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The 4f-4f transition Spectral Studies of Pr(III) with Hexafluoroacetylacetone and their Complexes

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ABSTRACT

Studies on the difference in energy interaction parameters and comparative absorption spectroscopy, involving 4f-4f transition spectra of praseodymium with hexafluoroacetylacetone [$C_5H_2O_2F_6$], and their complexes with aniline [C_6H_7N], chloroaniline [C_6H_6NCl] and bromoaniline [C_6H_6NBr]. The absorption spectrum were recorded in different solvents like methanol (CH_3OH), acetonitrile (CH_3CN) and dimethylformamide [$(CH_3)_2NCOH$]. 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_K,E^K), 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 of the 4f-4f transitions have been evaluated in order to investigate the formation and the type of bonding in lanthanide ligand complexes in methanol, acetonitrile and dimethylformamide. The energy interaction and Salter Condon parameters were computed on computer using partial multiple regression analysis method.

Key words: Absorption spectra, hexafluoroacetylacetone, nephelauxetic effect, pseudo hypersensitive.

INTRODUCTION

The trivalent lanthanide praseodymium 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. Some complexes of lanthanide are used in radiological analysis (M R I) 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] studied the complexes of o-phenanthroline, bipyridine and pyridine, they are concluded 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) from mononucleotide and mononucleosides, 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].

The present study deals with comparative absorption spectral studies of Pr(III) with hexafluoroacetylacetone and their adducts with aniline, chloroaniline and bromoaniline. Their 4f-4f absorption spectra of Pr(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 Pr(III) metal and ligand complexes.

MATERIALS AND METHODS

Pr(III) chloride heptahydrated of 99.9% purity from M/s Indian Rare Earths Ltd., hexafluoroacetylacetone of AR grade from Aldrich USA, nitrogen donor ligands viz.,aniline chloroaniline and bromoaniline were from Sisco Chemical Laboratory. The CH_3OH, DMF and CH_3CN 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 Strada Rivoltand 200 9D Rodono Italy, at CSMCRI Bhavnagar. Pr (III) contents were determined gravimetrically as Oxalate 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 in10^{-2} M.

Synthesis of [Pr (HFAA)$_3$(H$_2$O)$_2$]

Pr(III) chloride heptahydrate 3.734 gm was dissolved in distilled water, the methanolic solution of hexafluoroacetylacetone 6.24gm (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 [Pr HFAA)$_3$ (an)$_2$]

The [Pr (hfaa)$_3$ (H$_2$O)$_2$]of 4.15 gm added into methanolic solution of 0.50 gm of aniline 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 chloroaniline and bromoaniline complexes have also been synthesized by similar procedure. These adducts have been synthesized and characterized by elemental analysis and molecular weight determination, the elemental analysis and molecular weight determination carried out at CSMCRI, Bhavnagar. Molecular weight and Analytical data are shown in Table 1 and Table 2. Metal Pr(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,

$$E = f^k . F_k + A_{so} . \xi_{4f}$$

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 (F_2, F_4, F_6), G. Racah [9, 10]. (E^1, E^2, E^3) and spin orbit interaction parameter, Lande spin orbit coupling (ξ_{4f}) as a first approximation. The energy E_j of the j^{th} level is given by the following equation,

$$E_j(F_k . \xi_{4f}) = E_{oj}(F^0_k . \xi_{4f}) + \sum_{k=2,4,6} (\delta E_j/\delta F_k)\, \Delta F_k + (\delta E_j/\delta \xi_{4f}) \Delta \xi_{4f}$$

Where, E_{oj} is the zero order energy of the j^{th} level 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,

$$\beta = F^c_k / F^f_k$$

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 [13-19],

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

S. P. Sinha [20-21] 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,

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

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

RESULT AND DISCUSSION

The Fig. 1 shows comparative absorption spectra of Pr(III) complexes in dimethylformamide. There is marginal red shift observed in 4*f*-4*f* transition bands of [Pr(hfaa)$_3$ (H$_2$O)$_2$] and blue shift observed in chloroaniline, the enhancement is more in case aniline indicating that aniline is a better ligand than bromoaniline and chloroanline when recorded in dimethylformamide. The intensity order of Pr(III) complexes is $^3H_4 \rightarrow {}^3P_2 > {}^3H_4 \rightarrow {}^3P_1 > {}^3H_4 \rightarrow {}^3P_0 > {}^3H_4 \rightarrow {}^1D_2$ [22-25].

