

## Research Paper—



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## CALCULATION OF ENERGY INTERACTION PARAMETERS FOR THE COMPLEXATION OF PR(III) WITH B-DIKETONE COMPLEXES BY 4f-4f ABSORPTION SPECTRAL ANALYSIS



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## A B S T R A C T

*In the present study, absorption difference and comparative absorption spectroscopic studies involving 4f-4f transitions of Pr(III) with benzoylacetone [Pr(bzac)<sub>3</sub>(H<sub>2</sub>O)<sub>2</sub>] and their adducts with nitrogen donors ligands like pyridine, 2-acetylpyridine, 3-acetylpyridine, 4-acetylpyridine, chloropyridine, bromopyridine and dinitrogen ligands like o-phenanthroline, bipyridyl complexes in CH<sub>3</sub>OH, DMF, CH<sub>3</sub>CN, isopropanol solvents have been carried out. Variations in the spectral energy parameters like Slater Condon ( $F_k$ ), Lande spin orbit coupling ( $\xi_{4f}$ ), nephelauxetic ratio ( $\beta$ ) and bonding parameter ( $b^{1/2}$ ) and percent covalency ( $\beta$ ) are calculated. These spectral energy parameters were correlated with the interaction of Pr(III) with structurally related  $\beta$ -diketone complexes. The marginal decrease in the values of Slater Condon ( $F_k$ ), Lande spin orbit coupling ( $\xi_{4f}$ ) are correlated with the small increase in the value of nephelauxetic ratio ( $\beta$ ).*

**Key words:** Absorption spectra,  $\beta$ -diketones, nephelauxetic effects**Introduction**

The use of lanthanides as absorption spectral probe in several biochemical reactions involving Ca<sup>2+</sup> and Mg<sup>2+</sup> has open up a new dimension for the fast developing field of optical spectroscopy. During the last three decades, new field of application have been found for the lanthanide coordination compounds in solution viz., in construction of liquid laser in studying transuranic element, as unique spectral models in examining structure and function [1] and reactivity of the biosystems involving lanthanides as spectral probe [2, 3]. The hard metal acceptors like lanthanides(III) prefer oxygen and nitrogen donor ligands for stable complexes with predominantly ionic character,

although the affinity for oxygen donor ligand is more [4]. Shah studied comparative 4f-4f transition spectra of Pr(III) with lysozyme by using energy interaction parameters to explain the behavior of binding between them. Studies on Ln(III) complexes derived from nitrogen donor ligands have shown that the Ln-N interaction is stronger than that previously believed. It has been found that the number of coordinated ligands to the lanthanides depends upon the ability of anion to compete for the coordination sites and there relative size of the ligands [5].

In the present study, [Pr(bzac)<sub>3</sub>(H<sub>2</sub>O)<sub>2</sub>] and their adducts with structurally related nitrogen donors

ligands complexes, their spectroscopic studies involving 4f-4f transitions spectra of Pr(III) have been found to exhibit significant sensitivity towards even minor changes in the immediate coordination environment around the lanthanide ion through variation in the absorption spectral pattern, degree of red shift and intensification of 4f-4f transitions. Variations in the spectral energy parameters like Slater Condon ( $F_k$ ), Lande spin orbit coupling ( $\xi_{4f}$ ), nephelauxetic ratio ( $\beta$ ) and bonding parameter ( $b^{1/2}$ ) and percent covalency ( $\delta$ ) are calculated, which gives information about the nature of complexation.

### Experimental

Praseodymium(III) chloride heptahydrate of 99.9% purity from M/s Indian Rare Earths Ltd., benzoyl acetone (bzac) of AR grade from Qualigens, nitrogen donors ligands viz., pyridine, 2-acetylpyridine, 3-acetylpyridine, 4-acetylpyridine, chloropyridine, bromopyridine and dinitrogen ligands as o-phenanthroline, bipyridyl were from Sisco chemical laboratory. The CH<sub>3</sub>OH, DMF, CH<sub>3</sub>CN, and isopropanol solvents used for recording the spectra of AR grade from E. Merk. They are double distilled before use. All the spectra are recorded on Perkin Elmer Lambda-2 UV-Visible spectrophotometer in the range 380-620nm in the concentration of 0.01M.

### Synthesis of Praseodymium (III) $\beta$ -diketonate complexes

Praseodymium chloride heptahydrate 3.734gm was dissolved in water. The methanolic solution of benzoyl acetone 4.878gm was added very slowly with constant stirring which resulted in isolation of a yellow crystalline solid after neutralizing the contents with ammonia.

