Absorption spectral studies of Pr (III) with Acetyl acetone and their complexes with pyridine, bromopyridine and chloropyridine

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ABSTRACT

In the present investigation, the absorption difference and comparative absorption spectroscopic studies involving 4f-4f transitions of Pr(III) with acetyl acetone [Pr(acac)₃(H₂O)₂] and their adducts with structurally related ligands like pyridine (py), bromopyridine (Brpy) and chloropyridine (Clpy) complexes in different solvents like CH₃OH, CH₃CN and 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 (ξ_{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 difference in the energy parameters with respect to ligands atoms and with various solvents reveals that the chemical environment around the Pr(III) ion has great influence on 4f-4f transition and any change in the environment results in modification of the absorption spectra.

Key words: Electronic spectra, nephelauxetic effects, acetyl acetone.
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INTRODUCTION

Analysis of intra $4f$-$4f$ transition has been used successfully in elucidating the structure of lanthanide complexes with ligands [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. 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 transuanic element, as unique spectral models in examining structure and function [2, 3, 4].

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S. N. Misra et al [4-6] studies the solid complexes of Pr(III) and Nd(III) from mononucleotide and mononucleosides were dissolved in organic solvents and their spectra were recorded. The results suggest that these complexes, when dissolved in the solvents, retained their nonacoordinationated stereochemistry possessed 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 determined from observed $4f$-$4f$ transitions indicates minor coordination changes around Pr(III) and Nd(III) as a result of slight differences in binding capabilities of these structurally related ligands. This change depends on the nature of solvents mixture and varying affinities of ligands.

In the present study, we have prepared the $[Pr(acac)_3(H_2O)_2]$ complexes and their adducts with structurally related nitrogen donor ligands like pyridine, bromopyridine and chloropyridine 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 ($b^{1/2}$) 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., pyridine (py), bromopyridine (Brpy) and chloropyridine (Clpy) 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 double 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 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)$_3$ (H$_2$O)$_2$]
Pr(III) chloride heptahydrate 3.734 gm was dissolved in water, the methanolic solution of acetyl acetone 6.79 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)$_3$ (H$_2$O)$_2$] of 4.72 gm added into methanolic solution of 1.58 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 micro crystalline solid obtained by purified by recrystallization form methanol, the bromopyridine (Brpy) and chloropyridine (Clpy) 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

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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 $4f^n$ 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 [7,8] (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 jth 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 jth level is given by Wong [9, 10]. 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,

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

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 [11-15],

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

S. P. Sinha [16, 17] 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,

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

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

RESULTS AND DISCUSSION

The figure 1 shows comparative absorption spectra of Pr(III) complexes in methanol. There is marginal red shift of $4f$-$4f$ transition bonds in [Pr (acac)$_3$ (H$_2$O)$_2$] the enhancement is more in case chloropyridine (Clpy) indicating a better ligand than bromopyridine (Brpy) when recorded in methanol. The intensity of $^3H_4 \rightarrow {}^3P_2 > {}^3H_4 \rightarrow {}^3P_1 > {}^3H_4 \rightarrow {}^3P_0 > {}^3H_4 \rightarrow {}^1D_2$ [18].

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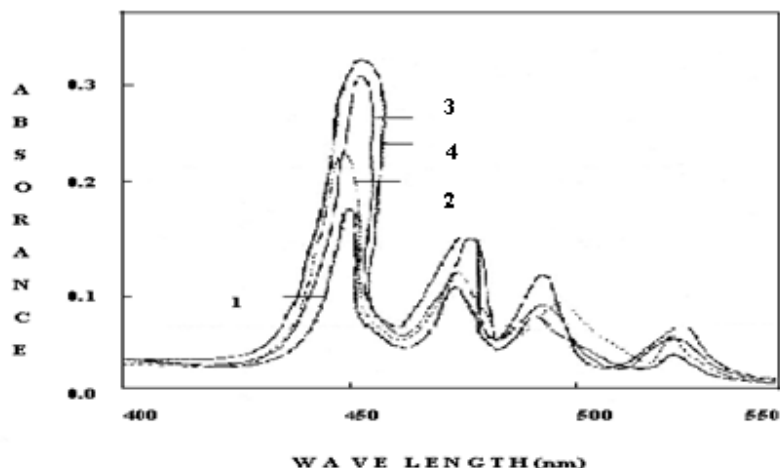
**Fig. 1 Comparative absorption spectra of 1) [Pr(acac)$_3$(py)$_2$] 2)[Pr(acac)$_3$(Brpy)$_2$], 3)[Pr(acac)$_3$(H$_2$O)$_2$] and 4]
[Pr(acac)$_3$(Clpy)$_2$] complexes in methanol.**

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.

