Available online at www.pelagiaresearchlibrary.com

Pelagia Research Library

Advances in Applied Science Research, 2012, 3 (2):1895-1899

ISSN: 0976-8610
CODEN (USA): AASRFC

Absorption Spectral Studies of Pr (III) with Acetyl acetone and their complexation with o-phenanthroline and bipyridyl

Kiran G. Chaudhari[1], Padmakar A. Savale[2]

Department of Chemistry[1], Arts and Science College, Bhalod, Tal. Yawal Dist. Jalgaon (MS) India
Department of Physics[2], Arts and Science College, Bhalod, Tal. Yawal Dist. Jalgaon (MS) India

---

ABSTRACT

In present study, absorption spectral studies of Pr(III) with acetyl acetone $[C_5H_8O_2]$ *and their adducts with dinitrogen donor ligands like, o-phenanthroline* $[C_{12}H_{10}N_2O]$ *and bipyridyl* $[C_{10}H_8N_2]$ *in methanol* $[CH_3OH]$*, dimethyl formamide* $[C_3H_7NO]$ *and acetonitrile* $[CH_3CN]$ *was carried out. The intra 4ƒ-4ƒ 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.*

Key words: Electronic spectra, nephelauxetic effects, dinitrogen donor ligands.

INTRODUCTION

The sharp line bands arising from 4f transition among different levels of 4f configuration exhibit red shift as well as some broadening when Pr (III) undergoes complexation. Judd Ofelt theory of lanthanide intensities have led to an upsurge in the quantitative analysis of spectral behavior of Pr (III) in crystalline state [1, 2].

S. N. Misra et al studies the interactions of adenine and adenosine with Pr (III) in different ratio, they observed similar type of absorption spectral pattern with small changes in the intensity, energy parameters of transition and marginal increase in wavelength. It was reported that adenosine appears to be a better ligand than adenine. The reasons are either increase in intensity parameters from adenine to adenosine or overlap of orbital and shortening of the metal ligand distance [3-8].

The formation of lanthanide ligand bond mainly depends on electronegativity of the bonding atom in the ligand. It is in the order of $F^- > OH^- > H_2O > NO_3 > Cl^-$ for ligands, when they can form chelate ring through their oxygen atom in β diketonates. When the ligand binds through either nitrogen atom or sulphur atom, they are unable to complete with water for the position in coordination sphere. Therefore, their compounds can be synthesized only in non aqueous media [9].

In the present study, absorption spectral studies of Pr (III) with acetyl acetone and their adducts with dinitrogen donor ligand like, o-phenanthroline and bipyridyl in methanol, dimethyl formamide and acetonitrile was carried out. The intra 4ƒ-4ƒ 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.

MATERIAL 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 like o-phenanthroline and bipyridyl 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 in10^{-2} M.

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

Pr (III) chloride heptahydrate 3.74 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)$_3$ (bipy)]

The [Pr (acac)$_3$ (H$_2$O)$_2$] of 4.77 gm added into methanolic solution of 1.56 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 o-phenothroline 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 [10].

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 [11-12]

(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,

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

Where, E_{oj} is the Zero order energy of the jth level is given by E. Y. Wong [13-14]. 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 [15-19],

$$b^{1/2} = [1 – \beta/ 2]^{1/2}$$

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,

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

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 4*f*-4*f* transition bonds in $[Pr(acac)_3\ (H_2O)_2]$ the enhancement is more in case o-phenthroline indicating a better ligand than bipyridyl when recorded in CH_3OH. The intensity of $^3H_4 \rightarrow\ ^3P_2 >\ ^3H_4 \rightarrow ^3P_1 >\ ^3H_4 \rightarrow ^3P_0 > ^3H_4 \rightarrow ^1D_2$ [22-24].

