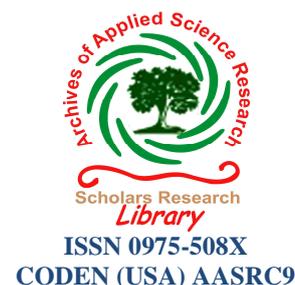




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Studies of Judd Oflet intensity parameters of Pr(III) with hexafluoroacetylacetone and their complexes

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ABSTRACT

Absorption spectroscopy has been used as tool to understand the coordination of mixed ligand complexes of praseodymium (III) $[\text{PrCl}_3(\text{H}_2\text{O})_7]$, with hexafluoroacetylacetone $[\text{C}_5\text{H}_2\text{O}_2\text{F}_6]$ and their complexes with pyridine $[\text{C}_5\text{H}_6\text{N}]$, chloropyridine $[\text{C}_5\text{H}_6\text{NCl}]$ & bromopyridine $[\text{C}_5\text{H}_6\text{NBr}]$. Using comparative absorption spectroscopy involving 4f-4f transitions in various solvents, like methanol (CH_3OH), acetonitrile (CH_3CN) and dimethylformamide $[(\text{CH}_3)_2\text{NCOH}]$. 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 (ζ_{4f}), nephelauxetic ratio (β), bonding parameter ($b^{1/2}$), percent covalency (δ), oscillator strength were calculated and the Judd-Oflet intensity parameters of 4f-4f transition have been computed on computer using partial multiple regression analysis. The intensity of hypersensitive transitions has been used to distinguish between outer and inner sphere coordination, in identifying the coordinating sites of ligands. These parameters oscillator strengths electronic dipole parameter gives information about nature of binding between lanthanide metal and ligands complexes in different solvents.

Key words: Electronic spectra, nephelauxetic effects, hexafluoroacetylacetone

INTRODUCTION

The coordination chemistry of lanthanides has become most significance in last two decades. The magnetic resonance imaging (MRI) technique has become very useful tool of diagnostic medicine. The lanthanides paramagnetic metal complexes used as image enhancement agents. Tremendous upsurge in the lanthanide spectral and magnetic characteristics has resulted because of the fact that these lanthanides ions have useful physical and chemical property and closely resemble with divalent calcium and magnesium in their chemical behavior. 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.[1,2]

The 4f-4f transition spectra are used to assess the effect of the strength of Lanthanide (III) ligand interaction, the geometry of octacoordination ligand structure and chelate-solvent interaction. These characteristic features are exhibited by hypersensitive transition in the absorption spectra of trivalent lanthanide. β -diketones have been receiving much attention because of their bright optical properties in visible region,. lanthanides β -diketones are used as light converting optical materials, light emitting diodes. The lanthanide chelates of ligands possessing oxygen and nitrogen donor atom find application as bactericides and fungicides. In lanthanides the electrons are successively added to inner lying 4f sub shell is filled up, by strongly positive and large sized ion undergoes

shrinkage in ionic size known as lanthanide contraction. This shrinkage influences the coordination chemistry of lanthanide and affects both coordination number and coordination geometry. [3, 4]

S. N. Misra et al [5, 6] studies the solid complexes of Pr(III) and Nd(III) from mononucleotide and mononucleosides were dissolved in 80:20 organic solvents(DMF:H₂O, MeOH:H₂O, MeCN:H₂O) 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 4*f*-4*f* bands as well as the changes in magnitude of Judd Ofelt intensity parameters determined from the observed 4*f*-4*f* transition indicate minor coordination changes around Pr(III) & Nd(III) as a result of slight differences in the binding capabilities of these structurally related ligands. This change depends on the nature of solvents mixture and varying affinities of ligands.

In the present research work, I have prepared the [Pr(hfaa)₃(H₂O)₂] complex and their adducts with structurally related nitrogen donor ligands like pyridine chloropyridine and bromopyridine their absorption spectra of Pr(III) have been interpreted in terms of various parameters namely Salter-Condon (F_k), Lande spin orbit coupling (ξ_{4*f*}), Racah (E^K), nephelauxetic ratio (β), bonding parameter (b^{1/2}), percent covalency (δ), oscillator strength were calculated and Judd Ofelt intensity parameters have been computed on computer using partial multiple regression analysis, which gives information about the nature of bonding between lanthanide metal and ligands 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., pyridine, chloropyridine and bromopyridine were from Sisco Chemical Laboratory. The CH₃OH, DMF and 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 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 [Pr (HFAA)₃(H₂O)₂]

Pr(III) chloride heptahydrate 3.74gm 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 (py)₂]

The [Pr (HFAA)₃ (H₂O)₂] of 4.15gm added into methanolic solution of 0.50 gm of pyridine 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 from methanol, the chloropyridine and bromopyridine 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 Oxinate by using 8-hydroxy quinoline method.