Compound	Cal. MW	Obs. MW
Pr (acac)$_3$(H$_2$O)$_2$	477.26	474.18
Pr (acac)$_3$(py)$_2$	601.51	599.98
Pr (acac)$_3$(Brpy)$_2$	756.60	753.15
Pr (acac)$_3$(Clpy)$_2$	667.97	665.19

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$_3$OH, DMF and CH$_3$CN solvents. The r.m.s. deviation σ are varies from 107.09 to 173.73 showing that accuration of the various energy interaction parameters.

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

Compound	% metal		%Carbon		% Hydrogen		% Nitrogen	
	Obs	Cal	Obs	Cal	Obs	Cal	Obs	Cal
Pr (acac)$_3$(H$_2$O)$_2$	29.52	29.68	36.71	37.80	4.88	5.05	-	-
Pr (acac)$_3$(Py)$_2$	22.48	2348	49.66	50.11	5.44	5.60	4.51	4.60
Pr(acac)$_3$(Brpy)$_2$	18.55	18.62	39.60	39.60	4.44	4.25	2.88	2.16
Pr(acac)$_3$(Clpy)$_2$	21.11	21.21	44.39	44.93	4.80	4.79	4.01	4.11

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$_3$OH, DMF and CH$_3$CN solvents. It shows that the values of nephelauxetic effect (β) in Pr(III) complexes were vary from 0.9421 to 0.9470 which is less than unity. The value of bonding parameters (b$^{1/2}$) were varies from 0.1662 to 0.1689 and which is positive indicate covalent bonding between Pr(III) and ligand.

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Table 3 Observed and calculated energies (cm $^{-1}$) of Pr(III) complexes in CH$_3$OH, DMF and CH$_3$CN 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$_3$OH									
Pr (acac)$_3$(H$_2$O)$_2$	22489	22424	21311	21215	20736	20660	16893	17117	131.30
Pr (acac)$_3$(py)$_2$	22536	22375	21361	21225	20772	20770	16937	17111	136.90
Pr (acac)$_3$(Brpy)$_2$	22537	22407	21357	21237	20778	20768	16937	17120	127.09
Pr (acac)$_3$(Clpy)$_2$	22508	22390	21316	21176	21028	20669	16837	17091	137.38
DMF									
Pr (acac)$_3$(H$_2$O)$_2$	22432	22557	21254	21128	20690	20690	16836	17107	173.73
Pr (acac)$_3$(py)$_2$	22524	22381	21350	21224	20756	20752	16930	17108	129.80
Pr (acac)$_3$(Brpy)$_2$	22504	22316	21328	21173	20744	20737	16894	17071	149.50
Pr (acac)$_3$(Clpy)$_2$	22498	22328	21318	21181	20740	20738	16882	17076	141.36
CH$_3$CN									
Pr (acac)$_3$(H$_2$O)$_2$	22914	22392	21363	21261	20776	20774	16932	17118	128.18
Pr (acac)$_3$(py)$_2$	22531	22390	21361	21238	20778	20736	16946	17119	130.60
Pr (acac)$_3$(Brpy)$_2$	22528	22375	21351	21122	20770	20770	16917	17001	109.70
Pr (acac)$_3$(Clpy)$_2$	22522	22370	21354	21232	20767	20755	16974	17156	107.81

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$_3$OH, DMF and CH$_3$CN solvents.

Complexes and Solvent	F$_2$	F$_4$	F$_6$	(ξ$_{4f}$)	β	(b$^{1/2}$)	(δ)
CH$_3$OH							
Pr (acac)$_3$(H$_2$O)$_2$	308.8561	42.6863	4.6686	719.6470	0.9445	0.1668	5.8904
Pr (acac)$_3$(py)$_2$	308.8670	42.6278	4.6637	719.8653	0.9445	0.1666	5.8710
Pr (acac)$_3$(Brpy)$_2$	308.8670	42.8998	4.6656	721.1446	0.9448	0.1668	5.8220
Pr (acac)$_3$(Clpy)$_2$	308.8800	42.4890	4.6660	720.1447	0.9446	0.1662	5.8220
DMF							
Pr (acac)$_3$(H$_2$O)$_2$	308.1064	42.5441	4.6534	719.3510	0.9421	0.1688	6.0329
Pr (acac)$_3$(py)$_2$	308.1108	42.5452	4.6653	778.9200	0.9430	0.1689	6.0495
Pr (acac)$_3$(Brpy)$_2$	308.2128	42.5577	4.6654	718.9476	0.9430	0.1689	6.0494
Pr (acac)$_3$(Clpy)$_2$	308.1735	42.5392	4.6519	719.2825	0.9431	0.1688	6.0447
CH$_3$CN							
Pr (acac)$_3$(H$_2$O)$_2$	308.1788	42.5304	4.6500	720.0623	0.9431	0.1666	5.9530
Pr (acac)$_3$(py)$_2$	308.2608	42.5404	4.6530	720.9980	0.9430	0.1667	5.8818
Pr (acac)$_3$(Brpy)$_2$	308.3394	42.5654	4.6652	721.3840	0.9470	0.1662	5.8818
Pr (acac)$_3$(Clpy)$_2$	308.2880	42.4206	4.6400	721.3334	0.9430	0.1684	6.0192