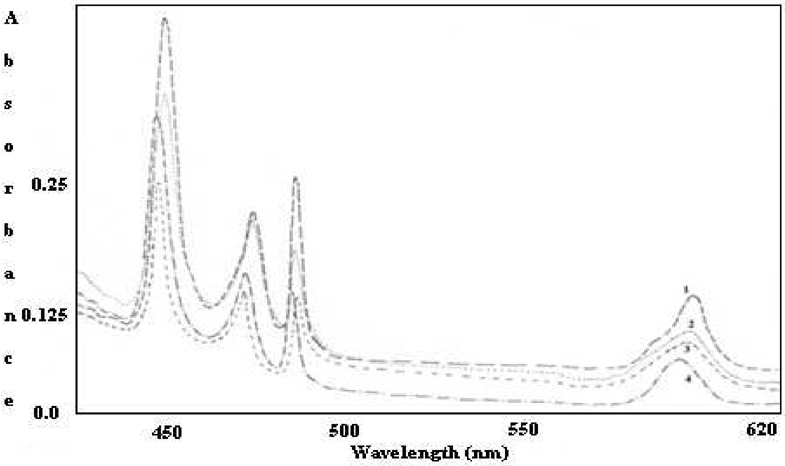

Fig. 1 Comparative absorption spectra of 1)[Pr(hfaa)$_3$(H$_2$O)$_2$]2)[Pr(hfaa)$_3$(an)$_2$] 3)[Pr(hfaa)$_3$(clan)$_2$] and 4)[Pr(hfaa)$_3$(bran)$_2$], complexes in methanol.

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

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

Complexes	Cal. MW	Obs. MW
Pr (hfaa)$_3$(H$_2$O)$_2$	829.40	828.20
Pr (hfaa)$_3$(an)$_2$	1007.40	1005.64
Pr (hfaa)$_3$(clan)$_2$	1066.56	1064.89
Pr (hfaa)$_3$(bran)$_2$	1155.48	1152.67

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

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
Pr $(hfaa)_3(H_2O)_2$	16.46	16.20	20.08	21.71	1.08	1.21	-	-
Pr $(hfaa)_3(an)_2$	13.18	13.98	31.25	32.16	1.58	2.87	2.52	2.77
Pr $(hfaa)_3(clan)_2$	13.62	13.21	30.20	30.37	1.56	2.53	1.40	2.62
Pr $(hfaa)_3(bran)_2$	12.35	12.19	29.02	28.04	2.54	2.34	2.54	2.42

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 119.70 to 170.80 this shows the accuracy of the various energy interaction parameters.

Table 3 Observed and calculated energies (cm $^{-1}$) of Pr(III) complexes in CH_3OH, DMF and CH_3CN solvents.

Complexes and Solvents	$^3P_2$		$^3P_1$		$^3P_0$		$^1D_2$		σ r.m.s.
	Obs	Cal	Obs	Cal	Obs	Cal	Obs	Cal	
CH_3OH									
Pr $(hfaa)_3(H_2O)_2$	22538	22386	21360	21233	20777	20774	16930	17118	128.28
Pr $(hfaa)_3(an)_2$	22532	22391	21362	21243	20771	20733	16946	17121	127.55
Pr $(hfaa)_3(clan)_2$	22525	22378	21359	21127	20768	20768	16923	17012	119.70
$Pr(hfaa)_3(bran)_2$	22543	22387	21369	21132	20776	20766	16913	17089	120.79
DMF									
Pr $(hfaa)_3(H_2O)_2$	22532	22382	21232	21351	20760	20756	16920	17110	133.28
Pr $(hfaa)_3(an)_2$	22539	22379	21237	21362	20752	20754	16936	17113	137.60
Pr $(hfaa)_3(clan)_2$	22543	22368	21230	21310	20749	20746	16868	17121	154.48
$Pr(hfaa)_3(bran)_2$	22512	22364	21215	21321	20756	20739	16876	17132	145.67
CH_3CN									
Pr $(hfaa)_3(H_2O)_2$	22421	22446	21243	21116	20689	20681	16827	17110	170.80
Pr $(hfaa)_3(an)_2$	22523	22373	21342	21221	20755	20751	16931	17116	129.97
Pr $(hfaa)_3(clan)_2$	22514	22332	21331	21198	20731	20733	16901	17085	137.46
$Pr(hfaa)_3(bran)_2$	22512	22341	21336	21189	20743	20723	16911	17076	134.53