The Coulombic and magnetic interaction between 4*fⁿ* electrons leads to energy level of 4*fⁿ* configuration and these interaction can be expressed in terms of the electronic repulsion parameters Salter-Condon (F₂, F₄, F₆), G, Racah [10, 11] (E¹, E², E³) and spin orbit interaction parameter, Lande spin orbit coupling (ξ_{4*f*}) as a first approximation. The energy E_j of the jth level is given by the following equation,

$$E_j[F_k \xi_{4f}] = E_{0j}[F_k^0 \xi_{4f}] + \sum_{k=2,4,6} \left[\frac{\delta E_j}{\delta F_k} \right] \Delta F_k + \left[\frac{\delta E_j}{\delta \xi_{4f}} \right] \Delta \xi_{4f}$$

Where, E_{0j} is the zero order energy of the j^{th} level is given by Wong [12, 13]. The zero order energy values of E_{0j} , partial derivative $\left[\frac{\delta E_j}{\delta F_k}\right]$ and $\left[\frac{\delta E_j}{\delta \xi^{4f}}\right]$, 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

$$\text{Defined as, } \beta = \frac{F_k^c}{F_k^f}$$

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 [14, 16],

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

S. P. Sinha [17, 18] introduced another parameter, percentage covalency parameter (δ) as, $\delta = \left[\frac{1-\beta}{\beta}\right] \times 100$

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

$$P_{\text{exp}} = 4.6 \times 10^{-9} \epsilon_m(\bar{\nu}) d\bar{\nu}$$

Where, ϵ_m is the molar extinction coefficient of corresponding 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 and most intensification observed in $[\text{Pr}(\text{hfaa})_3(\text{H}_2\text{O})_2]$. The enhancement is more in case of chloropyridine (clpy) indicating a better ligand than bromopyridine (brpy) 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, 28].

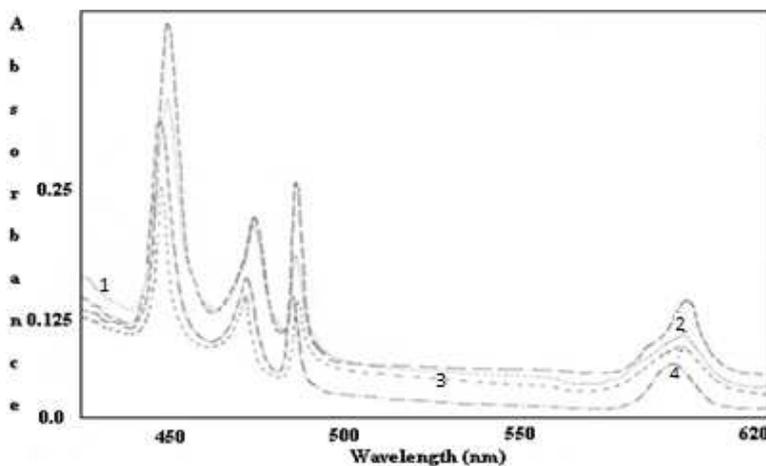


Fig. 1 Comparative absorption spectra of 1) $[\text{Pr}(\text{hfaa})_3(\text{H}_2\text{O})_2]$ 2) $[\text{Pr}(\text{hfaa})_3(\text{py})_2]$ 3) $[\text{Pr}(\text{hfaa})_3(\text{clpy})_2]$ and 4) $[\text{Pr}(\text{hfaa})_3(\text{brpy})_2]$, complexes in methanol.

