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Absorption Spectral Studies of Pr (III) with Acetyl Acetone and their Complexes with Nitrogen Donor Ligands

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ABSTRACT

In the present research work, the absorption difference and comparative absorption spectroscopic studies involving 4f-4f transitions of Pr(III) with acetyl acetone $[\text{Pr}(\text{acac})_3(\text{H}_2\text{O})_2]$ and their adducts with structurally related ligands viz., aniline (an), bromoaniline (Bran) and chloroaniline (Clan) complexes in different solvents like methanol (CH_3OH), acetonitrile (CH_3CN) and dimethyl formamide (DMF) have been carried out. The intra 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) were calculated and intensity parameters have been computed on computer using partial multiple regression analysis. The obtained results are used to determine the probable geometry of complexes in solution and nature of the bond between Pr (III) ion and ligands, the inner sphere coordination of 4f-4f transition.
Key words: Electronic spectra, nephelauxetic effects, acetyl acetone

INTRODUCTION

During the past three decades, new fields of applications have been found for the lanthanide coordination compounds in solutions viz., in constructions of liquid laser in studying transuranic element, as unique spectral models in examining structure and function [1-3]. 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.

S. N. 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, 7].

In the present research work, we have prepared the $[\text{Pr}(\text{acac})_3(\text{H}_2\text{O})_2]$ complexes and their adducts with structurally related nitrogen donor ligands like aniline, bromoaniline and chloroaniline their absorption spectra of Pr(III) have been interpreted in terms of various parameters namely Salter-Condon (F_K), Lande spin orbit coupling (ζ_{4f}), Racah (E^K), nephelauxetic ratio (β), bonding parameter ($b^{1/2}$) and percent covalency (δ) were calculated and intensity

parameters have been computed on computer using partial multiple regression analysis, which gives information about the nature of complexation.

MATERIALS AND METHODS

Pr(III) chloride heptahydrate of 99.9% purity from M/s Indian Rare Earths Ltd., acetyl acetone of AR grade from Qualigens, nitrogen donor ligands viz., aniline, bromoaniline and chloroaniline 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 double 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 M.

Synthesis of [Pr (acac)₃ (H₂O)₂]

Pr(III) chloride heptahydrate 3.734 gm was dissolved in water, the methanolic solution of acetyl acetone 3.2 gm was added very slowly with constant stirring with resulted in isolation of yellow crystalline solid. After neutralizing the contents with ammonia the product was filtered and washed thoroughly with methanol and was purified by recrystallization with methanol.

Synthesis of [Pr (acac)₃ (py)₂]

The [Pr (acac)₃ (H₂O)₂] of 4.77 gm added into methanolic solution of 1.96 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 micro crystalline solid was obtained and they were recrystallized from methanol, the bromoaniline and chloroaniline 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,

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

Where, E_{0j} is the Zero order energy of the jth level is given by E. Y. Wong [10, 11]. The values of E_{0j}, partial derivative (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

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

curve analysis using the following relationship,

Where C_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 $[\text{Pr}(\text{acac})_3(\text{H}_2\text{O})_2]$ the enhancement is more in case chloroaniline (Clan) indicating a better ligand than bromoaniline (Bran) 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].

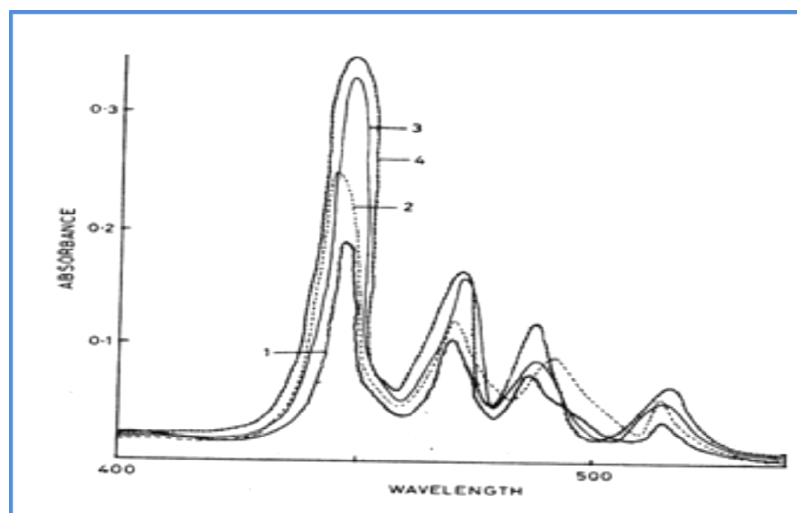


Fig. 1 Comparative absorption spectra of 1) $[\text{Pr}(\text{acac})_3(\text{an})_2]$ 2) $[\text{Pr}(\text{acac})_3(\text{Bran})_2]$, 3) $[\text{Pr}(\text{acac})_3(\text{H}_2\text{O})_2]$ and 4) $[\text{Pr}(\text{acac})_3(\text{Clan})_2]$ complexes in methanol.

Table 1 shows the observed and calculated values of molecular weight of Pr (III) complexes. This indicates that the observed and calculated values of molecular weight are nearly same; it means that the complexation is proper.

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

Complexes	Cal. MW	Obs. MW
$\text{Pr}(\text{acac})_3(\text{H}_2\text{O})_2$	477.36	474.18
$\text{Pr}(\text{acac})_3(\text{an})_2$	539.20	534.10
$\text{Pr}(\text{acac})_3(\text{Bran})_2$	617.55	616.16
$\text{Pr}(\text{acac})_3(\text{Clan})_2$	576.90	570.16

Table 2 shows the observed and calculated values of analytical data whereas 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 107.86 to 173.73 showing that accuracy of the various energy interaction parameters.