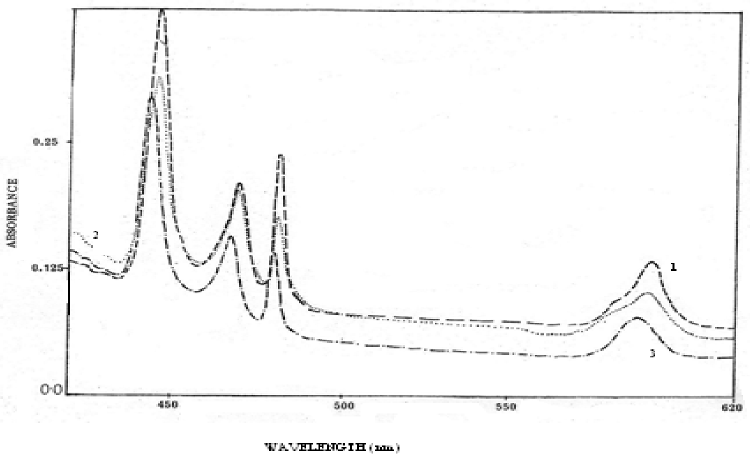

Fig. 1 Comparative absorption spectra of 1) $[Pr(acac)_3(H_2O)_2]$ 2) $[Pr(acac)_3($ o - ph$)]$ and 3) $[Pr(acac)_3(Bipy)]$ complexes in methanol.

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 matched means that the complexation is proper.

Table 1 Observed and calculated values of molecular weight of Pr(III) complexes.

Complexes	Cal. MW	Obs. MW
Pr $(acac)_3(H_2O)_2$	477.36	474.18
Pr $(acac)_3$(oph)	639.50	638.01
Pr $(acac)_3$(Bipy)	567.46	566.30

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
$Pr(acac)_3(H_2O)_2$	29.52	29.68	36.71	37.80	4.88	5.05	-	-
Pr $(acac)_3$(oph)	21.56	22.03	49.68	50.66	500	5.05	4.11	4.38
Pr $(acac)_3$(Bipy)	23.90	24.83	51.90	53.74	5.98	6.20	4.80	4.94

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 108.97 to 173.73 showing that accuration of the various energy interaction parameters.

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 vary from 0.927 to 0.946

which is less than unity. The value of bonding parameters ($b^{1/2}$) were varies from 0.126 to 0.168 and which is positive indicate covalent bonding between Pr (III) and ligand.

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.**
CH_3OH	**Obs**	**Cal**	**Obs**	**Cal**	**Obs**	**Cal**	**Obs**	**Cal**	
$Pr(acac)_3(H_2O)_2$	22489	22424	21311	21215	20736	20660	16893	17117	131.30
$Pr\ (acac)_3(o\text{-}ph)$	22506	22356	21333	21206	20755	20756	16917	17077	126.72
$r(acac)_3(Bipy)$	22537	22415	21360	21252	20772	20770	16972	17110	108.97
DMF									
$Pr(acac)_3(H_2O)_2$	22432	22557	21254	21128	20690	20690	16836	17107	173.73
$Pr\ (acac)_3(o\text{-}ph)$	22436	22250	21263	21119	20708	20705	16820	17034	159.02
$Pr(acac)_3(Bipy)$	22437	22248	21258	21126	20709	20707	16821	17033	154.47
CH_3CN									
$Pr(acac)_3(H_2O)_2$	22414	22392	21363	21261	20776	20774	16932	17118	128.18
$Pr\ (acac)_3(o\text{-}ph)$	22532	22310	21353	21236	20755	20751	16855	17065	143.20
$Pr(acac)_3(Bipy)$	22530	22401	21341	21190	20748	20755	16943	17101	144.66

S. N. Misra et al [25-27] 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 $^3H_4 \rightarrow {}^3P_2$, $^3H_4 \rightarrow {}^3P_{1,}$ $^3H_4 \rightarrow {}^3P_0$, $^3H_4 \rightarrow {}^1D_2$ 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 $^3H_4 \rightarrow {}^1D_2$. 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 [28, 29].

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							
$Pr\ (acac)_3(H_2O)_2$	308.85	42.68	4.66	719.64	0.944	0.166	5.890
$Pr\ (acac)_3(o\text{-}ph)$	311. 12	41.98	4.70	651.77	0.927	0.128	3.358
$Pr\ (acac)_3(Bipy)$	311.50	42.02	4.71	658.37	0.929	0.126	3348
DMF							
$Pr\ (acac)_3(H_2O)_2$	308.10	42.54	4.65	719.35	0.941	0.168	6.032
$Pr\ (acac)_3(o\text{-}ph)$	311.65	43.10	4.68	668.54	0.945	0.129	3.444
$Pr\ (acac)_3(Bipy)$	311.20	42.92	4.78	863.11	0.946	0.130	3.446
CH_3CN							
$Pr\ (acac)_3(H_2O)_2$	308.17	42.53	4.65	720.06	0.943	0.166	5.953
$Pr\ (acac)_3(o\text{-}ph)$	311.62	43.00	4.68	665.56	0.933	0.130	3.391
$Pr\ (acac)_3(Bipy)$	311.23	42.95	4.71	683.11	0.944	0.128	3.610

