66	34.89	11.01	8.96	7.84	7.83	11.22	10.75	1.87
Pr(hfaa) ₃ (bipy)	32.33	31.55	9.83	6.87	6.73	6.77	9.66	9.43	1.54

Table 6 shows Judd Ofelt intensity parameters. These parameters are derived from the observed oscillator strength. The variation of T₂, T₄, T₆ parameters clearly indicates the high sensitivity towards coordination. The symmetry of complexes changes as a result of the nature and position of the substituent, as well as the nature of solvent. The T₄/T₆ ratio varies between 0.15 to 0.34 which indicates the wide variation of oscillator strength of pseudo hypersensitive transitions.

Table 6 Judd Ofelt parameters ($T \times 10^{10}$) for Pr(III) Complexes in different solvents.

Complexes and Solvent	T ₂	T ₄	T ₆	T ₄ /T ₆
CH ₃ OH				
Pr (hfaa) ₃ (H ₂ O) ₂	141.60	11.18	41.39	0.27
Pr (hfaa) ₃ (oph)	641.20	28.39	138.25	0.21
Pr (hfaa) ₃ (bipy)	865.01	25.30	96.15	0.26
DMF				
Pr (hfaa) ₃ (H ₂ O) ₂	510.60	24.25	83.36	0.29
Pr (hfaa) ₃ (oph)	620.80	44.50	130.40	0.34
Pr (hfaa) ₃ (bipy)	198.98	23.80	109.68	0.22
CH ₃ CN				
Pr (hfaa) ₃ (H ₂ O) ₂	165.55	9.68	31.98	0.30
Pr (hfaa) ₃ (oph)	140.44	24.80	109.90	0.22
Pr (hfaa) ₃ (bipy)	146.40	14.88	96.88	0.15

S. N. Misra et al [21-23] 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 Pr(III) complexes with β -diketones viz., bzac, acac, dbm, ttfa and nitrogen donor ligands viz., aniline, bromoaniline and chloroaniline and their $^3H_4 \rightarrow ^3P_2$, $^3H_4 \rightarrow ^3P_1$, $^3H_4 \rightarrow ^3P_0$, $^3H_4 \rightarrow ^1D_2$ transitions are not hypersensitive in orthodox sense [24-26].

All these four transitions of Pr(III) $^3H_4 \rightarrow ^3P_2$, $^3H_4 \rightarrow ^3P_1$, $^3H_4 \rightarrow ^3P_0$ and $^3H_4 \rightarrow ^1D_2$ shows substantial variation of oscillator strength which confirm the ligand mediated pseudohypersensitivity of these pseudohypersensitive transitions. Karaker shows that the shape, energy and oscillator strength of hypersensitive and pseudohypersensitive transition could be correlated with diagnostic of the immediate coordination environment around the lanthanide ions and coordination number [27].

CONCLUSION

The results of this study reveals that the Pr(III) complexes with hexafluoroacetylacetonate and their adducts with nitrogen donor ligands viz., o-phenanthroline and bipyridyl complexes creates high degree of intensification to $^3H_4 \rightarrow ^3P_2$ pseudohypersensitive transitions, in different immediate coordination environment around lanthanide metal. The variation of T₂, T₄ and T₆ parameters clearly shows the high sensitivity towards the coordination. The change in the stereochemistry could change the distance between lanthanide metal and ligands.

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