### Synthesis of adduct Praseodymium (III) $\beta$ -diketonate with nitrogen donor ligands

The addition of 2.5ml of acetyl pyridine in methanol (5ml) to methanolic solution of [Pr(bzac)<sub>3</sub>(H<sub>2</sub>O)<sub>2</sub>] 6.634gms in methanol on constant stirring yielded yellow precipitate. The amount of precipitate increased tremendously on addition of ammonia solution drop wise. The yellow microcrystalline solid obtained was purified by recrystallization from methanol and other adducts has also been synthesized by similar procedure. These

adducts have been synthesized and characterized by elemental analysis. Elemental analysis was carried out on Carlo-Ebra Strumentazione Strada Rivoltand 200 9D Ronodo Italy. Metal Pr(III) was estimated first by decomposing the chelate by concentrated nitric acid and evaporating it to dryness. The dried mass extracted with dilute HCl and the metal was precipitated as oxinate by using 8-Hydroxy quinoline method and Analytical data are summarized. The complexes were synthesized by using the method available in literature [6]. The nephelauxetic effects ( $\beta$ ), a measure of covalency have been interpreted in terms of Slater-Condon and Racah parameters as well as by the ratio of the free ion and complex ion respectively.

$$\beta = F_k^c / F_k^f \text{ or } F_c^k / F_f^k \quad [1]$$

The bonding parameter ( $b^{1/2}$ ) is derived from the nephelauxetic effect as,

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

Sinha [7, 8] introduced a percentage covalency parameter ( $\delta$ ) can be derived from using the equation 1.

$$\delta = [1 - \beta / \beta] \times 100 \quad [3]$$

Condon and Shortly [9] redefined  $F_k$  integrals in terms of reduced integral  $F_k$  related to each other and the relation is

$$F_k = F^k / D_k \quad [4]$$

The Racah [10] energy interaction parameter  $E^k$  are linear combinations of  $F_k$  is given by,

$$E^1 = (70 \times F_2 + 231F_4 + 20.02 F_6) / 9$$

$$E^2 = (F_2 - 3F_4 + 7 F_6) / 9$$

$$E^3 = (5 F_2 + 6F_4 - 9 F_6) / 3 \quad [5]$$

Assuming hydrogenic wave function, the equation 5 for calculation of Racah parameters  $E^1, E^2, E^3$  in case of Pr(III) complexes reduced to,

$$E^1 = 14.6816 \times F_2$$

$$E^2 = 0.0768 \times F_2$$

$$E^3 = 1.4844 \times F_2 \quad [6]$$

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

$$P_{obs} = 4.60 \times 10^{-9} \epsilon_m (\bar{\nu}) d\nu \quad [7]$$

Where  $\epsilon_m$  is the molar extinction coefficient [11, 12] corresponding to energy ( $\bar{\nu}$ ). The energy  $E_{so}$  arising from the most important magnetic interactions, which are spin orbit interactions, may be written as,

$$E_{so} = A_{so} \xi_{4f} \quad [8]$$

Where  $A_{so}$  is the angular part of spin orbit interaction and  $\xi_{4f}$  is the radial integral and is known Lande's parameter by first order approximation the energy  $E_j$  of the  $j^{th}$  level is given by Wong as [13,14],  $E_j(F_k, \xi_{4f}) = E_{oj}(F_k, \xi_{4f}) + (\delta E_j / \delta F_k) \Delta F_k + (\delta E_j / \delta \xi_{4f}) \Delta \xi_{4f}$  [9]

Where,  $E_{oj}$  is the Zero order energy of the  $j^{th}$  level. The value of  $F_k$  and  $\xi_{4f}$  are given by,

$$F_k = F_k^0 + \delta F_k \quad [10]$$

$$\xi_{4f} = \xi_{4f}^0 + \delta \xi_{4f}$$

The difference between the observed values of  $E_j$  and  $E_{oj}$  and  $\Delta E_j$  is evaluated by,

$$\Delta E_j = \sum_{k=2,4,6} (\delta E_j / \delta F_k) \Delta F_k + (\delta E_j / \delta \xi_{4f}) \Delta \xi_{4f} \quad [11]$$

The above equation can be transformed into the general equation  $y_n = a + xnb$ . Where,  $n = 1, 2, 3$  and  $4$ . The values for  $x$  and  $y$  can be obtained statistically. The value  $F_4$  and  $F_6$  can also be evaluated from the relation [15-19]

$$F_4/F_2 = 0.1380 \text{ and } F_4/F_2 = 0.0151 \quad [12]$$

### Result and Discussion

The sensitivity of any transition is judged by the percentage variation of the oscillator strength and not by the variation of the absolute value of oscillator strength. Hence, the following transitions are behaving like hypersensitive transition as these are showing wide variation of intensities with minor changes in the immediate coordination environment around metal in these structurally related compounds, the variation of oscillator strength of these pseudohypersensitive transitions given below.