CONCLUSION

The results of this study reveals that the Pr(III) complexes with acetyl acetone and their adducts with nitrogen donor ligands like o-phenanthroline and bipyridyl complexes creates high degree of intensification to different pseudohypersensitive transitions in different immediate coordination environment. It is quite apparent the stereochemistry possible for octacoordination. 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.

REFERENCES

[1] Martin RB, *Int. Ed. T. G. Spiro structural chemistry and calcium, Lanthanides as Probe in Calcium in Biology*, New York Marcel Decker, **1983**.
[2] Khan AA, Ittikar K, *Indian J of Chem*, **2000**, 39A, 1286.

[3] Misra SN, Joshi GK, Bhutra MP, *J of Inorg Nucl Chem*, **1981**, 43, 527.
[4] Mishra SN, Mehta SB, Venkatasubramaniyan K, *Asian J of Chem Rev*, **1991**, Vol.2 No.2, 100.
[5] Misra SN, *J Scient Ind Res*, **1985**, 44, 367.
[6] Misra SN, Gagnani MA, Indira Devi M, Shukla RS, *Bioinorg Chem Appl*, **2004,** 2 (3-4), 155.
[7] Judd BR, *Phys Rev*, **1962**,127, 750.
[8] Oflet GS, *J of Chem Phys*, **1962**, 37, 511.
[9] Chaudhari KG, *Ph. D. Thesis*, **1992.**
[10] Chaudhari KG, Savale PA, *Science Research Link-73*, **2010**, Vol-IX (2), 9.
[11] Racha G, *Physics Rev*, **1949**, 76, 1352.
[12] Racha G, *Physics Rev*, **1942**, 61, 165.
[13] Wong EY, *J of Chem Physics*, **1963**, 38, 976.
[14] Wong EY, *J of Chem Physics*, **1961**, 35, 544.
[15] Shah KJ, Shah MK, *Bull of Pure Appl Sci*, **2001**, C20, 81.
[16] Chaudhari KG, Savale PA, *Int Research J Research Analysis and Evolution*, **2009**, Vol I Issue 3 and 4,132.
[17] Devid Th, Sumitra Ch, Bag GC, Indira Devi M, Singh NR, *Spectrochim Acta*, **2006**, 63A, 154.
[18] Carnall WT, Field PR, Wybourne BG, *J of Chem Phys*, **1965**, 42, 3797.
[19] Yaiphaba N, Devid Singh Th, Indira Devi M, Rajmubhan Singh N, *Asian J of Chem*, **2008**,20, No. 2, 901.
[20] Sinha SP, Schmidtke HH, *Mol Phy*, **1965**, 38, 2190.
[21] Sinha SP, *Spectrochim Acta*, **1966**, 22A, 57.
[22] Chaudhari KG, Savale PA, *Scholars Research Library, Archives of Applied Science Research*, **2010**, 2(2), 162.
[23] Misra SN, Joshi GK, Bhutra MP, *J of Inorg Nucl Chem*, **1981**, 43, 527.
[24] Chaudhari KG, Savale PA, *Scholars Research Library, Archives of Applied Science Research*, **2011**, 3(6), 327.
[25] Misra SN, Joseph G, Anjaiah K, Abdi SHR, *Indian J of Biochem. Biophys*, **1992**, 29, 70.
[26] Misra SN, Mehta SB, *Bull of Chem Soc*, Japan, **1991,** 64, 3653.
[27] Misra SN, Mehta SB, Mathew Suma, John Koshy, *Proc of Indian Nata, Sci Acad*, **1992,** 58A, 29.
[28] Kararker DG, *Inorg Chem*, **1967,** 6, 1863.
[29] Kararker DG, *Inorg Chem*, **1968,** 7, 473.