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Comparative absorption spectral studies of Pr (III) with thenoyltrifluoroacetone and their adducts with o-phenanthroline and bipyridyl

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ABSTRACT

The interaction of Pr (III) with thenoyltrifluoroacetone [C₈H₅F₃O₂S] has been explored in presence of o-phenanthroline [C₁₂H₈N₂] and bipyridyl [C₁₀H₈N₂]. Using comparative absorption spectroscopy involving 4f-4f transition in various solvents like methanol (CH₃OH), acetonitrile (CH₃CN) and dimethylformamide [(CH₃)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 were calculated and intensity parameters have been computed on computer using partial multiple regression analysis.

Key words: Electronic spectra, nephelauxetic effects,) Thenoyltrifluoroacetone

INTRODUCTION

A great deals of work has been carried out on electronic spectra of praseodymium and neodymium complexes, especially on oxygen and nitrogen donor ligands in order to understand, the factor responsible for the presence of a large number of narrow weak absorption bands in visible and near IR region [1,2]. 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. In such cases it is quite useful to substitute these metal ions by paramagnetic ions like lanthanides with similar preference for binding sites of organic moieties and showing somewhat similar biological activity. Lanthanides are used as substitutes for Ca(II) because they possess certain advantages like exhibiting electronic transitions in the visible region [3 ,7].

In the present research work, The preparation of [Pr(ttfa)₃(H₂O)₂] complex and their adducts with structurally related nitrogen donor ligands, like o-phenanthroline and bipyridyl their 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, The intensity parameters have been computed on computer using partial multiple regression analysis, which gives information about the nature of complexes.

MATERIALS AND METHODS

Pr(III) chloride heptahydrate of 99.9% purity from M/s Indian Rare Earths Ltd., Thenoyltrifluoroacetone of AR grade from Aldrich USA, nitrogen donor ligands viz., o-phenanthroline and bipyridyl 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 380-620 nm, in the concentration of Pr(III) complexes in 10⁻² M.

Synthesis of [Pr (ttfa)₃(H₂O)₂]

Pr(III) chloride heptahydrate 3.734 gm was dissolved in distilled water, the methanolic solution of thenoyltrifluoroacetone 6.69 gm 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(ttfa)₃ (oph)]

The [Pr (ttfa)₃ (H₂O)₂] of 4.612 gm added into methanolic solution of 0.988 gm of 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. 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 4fⁿ electrons leads to energy level of 4fⁿ configuration and these interaction can be expressed in terms of the electronic repulsion parameters Salter-Condon (F₂, F₄, F₆), G. Racah [8,9](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,

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

Where, E_{oj} is the zero order energy of the jth level is given by Wong [10,11]. The values of zero order energy E_{oj}, partial derivative of Pr (III) (δE_j/δF_k) and (δE_j/δξ_{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 [12,16].

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

S. P. Sinha [17, 18] 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,

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

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 $[\text{Pr}(\text{tfa})_3(\text{H}_2\text{O})_2]$, the enhancement is more in case bipyridyl (bipy) indicating a better ligand than o-phenanthroline (oph) when recorded in methanol.

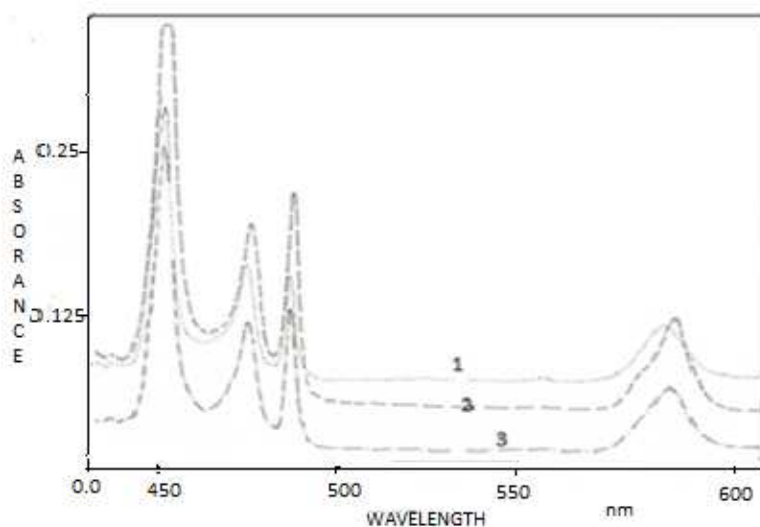


Fig. 1 Comparative absorption spectra of 1) $[\text{Pr}(\text{tfa})_3(\text{H}_2\text{O})_2]$ 2) $[\text{Pr}(\text{tfa})_3(\text{Bipy})]$ and 3) $[\text{Pr}(\text{tfa})_3(\text{oph})]$ complexes in methanol.