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 parameter (δ) for Pr(III) complexes in CH_3OH, DMF and CH_3CN solvents. It shows that the values of nephelauxetic effect (β) in Pr(III) complexes were varies from 0.921 to 0.943 which is less than unity. The value of bonding parameters ($b^{1/2}$) were varies from 0.125 to 0.145and which is positive indicate covalent bonding between Pr(III) and ligand.

S. N. Misra et al [26-30] 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 (bzac, ttfa, acac, etaa, dbm) and nitrogen donor ligand aniline, bromoaniline and chloroaniline. 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, yet these shows high degree of intensification and wide variation in the values of oscillator strength.

Table 4 Computed values of energy interaction parameters Slator 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 CH_3OH, DMF and CH_3CN solvents.

Complexes and Solvent	F_2	F_4	F_6	(ξ_{4f})	β	($b^{1/2}$)	(δ)
CH_3OH							
Pr $(hfaa)_3(H_2O)_2$	311.63	42.98	4.70	672.75	0.923	0.131	3.621
Pr $(hfaa)_3(an)_2$	311.61	4311	4.73	676.32	0.927	0.133	3.523
Pr $(hfaa)_3(clan)_2$	311.70	43.13	4.76	670.63	0.924	0.128	3.339
Pr $(hfaa)_3(bran)_2$	311.74	41.98	4.82	671.71	0.931	0.132	3.453
DMF							
Pr $(hfaa)_3(H_2O)_2$	311.70	43.01	4.70	652.68	0.924	0.128	3.359
Pr $(hfaa)_3(an)_2$	311.69	43.13	4.72	662.43	0.928	0.129	3.358
Pr $(hfaa)_3(clan)_2$	311.78	43.11	4.73	571.39	0.922	0.132	3.535
Pr $(hfaa)_3(bran)_2$	311.86	43.01	4.69	631.37	0.921	0.125	3.457
CH_3CN							
Pr $(hfaa)_3(H_2O)_2$	311.08	42.98	4.70	655.58	0.924	0.131	3.531
Pr $(hfaa)_3(an)_2$	311.53	42.96	4.74	676.41	0.938	0.145	3.521
Pr $(hfaa)_3(clan)_2$	311.43	42.92	4.71	670.68	0.937	0.139	3.524
Pr $(hfaa)_3(bran)_2$	311.33	41.97	4.72	670.88	0.943	0.136	3.621

All these four transitions of Pr (III) $\mathbf{^3H_4 \rightarrow {}^3P_2}$, $\mathbf{^3H_4 \rightarrow {}^3P_1}$,

$\mathbf{^3H_4 \rightarrow {}^3P_0}$ **and** $\mathbf{^3H_4 \rightarrow {}^1D_2}$ are showing substantial variation of oscillator strength which confirms the ligand mediated pseudohypersensitivity of these pseudohypersensitive transitions. Karrakar shows that the shape, energy and oscillator strength of hypersensitive and pseudohypersensitive transition can be correlated with coordination number [31-33].

Table 5 shows experimental and computed values of Oscillator strength the (σ) r. m. s. deviation varies from 0.78 to 2.89.

Table 5 Experimental and computed values of Oscillator strength (Px10^6) in CH3OH, DMF, CH3CN.