Table 2 Observed and calculated values of analytical data Pr (III) complexes.

Complexes	% metal		%Carbon		%Hydrogen		% Nitrogen	
	Obs	Cal	Obs	Cal	Obs	Cal	Obs	Cal
$\text{Pr}(\text{acac})_3(\text{H}_2\text{O})_2$	29.52	29.68	36.71	37.80	4.88	5.05	-	-
$\text{Pr}(\text{acac})_3(\text{an})_2$	24.11	26.25	60.44	59.66	6.74	6.70	5.14	5.21
$\text{Pr}(\text{acac})_3(\text{Bran})_2$	24.61	24.51	55.66	56.60	6.11	6.29	4.89	4.91
$\text{Pr}(\text{acac})_3(\text{Clan})_2$	21.77	22.76	51.88	52.63	5.77	5.85	4.46	4.54

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 (acac) ₃ (H ₂ O) ₂	22489	22424	21311	21215	20736	20660	16893	17117	131.30
Pr (acac) ₃ (an) ₂	22435	22245	21258	21162	20722	20734	16878	17044	135.20
Pr (acac) ₃ (Bran) ₂	22446	22287	21304	21156	20741	20741	16835	16959	133.98
Pr (acac) ₃ (Clan) ₂	22452	22289	21281	21156	20727	20729	16821	17040	156.18
DMF									
Pr (acac) ₃ (H ₂ O) ₂	22432	22557	21254	21128	20690	20690	16836	17107	173.73
Pr (acac) ₃ (an) ₂	22528	22390	21361	21238	20775	20735	16945	17117	129.05
Pr (acac) ₃ (Bran) ₂	22542	22394	21357	21247	20712	20770	16949	17115	107.86
Pr (acac) ₃ (Clan) ₂	22532	22383	21354	21231	20771	20767	16921	1712	133.98
CH₃CN									
Pr (acac) ₃ (H ₂ O) ₂	22914	22392	21363	21261	20776	20774	16932	17118	128.18
Pr (acac) ₃ (an) ₂	22524	22319	21350	21221	20754	20755	16930	17106	129.95
Pr (acac) ₃ (Bran) ₂	22512	22352	21331	21201	20746	20741	16903	17108	145.85
Pr (acac) ₃ (Clan) ₂	22502	22342	21321	21191	20741	20740	16901	17086	138.41

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 vary from 0.921 to 0.944 which is less than unity. The value of bonding parameters (b^{1/2}) were varies from 0.128 to 0.168 and which is positive indicate covalent bonding between Pr (III) and ligand.

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 (acac) ₃ (H ₂ O) ₂	308.85	42.68	4.66	719.64	0.944	0.166	5.890
Pr (acac) ₃ (an) ₂	311.80	43.04	4.69	651.28	0.929	0.129	3.428
Pr (acac) ₃ (Bran) ₂	311.88	43.06	4.71	658.45	0.921	0.128	3.799
Pr (acac) ₃ (Clan) ₂	311.71	43.03	4.70	653.68	0.925	0.128	3.359
DMF							
Pr (acac) ₃ (H ₂ O) ₂	308.10	42.54	4.65	719.35	0.94	0.168	6.032
Pr (acac) ₃ (an) ₂	311.70	43.03	4.70	676.74	0.928	0.132	3.519
Pr (acac) ₃ (Bran) ₂	311.53	43.00	4.68	678.25	0.925	0.131	3.551
Pr (acac) ₃ (Clan) ₂	311.66	43.05	4.77	689.30	0.924	0.134	3.561
CH₃CN							
Pr (acac) ₃ (H ₂ O) ₂	308.17	42.53	4.65	720.06	0.943	0.166	5.953
Pr (acac) ₃ (an) ₂	311.34	42.95	4.71	671.51	0.935	0.136	3.521
Pr (acac) ₃ (Bran) ₂	311.36	42.98	4.73	671.53	0.936	0.136	3.521
Pr (acac) ₃ (Clan) ₂	311.37	42.99	4.78	672.73	0.931	0.137	3.524

S. N. Misra et al [21-24] 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-diketone and donor ligand aniline, bromoaniline and chloroaniline. Their ³H₄ → ³P₂, ³H₄ → ³P₁, ³H₄ → ³P₀, ³H₄ → ¹D₂ transitions are not hypersensitive in orthodox sense, yet these high intensification and wide variation of oscillator strength.

³H₄ → ³P₂, ³H₄ → ³P₁, ³H₄ → ³P₀ and ³H₄ → ¹D₂. All these four transitions are showing substantial variation of oscillator strength which conform the ligand mediated pseudohypersensitivity of these pseudohypersensitive transitions. D. G. Karaker shows that the shape, energy and oscillator strength of hypersensitive and pseudohypersensitive transition can be correlated with coordination number [25, 26].

CONCLUSION

The results of this study reveals that the Pr (III) complexes with acetyl acetone and their adducts with nitrogen donor ligands like aniline, bromoaniline and chloroaniline complexes creates high degree of intensification to different pseudohypersensitive transitions in different immediate coordination environment. It is quite apparent the

stereochemistry possible for octacoordination and are interconvertible. The change in the stereochemistry could change the distance between lanthanide and ligands. Hence, this could change the extent of interactions between lanthanide and ligands.

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