The order of intensity for transitions ${}^3\text{H}_4 \rightarrow {}^3\text{P}_2 > {}^3\text{H}_4 \rightarrow {}^3\text{P}_1 > {}^3\text{H}_4 \rightarrow {}^3\text{P}_0 > {}^3\text{H}_4 \rightarrow {}^1\text{D}_2$. The bipyridyl and o-phenanthroline have been found to be monomeric and an octacoordinated environment has been proposed around Pr (III) metal in these complexes again. The significant increase in the intensity of hypersensitive transition can be attributed to decrease in the coordination geometry from nona coordinated haloacetates to octacoordinated bipyridyl and o-phenanthroline complexes [19, 21].

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
$\text{Pr}(\text{tfa})_3(\text{H}_2\text{O})_2$	911.27	909.58
$\text{Pr}(\text{tfa})_3(\text{oph})$	1073.18	1072.10
$\text{Pr}(\text{tfa})_3(\text{bipy})$	1031.27	1030.22

Table 2 shows the observed and calculated values of analytical data for the complexes.

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	% metal		% Carbon		% Hydrogen		% Nitrogen	
	Obs	Cal	Obs	Cal	Obs	Cal	Obs	Cal
$\text{Pr}(\text{tfa})_3(\text{H}_2\text{O})_2$	17.10	15.80	34.14	32.81	2.24	2.08	-	-
$\text{Pr}(\text{tfa})_3(\text{oph})$	14.32	12.86	42.95	41.65	2.28	2.09	2.78	2.60
$\text{Pr}(\text{tfa})_3(\text{bipy})$	14.96	12.98	42.33	41.38	2.38	2.10	2.90	2.20

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 100.20 to 162.26 this shows the 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 (ttfa) ₃ (H ₂ O) ₂	22482	22303	21312	21163	20746	20743	16857	17068	155.97
Pr (ttfa) ₃ (oph)	22451	22276	21285	21147	20733	20731	16866	17059	148.51
Pr (ttfa) ₃ (bipy)	22466	22268	21303	21220	20742	20740	16854	17055	142.51
DMF									
Pr (ttfa) ₃ (H ₂ O) ₂	22441	22264	21272	21113	20712	20710	16832	17022	152.24
Pr (ttfa) ₃ (oph)	22418	22318	21253	21150	20699	20729	16815	17075	100.20
Pr (ttfa) ₃ (bipy)	22421	22230	21258	21151	20669	20708	16815	17033	120.30
CH₃CN									
Pr (ttfa) ₃ (H ₂ O) ₂	22527	22333	21344	21188	20755	20734	16949	17084	141.39
Pr (ttfa) ₃ (oph)	22527	22332	21349	21186	20759	20751	16928	17081	148.15
Pr (ttfa) ₃ (bipy)	22466	22370	21299	21284	20733	20770	16846	17006	162.26

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) in Pr (III) complexes were Varies from 0.921 to 0.939, which is less than unity. The value of bonding parameters (b^{1/2}) were varies from 0.123to 0.131 and which is positive indicate covalent bonding between Pr(III) and ligand.

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 CH₃OH, DMF and CH₃CN solvents.

Complexes and Solvent	F ₂	F ₄	F ₆	(ξ_{4f})	β	(b ^{1/2})	(δ)
CH₃OH							
Pr (ttfa) ₃ (H ₂ O) ₂	311.73	43.02	4.71	656.69	0.921	0.128	3.156
Pr (ttfa) ₃ (oph)	311.56	43.01	4.71	654.30	0.932	0.123	3.145
Pr (ttfa) ₃ (bipy)	311.52	43.00	4.71	653.87	0.924	0.123	3.145
DMF							
Pr (ttfa) ₃ (H ₂ O) ₂	311.32	42.96	4.70	654.31	0.939	0.123	3.146
Pr (ttfa) ₃ (oph)	311.59	53.01	4.71	661.90	0.936	0.123	3.56
Pr (ttfa) ₃ (bipy)	311.55	43.01	4.71	661.56	0.936	0.126	3.327
CH₃CN							
Pr (ttfa) ₃ (H ₂ O) ₂	311.32	42.96	4.70	668.12	0.933	0.131	3.562
Pr (ttfa) ₃ (oph)	311.49	43.00	4.71	665.49	0.925	0.128	3.530
Pr (ttfa) ₃ (bipy)	311.58	43.04	4.71	669.67	0.935	0.127	3.460