$^3H_4 \rightarrow ^3P_2$	$9.434 \times 10^6$ to $44.174 \times 10^6$
$^3H_4 \rightarrow ^3P_1$	$4.355 \times 10^6$ to $19.899 \times 10^6$
$^3H_4 \rightarrow ^3P_0$	$3.105 \times 10^6$ to $15.279 \times 10^6$
$^3H_4 \rightarrow ^1D_2$	$3.786 \times 10^6$ to $15.709 \times 10^6$

None of this transition follows the selection rule for Pr(III), yet these are showing high sensitivity and hence these are considered as pseudohypersensitive transitions [16].

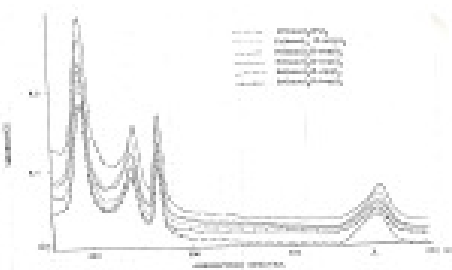


Fig.1 The comparative absorption spectra of Pr(III) complexes in methanol.

Karaker [20] shows that the shape energy and oscillator strength of hypersensitive and pseudohypersensitive transition can be correlated with co-ordination number. The Fig. 1 shows the maximum absorbance observed in methanol in  $[Pr(bzac)_3(Py)_2]$  and minimum absorbance is observed in  $[Pr(bzac)_3(bipy)]$ . The Fig. 2 shows the maximum absorbance observed in isopropanol in  $[Pr(bzac)_3(Py)_2]$  where as minimum absorbance is observed in  $[Pr(bzac)_3(3-acpy)_2]$ . The comparative absorption spectra of  $[Pr(bzac)_3(2-clpy)_2]$  in methanol, isopropanol and acetonitrile were shown in Fig.3.

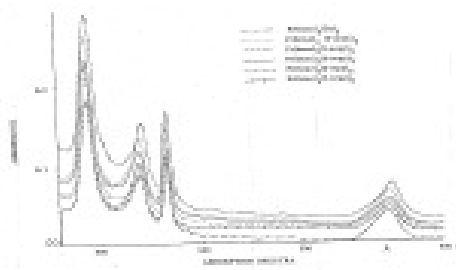


Fig.2. The comparative absorption spectra of Pr(III) complexes in isopropanol.

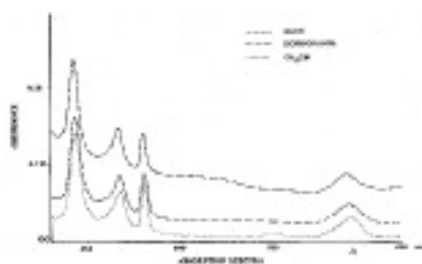


Fig. 3 The marginal absorbance observed in methanol and maximum absorbance in case of solvent isopropanol.

Table 1 shows the observed and calculated values of analytical data Pr(III) complexes. The small variation is observed in the  $F_k$  and  $(\xi_{4f})$  and values of nephelauxetic ratio ( $\beta$ ) and percentage of covalency parameters ( $\delta$ ). The value of  $n$  is proportional to Nephelauxetic effect  $n = [1 - \beta^{1/2} / \beta^{1/2}]$  as a function of two variables  $SR^*$  and  $N$  which varies with

changes in the lanthanide ligand distance in opposite directions. Where  $S$  is the overlap integral,  $R^*$  is the radius of orbit and  $N$  is the coordination number. The Nephelauxetic effect increases as the coordination number decreases. The Ln-O distance shortens in spite of the additive nature of ( $\beta$ ) and decrease in number of the coordinating ligands.