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

Table 1 shows the obs. and cal. values of M.W. of Pr(III) complexes

Complexes	Cal. MW	Obs. MW
Pr (hfaa) ₃ (H ₂ O) ₂	829.40	828.20
Pr (hfaa) ₃ (py) ₂	921.76	922.45
Pr (hfaa) ₃ (clpy) ₂	1041.40	1040.21
Pr (hfaa) ₃ (brpy) ₂	1127.60	1126.65

Table 2 shows the observed and calculated values of analytical data whereas Table 3 shows experimental and computed values of Pr(III) complexes in CH₃OH, DMF and CH₃CN solvents. The r.m.s. deviation σ are varies from 120.18 to 170.80, clearly shows that accuration of various energy interaction parameters,

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 ₂ O) ₂	16.46	16.20	20.08	21.71	1.08	1.21	-	-
Pr (hfaa) ₃ (py) ₂	14.53	14.98	30.91	30.16	2.58	2.60	2.92	2.90
Pr (hfaa) ₃ (clpy) ₂	13.56	13.45	28.99	28.89	2.22	2.34	2.89	2.66
Pr (hfaa) ₃ (brpy) ₂	12.50	12.51	26.65	26.60	2.04	2.039	2.48	2.52

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	
CH ₃ OH									
Pr (hfaa) ₃ (H ₂ O) ₂	22538	22386	21360	21233	20777	20774	16930	17118	128.28
Pr (hfaa) ₃ (py) ₂	22496	22391	21356	21249	20777	20745	16955	17129	126.47
Pr (hfaa) ₃ (clpy) ₂	22528	22397	21367	21125	20757	20776	16927	17018	120.53
Pr(hfaa) ₃ (brpy) ₂	22547	22387	21375	21215	20778	20766	16917	17095	120.18
DMF									
Pr (hfaa) ₃ (H ₂ O) ₂	22532	22382	21232	21351	20760	20756	16920	17110	133.28
Pr (hfaa) ₃ (py) ₂	22541	22380	21241	21368	20762	20758	16941	17121	138.62
Pr (hfaa) ₃ (clpy) ₂	22544	22364	21232	21311	20751	20748	16862	17120	155.65
Pr(hfaa) ₃ (brpy) ₂	22521	22356	21218	21323	20767	20743	16878	17135	144.75
CH ₃ CN									
Pr (hfaa) ₃ (H ₂ O) ₂	22421	22446	21243	21116	20689	20681	16827	17110	170.80
Pr (hfaa) ₃ (py) ₂	22533	22369	21339	21223	20758	20753	16933	17118	128.91
Pr (hfaa) ₃ (clpy) ₂	22516	22334	21330	21189	20735	20733	16911	17088	136.55
Pr(hfaa) ₃ (brpy) ₂	22514	22343	21338	21186	20745	20725	16914	17072	133.61

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)
CH ₃ OH							
Pr (hfaa) ₃ (H ₂ O) ₂	311.63	42.98	4.70	672.75	0.923	0.131	3.621
Pr (hfaa) ₃ (py) ₂	311.56	43.12	4.74	675.34	0.928	0.133	3.534
Pr (hfaa) ₃ (clpy) ₂	311.72	43.21	4.76	670.53	0.925	0.129	3.328
Pr (hfaa) ₃ (brpy) ₂	311.54	41.97	4.83	671.73	0.932	0.132	3.464
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 (py) ₂	311.71	43.32	4.71	662.54	0.929	0.129	3.366
Pr (hfaa) ₃ (clpy) ₂	311.76	43.12	4.74	571.41	0.923	0.132	3.545
Pr (hfaa) ₃ (brpy) ₂	311.87	43.12	4.69	631.43	0.922	0.126	3.466
CH ₃ CN							
Pr (hfaa) ₃ (H ₂ O) ₂	311.08	42.98	4.70	655.58	0.924	0.131	3.531
Pr (hfaa) ₃ (py) ₂	311.55	42.97	4.75	676.45	0.939	0.146	3.532
Pr (hfaa) ₃ (clpy) ₂	311.53	42.93	4.72	670.69	0.938	0.138	3.533
Pr (hfaa) ₃ (brpy) ₂	311.38	41.98	4.73	670.85	0.941	0.135	3.630

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 covalency parameter (δ) for Pr(III) complexes in CH₃OH, DMF and CH₃CN solvents. It shows that the values of nephelauxetic effect (β) of Pr(III) complexes were less than unity. The value of

bonding parameters ($b^{1/2}$) were varies from 0.126 to 0.146 and which is positive indicate covalent bonding between Pr (III) metal and ligands.

S. N. 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 Pr(III) complexes with β -diketones (bzac, acac, tfa, dbm) and nitrogen donor ligand aniline, bromo aniline 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 high intensification and wide variation of oscillator strength.