Complexes and Solvents	$^3P_2$		$^3P_1$		$^3P_0$		$^1D_2$		σ r.m.s.
	Obs	Cal	Obs	Cal	Obs	Cal	Obs	Cal	
CH_3OH									
Pr $(hfaa)_3(H_2O)_2$	13.17	13.16	4.95	3.71	3.70	3.55	3.92	4.36	0.78
Pr $(hfaa)_3(an)_2$	42.23	43.14	19.29	17.58	16.79	15.45	15.46	15.40	1.78
Pr $(hfaa)_3(clan)_2$	30.38	31.42	11.99	9.83	9.15	8.69	13.14	12.74	1.48
Pr $(hfaa)_3(bran)_2$	31.43	32.23	12.67	10.56	9.89	9.14	12.24	13.21	1.89
DMF									
Pr $(hfaa)_3(H_2O)_2$	26.56	27.44	10.66	9.01	8.11	7.99	10.22	10.12	1.30
Pr $(hfaa)_3(an)_2$	36.36	35.87	13.58	8.34	8.18	8.22	10.94	11.23	2.89
Pr $(hfaa)_3(clan\ )_2$	18.77	17.89	7.63	5.13	5.18	4.97	6.48	6.57	1.48
Pr $(hfaa)_3(bran\ )_2$	19.54	18.99	10.70	9.43	8.67	7.67	7.34	7.12	1.79
CH_3CN									
Pr $(hfaa)_3(H_2O)_2$	10.98	11.44	4.55	3.51	3.22	3.56	3.57	3.88	0.78
Pr $(hfaa)_3(an)_2$	34.67	34.88	11.12	8.98	7.86	7.86	11.24	10.72	1.86
Pr $(hfaa)_3(clan)_2$	32.34	31.55	9.88	6.86	6.74	6.78	9.68	9.45	1.56
$Pr(hfaa)_3(bran)_2$	31.78	30.89	11.10	8.99	7.12	7.67	11.56	10.54	1.98

Table 6 Judd Ofelt parameters (Tx10^{10}) for Pr (III) Complexes in different solvents.

Complexes and Solvent	T_2	T_4	T_6	T_4/T_6
CH_3OH				
Pr $(hfaa)_3(H_2O)_2$	141.60	11.18	41.39	0.27
Pr $(hfaa)_3(an)_2$	642.34	28.52	131.54	0.22
Pr $(hfaa)_3(clan)_2$	863.21	25.74	96.34	0.26
$Pr(hfaa)_3(bran)_2$	776.34	26.31	121.67	0.21
DMF				
Pr $(hfaa)_3(H_2O)_2$	510.60	24.44	83.56	0.29
Pr $(hfaa)_3(an)_2$	621.67	45.58	136.44	0.33
Pr $(hfaa)_3(clan)_2$	199.98	23.87	109.89	0.22
$Pr(hfaa)_3(bran)_2$	221.34	21.98	115.45	0.19
CH_3CN				
Pr $(hfaa)_3(H_2O)_2$	165.55	9.68	31.98	0.30
Pr $(hfaa)_3(an)_2$	141.46	24.89	109.97	0.23
Pr $(hfaa)_3(clan)_2$	145.54	15.84	97.89	0.16
$Pr(hfaa)_3(bran)_2$	167.45	20.11	99.66	0.17

Table 6 shows Judd Ofelt intensity parameters are derived from the observed oscillator strength and T_4/T_6varies from 0.19 to 0.33 this shows the wide variation of oscillator strength of pseudo hypersensitive transitions. The variation of T_2, T_4, T_6 parameters clearly shows that, the high sensitivity towards coordination and position of the substituent as well as the nature of solvent

CONCLUSION

The results of this study reveals that the Pr(III) complexes with hexafluoroacetylacetone and their adducts with aniline, chloroaniline and bromoaniline, complexes are octacoordinated the six oxygen atom satisfying six coordination position and two positions are satisfies with nitrogen from nitrogen donor ligands. Creates high degree of intensification to $^3H_4 \rightarrow {}^3P_2$ pseudo hypersensitive transitions, in different immediate coordination environment around Pr (III), shows a 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 lanthanide metal and ligands. Hence, this could change the extent of interactions between lanthanide and ligands. The interaction between metal and ligands induced substantial changes in the intensities of 4f-4f transition bands and their perturbation was reflected through oscillator strength and Judd Oflet intensity parameters.

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