S. N. Misra et al [19-21] 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   pyridine(py), bromopyridine(Brpy) and chloropyridine(Clpy). 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.

$^3H_4 \rightarrow ^3P_2$, $^3H_4 \rightarrow ^3P_1$, $^3H_4 \rightarrow ^3P_0$ and $^3H_4 \rightarrow ^1D_2$.

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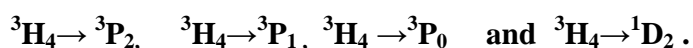
All these four transitions are showing substantial variation of oscillator strength which conform the ligand mediated pseudohypersensitivity of these pseudohypersensitive transitions. Karaker shows that the shape, energy and oscillator strength of hypersensitive and pseudohypersensitive transition can be correlated with coordination number [22, 23].

CONCLUSION

The results of this study reveals that the Pr(III) complexes with acetyl acetone and their adducts with nitrogen donor ligands like pyridine (py), bromopyridine (Brpy) and chloropyridine (Clpy) 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 metal and ligands.

REFERENCES

[1] RJP Williams; Structure and bonding, Springer Verlay Berlin, **1982,** 50, 79.
[2] AA Khan; K Ittikar; *Indian J. Of Chem*., **2000**, 39A, 1286.
[3] RB Martin. Int. Ed. T. G. Spiro structural chemistry and calcium, Lanthanides as Probe in Calcium in Biology, New York Marcel Decker, **1983**.
[4] SN Mishra; SB Mehta; K Venkatasubramaniyan; *Asian J. of Chem., Rev*., **1991**, Vol.2 No.2, 100.
[5] SN. Misra; GK Joshi; MP Bhutra; *J. Inorg. Nucl. Chem*., **1981**, 43, 527.
[6] SN Misra; *J. Scient. Ind. Res*., **1985**, 44,367.
[7] G Racha; *Physics Rev*., **1942**, 61,165.
[8] G Racha; *Physics Rev.,* **1949**, 76, 1352.
[9] EY Wong; *J. of Chem. Physics*., **1961**, 35, 544.
[10] EY Wong; *J. of Chem. Physics*., **1963**, 38,976.
[11] KJ Shah; MK Shah; *Bull. Of Pure Appl. Sci*., **2001**, C20, 81.
[12] WT Carnall; PR Field; BG Wybourne; *J. Chem. Phys*., **1965**, 42 ,3797.
[13] Th. Devid; Ch. Sumitra; GC. Bag; M. Indira Devi ; NR Singh; *Spectrochim Acta*., **2006** ,63A,154.
[14] KG. Chaudhari; PA Savale; *Int. Research J.Research Analysis and Evolution*, **2010**, Vol I Issue 3 and 4,132.
[15] N Yaiphaba; Th. Devid Singh; M, Indira Devi ; N. Rajmubhan Singh; *Asian J. of Chem..*, **2008**,20, No. 2, 901.
[16] SP Sinha; HH. Schmidtke; *Mol. Phy*., **1965**, 38, 2190.
[17] SP Sinha; *Spectrochim. Acta,* **1966**, 22A, 57.
[18] SN Misra; G Joseph; K Anjaiah; SHR Abdi; *Indian J. of Biochem. Biophys*, **1992, 29**, 70.
[19] SN Misra; GK Joshi; M. P. Bhutra; *J. Inorg. Nucl. Chem*., **1981**, 43,527.
[20] SN Misra; SB Mehta; *Bull. Chem. Soc*., Japan, **1991**, 64, 3653.
[21] SN. Misra; SB Mehta; Suma Mathew; Koshy John; *Proc., Indian Nata, Sci. Acad*., **1992**, 58A, 29.
[22] DG Kararker; *Inorg. Chem*., **1968**, 7, 473.
[23] DG Kararker; *Inorg. Chem*., **1967**, 6, 1863.