All these four transitions of Pr (III) $^3H_4 \rightarrow ^3P_2$, $^3H_4 \rightarrow ^3P_1$, $^3H_4 \rightarrow ^3P_0$ and $^3H_4 \rightarrow ^1D_2$ are showing substantial variation of oscillator strength which conform the ligand mediated pseudohypersensitivity of these pseudohypersensitive transitions. These transitions also show variation in intensification and wavelength which is observed by values of energies at various transitions. Karraker showed that the symmetry coordination number of lanthanide ion could be predicted from the shape, intensity and wavelength of hypersensitive transition in visible region. The energy and oscillator strength of hypersensitive and pseudohypersensitive transition can be correlated with coordination number [34-36].

Table no 5 shows experimental and computed values of Oscillator strength the σ r.m.s deviation varies from 0.78 to 2.86, of pseudo hypersensitive transitions. The variation of T_2, T_4, T_6 parameters clearly shows the high sensitivity towards coordination and symmetry changes as a result of the nature and position of the substituent as well as the nature of solvent.

Table 5 Experimental and computed values of Oscillator strength ($P \times 10^6$) 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	
CH ₃ OH									
Pr (hfaa) ₃ (H ₂ O) ₂	13.17	13.16	4.95	3.71	3.70	3.55	3.92	4.36	0.78
Pr (hfaa) ₃ (py) ₂	42.32	43.22	19.29	17.58	16.78	15.49	15.49	15.37	1.79
Pr (hfaa) ₃ (clpy) ₂	30.37	31.45	11.94	9.82	9.10	8.87	13.03	12.59	1.58
Pr (hfaa) ₃ (brpy) ₂	32.53	32.51	10.98	9.73	7.34	6.73	9.43	9.33	1.68
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 (py) ₂	36.37	35.87	13.54	8.33	8.19	8.20	10.94	11.22	2.86
Pr (hfaa) ₃ (clpy) ₂	18.73	17.85	7.64	5.19	4.98	4.68	6.47	6.59	1.44
Pr (hfaa) ₃ (brpy) ₂	26.94	26.93	10.55	6.21	6.01	6.07	9.031	9.21	2.12
CH ₃ CN									
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 (py) ₂	34.68	34.85	11.11	8.99	7.85	7.87	11.24	10.79	1.88
Pr (hfaa) ₃ (clpy) ₂	32.42	31.45	9.82	6.85	6.78	6.77	9.68	9.46	1.56
Pr (hfaa) ₃ (brpy) ₂	10.56	10.54	4.34	3.45	3.31	3.31	3.86	3.87	0.82

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	141.62	11.18	41.40	0.27
Pr (hfaa) ₃ (py) ₂	640.32	28.89	139.80	0.25
Pr (hfaa) ₃ (clpy) ₂	861.12	26.86	96.34	0.39
Pr (hfaa) ₃ (brpy) ₂	643.65	27.85	112.48	0.26
DMF				
Pr (hfaa) ₃ (H ₂ O) ₂	510.60	24.25	83.36	0.29
Pr (hfaa) ₃ (py) ₂	622.73	45.66	131.56	0.38
Pr (hfaa) ₃ (clpy) ₂	198.89	23.96	109.66	0.29
Pr (hfaa) ₃ (brpy) ₂	325.51	51.87	211.38	0.24
CH ₃ CN				
Pr (hfaa) ₃ (H ₂ O) ₂	165.55	9.68	31.98	0.30
Pr (hfaa) ₃ (py) ₂	142.19	24.96	109.78	0.22
Pr (hfaa) ₃ (clpy) ₂	146.69	15.84	97.89	0.24
Pr (hfaa) ₃ (brpy) ₂	155.45	19.43	98.52	0.19

Table no 6 shows Judd Ofelt intensity parameters are derived from the observed oscillator strength and T_4/T_6 varies between 0.19 to 0.35 this shows the wide variation of oscillator strength.

CONCLUSION

The Pr(III) complexes with hexafluoroacetylacetone and their adducts with nitrogen donor ligands like pyridine, chloropyridine and bromopyridine shows high degree of intensification to pseudohypersensitive transitions, in different immediate coordination environment around Pr(III). 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. In our studies the intensity of ${}^3\text{H}_4 \rightarrow {}^3\text{P}_2$ is higher than ${}^3\text{H}_4 \rightarrow {}^1\text{D}_2$, ${}^3\text{H}_4 \rightarrow {}^3\text{P}_1$, ${}^3\text{H}_4 \rightarrow {}^3\text{P}_0$ transitions. The comparative absorption spectra of Pr(III) clearly show that all the complexes consist of identical chromophore LnO_6N_2 and six oxygen atoms from β -diketone from a strong bond to lanthanide metal, while two lanthanide nitrogen are much weaker.

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