Table 1 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 (bzac) <sub>3</sub> (H <sub>2</sub> O) <sub>2</sub>	21.23	20.78	54.25	53.60	5.12	4.84	-	-
Pr (bzac) <sub>3</sub> (Py) <sub>2</sub>	17.94	16.80	61.10	59.88	5.09	4.88	3.56	2.96
Pr (bzac) <sub>3</sub> (2-acpy) <sub>2</sub>	15.63	15.70	58.60	57.70	5.05	4.76	3.12	2.86
Pr (bzac) <sub>3</sub> (3-acpy) <sub>2</sub>	15.63	15.76	58.60	57.87	5.05	4.64	3.12	2.80
Pr (bzac) <sub>3</sub> (4-acpy) <sub>2</sub>	15.63	15.79	58.60	57.77	5.05	4.89	3.12	2.88
Pr (bzac) <sub>3</sub> (2-clpy) <sub>2</sub>	16.48	15.96	56.16	55.10	4.68	4.32	3.27	2.67
Pr (bzac) <sub>3</sub> (2-brpy) <sub>2</sub>	14.93	13.86	50.90	50.20	4.03	3.89	2.96	2.32
Pr (bzac) <sub>3</sub> (Phen)	12.70	11.88	61.03	59.80	4.60	4.10	3.39	2.88
Pr (bzac) <sub>3</sub> (bipy)	17.98	16.77	61.25	60.15	5.10	4.80	3.57	2.92

Misra et al [21-23] observed decrease in the value of  $F_k$ ,  $E^k$  and  $(\xi_{4f})$  parameters as compared to corresponding parameter of aqueous ion. The value of Nephelauxetic effect ( $\beta$ ) in Pr(III) complexes is varies from 0.921 to 0.935 this is less than one. The values of bonding parameters ( $b^{1/2}$ ) in Pr(III) complexes are varies from 0.126

to 0.144 and are positive which indicates covalent bonding. Table 2 shows the information of calculated and observed values of energies for the four transition bands of Pr(III) complexes and the r.m.s. deviation ( $\sigma$ ) showing accuration of the various energy parameters. The r.m.s. deviation ( $\sigma$ ) varies from 107.81 to 191.84.

Table 2 Experimental and computed Energies (cm<sup>-1</sup>) of Pr(III) complexes in different solvents

Complexes and Solvents	<sup>3</sup> P <sub>2</sub>		<sup>3</sup> P <sub>1</sub>		<sup>3</sup> P <sub>0</sub>		<sup>1</sup> D <sub>2</sub>		$\sigma$ r.m.s.
	Obs	Cal	Obs	Cal	Obs	Cal	Obs	Cal	
Methanol									
Pr (bzac) <sub>3</sub> (H <sub>2</sub> O) <sub>2</sub>	22436	22244	21258	21161	20721	20733	16878	17042	135.29
Pr (bzac) <sub>3</sub> (Py) <sub>2</sub>	22247	22286	21303	21155	20742	20740	16835	16957	133.94
Pr (bzac) <sub>3</sub> (2-acpy) <sub>2</sub>	22471	22279	21299	21051	20743	20740	16832	17053	191.84
Pr (bzac) <sub>3</sub> (3-acpy) <sub>2</sub>	22507	22319	21326	21161	20755	20753	16857	17076	166.23
Pr (bzac) <sub>3</sub> (4-acpy) <sub>2</sub>	22451	22286	21281	21155	20729	20727	16823	17042	157.02
Pr (bzac) <sub>3</sub> (2-clpy) <sub>2</sub>	22482	22329	21308	21189	20746	20748	16837	17060	148.21
Pr (bzac) <sub>3</sub> (2-brpy) <sub>2</sub>	22483	22290	21303	21162	20746	20743	16846	17062	159.60
Pr (bzac) <sub>3</sub> (Phen)	22471	22310	21294	21195	20738	20756	16829	17082	144.83
Pr (bzac) <sub>3</sub> (bipy)	22492	22280	21321	21150	20751	20756	16889	17084	146.40
Isopropanol									
Pr (bzac) <sub>3</sub> (H <sub>2</sub> O) <sub>2</sub>	22542	22390	21362	21235	20779	20776	16932	17120	129.28
Pr (bzac) <sub>3</sub> (Py) <sub>2</sub>	22532	22391	21362	21238	20777	20735	16946	17118	130.05
Pr (bzac) <sub>3</sub> (2-acpy) <sub>2</sub>	22527	22375	21353	21122	20772	20770	16917	17001	109.70
Pr (bzac) <sub>3</sub> (3-acpy) <sub>2</sub>	22542	22395	21358	21247	20772	20770	16949	17116	107.97