S. N. Misra et al [22,25] 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, dbm) and nitrogen donor ligands aniline, bromoaniline and chloroaniline. These transitions ³H₄→³P₂, ³H₄→³P₁, ³H₄→³P₀, ³H₄→¹D₂ are not hypersensitive in orthodox sense, yet these high intensification and wide variation of oscillator strength.

All these four transitions of Pr (III) ³H₄→³P₂, ³H₄→³P₁,

³H₄→³P₀ and ³H₄→¹D₂ are showing substantial variation of oscillator strength which conform the ligand mediated pseudohypersensitivity of these pseudohypersensitive transitions. Karraker shows that the shape, energy and oscillator strength of hypersensitive and pseudohypersensitive transition can be correlated with coordination number [26, 27].

Table 5 shows 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	
CH₃OH									
Pr (ttfa) ₃ (H ₂ O) ₂	19.61	19.61	6.680	3.867	3.820	3.810	7.328	6.000	1.550
Pr (ttfa) ₃ (oph)	33.38	33.38	10.64	7.764	7.659	7.655	12.80	12.80	1.440
Pr (ttfa) ₃ (bipy)	21.18	21.18	8.165	5.389	5.313	5.312	6.741	6.742	1.380
DMF									
Pr (ttfa) ₃ (H ₂ O) ₂	32.89	32.89	8.449	6.906	6.807	6.807	10.74	10.86	0.770
Pr (ttfa) ₃ (oph)	37.72	36.80	11.76	9.320	9.198	9.188	12.29	12.29	1.310
Pr (ttfa) ₃ (bipy)	32.96	32.93	10.76	8.679	8.545	8.543	7.894	7.890	1.040
CH₃CN									
Pr (ttfa) ₃ (H ₂ O) ₂	15.52	15.52	4.618	2.638	2.610	2.593	4.628	5.501	0.941
Pr (ttfa) ₃ (oph)	28.99	27.59	8.760	8.643	6.145	6.145	9.290	9.289	1.440
Pr (ttfa) ₃ (bipy)	26.54	26.53	7.674	5.417	5.340	5.338	7.374	7.375	1.128

Table 5 shows experimental and computed values of Oscillator strength the σ r m s deviation varies from 0.770 to 1.550.

Table 6 shows Judd Ofelt intensity parameters are derived from the observed oscillator strength and T_4/T_6 varies from 0.147 to 0.234. This shows the wide variation of oscillator strength 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 6 shows 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
CH₃OH				
Pr (ttfa) ₃ (H ₂ O) ₂	69.23	10.63	61.52	0.172
Pr (ttfa) ₃ (oph)	698.8	21.37	104.0	0.205
Pr (ttfa) ₃ (bipy)	128.8	14.82	65.64	0.225
DMF				
Pr (ttfa) ₃ (H ₂ O) ₂	296.2	19.02	103.1	0.184
Pr (ttfa) ₃ (oph)	358.5	25.69	114.3	0.224
Pr (ttfa) ₃ (bipy)	-391.5	23.92	102.0	0.234
CH₃CN				
Pr (ttfa) ₃ (H ₂ O) ₂	223.0	7.23	48.92	0.147
Pr (ttfa) ₃ (oph)	190.38	17.13	90.41	0.189
Pr (ttfa) ₃ (bipy)	-77.3	14.90	83.18	0.179

CONCLUSION

The results of this study reveals that the Pr(III) complexes with thenoyltrifluoroacetone and their adducts with nitrogen donor ligands like o-phenanthroline and bipyridyl complexes shows high degree of intensification to $^3H_4 \rightarrow ^3P_2$ pseudohypersensitive transitions, in different immediate coordination environment around Pr(III) as a result 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 lanthanide metal and ligands. Hence, this could change the extent of interactions between lanthanide and ligands.

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