Pr (bzac) <sub>3</sub> (4-acpy) <sub>2</sub>	22532	22381	21353	21230	20772	20768	16923	17112	134.17
Pr (bzac) <sub>3</sub> (2-clpy) <sub>2</sub>	22537	22376	21362	21225	20772	20770	16937	17111	136.90
Pr (bzac) <sub>3</sub> (2-brpy) <sub>2</sub>	22537	22407	21358	21239	20777	20769	16937	17120	127.09
Pr (bzac) <sub>3</sub> (Phen)	22522	22360	21354	21234	20768	20756	16974	17156	107.81
Pr (bzac) <sub>3</sub> (bipy)	22581	22347	21312	21194	20746	20740	16860	17115	184.69
Acetonitrile									
Pr (bzac) <sub>3</sub> (H <sub>2</sub> O) <sub>2</sub>	22431	22256	21253	21126	20699	20690	16836	17106	174.79
Pr (bzac) <sub>3</sub> (Py) <sub>2</sub>	22522	22379	21349	21222	20755	20754	16931	17107	129.95
Pr (bzac) <sub>3</sub> (2-acpy) <sub>2</sub>	22512	22352	21331	21200	20746	20743	16903	17109	145.95
Pr (bzac) <sub>3</sub> (3-acpy) <sub>2</sub>	22502	22342	21321	21193	20742	20740	16900	17086	138.36
Pr (bzac) <sub>3</sub> (4-acpy) <sub>2</sub>	22487	22324	21312	21179	20738	20736	16883	17076	142.75
Pr (bzac) <sub>3</sub> (2-clpy) <sub>2</sub>	22502	22316	21326	21171	20742	20737	16894	17070	149.68
Pr (bzac) <sub>3</sub> (2-brpy) <sub>2</sub>	22492	22327	21317	21182	20742	20740	16883	17078	144.46
Pr (bzac) <sub>3</sub> (Phen)	22461	22328	21290	21181	20728	20726	16843	17078	145.59
Pr (bzac) <sub>3</sub> (bipy)	22476	2298	21303	21159	20729	20724	1852	17062	155.56

**Table 3 Energy interaction (cm<sup>-1</sup>), Slater Condon (F<sub>k</sub>), Lande spin orbit interaction (ξ<sub>4f</sub>), nephelauxetic ratio (β), bonding parameters (b<sup>1/2</sup>) and covalency parameter (δ) for Pr(III) complexes in methanol, isopropanol and acetonitrile solvents.**

Complexes and Solven	F <sub>2</sub>	F <sub>4</sub>	F <sub>6</sub>	(ξ <sub>4f</sub> )	E <sup>1</sup>	E <sup>2</sup>	E <sup>3</sup>	β	(b <sup>1/2</sup> )	(δ)
Methanol										
Pr (bzac) <sub>3</sub> (H <sub>2</sub> O) <sub>2</sub>	311.66	43.02	4.71	646.00	4575.72	23.94	462.63	0.926	0.127	3.359
Pr (bzac) <sub>3</sub> (Py) <sub>2</sub>	311.80	43.04	4.71	652.12	4577.78	23.95	462.83	0.928	0.129	3.412
Pr (bzac) <sub>3</sub> (2-acpy) <sub>2</sub>	311.87	43.05	4.70	649.97	4578.81	23.95	465.94	0.925	0.126	3.359
Pr (bzac) <sub>3</sub> (3-acpy) <sub>2</sub>	311.82	43.05	4.71	658.44	4578.07	23.95	462.86	0.921	0.128	3.799
Pr (bzac) <sub>3</sub> (4-acpy) <sub>2</sub>	311.71	43.03	4.70	653.68	4576.46	23.94	462.70	0.925	0.127	3.359
Pr (bzac) <sub>3</sub> (2-clpy) <sub>2</sub>	311.69	43.03	4.71	663.24	4576.17	23.94	462.67	0.925	0.128	3.359
Pr (bzac) <sub>3</sub> (2-brpy) <sub>2</sub>	311.85	43.05	4.71	652.37	4578.52	23.95	462.91	0.926	0.128	3.359
Pr (bzac) <sub>3</sub> (Phen)	311.63	43.02	4.71	663.37	4575.28	23.93	462.58	0.926	0.128	3.359
Pr (bzac) <sub>3</sub> (bipy)	311.78	43.02	4.71	650.50	4577.49	23.94	462.80	0.925	0.128	3.359
Isopropanol										
Pr (bzac) <sub>3</sub> (H <sub>2</sub> O) <sub>2</sub>	311.73	43.02	4.71	673.75	4576.75	23.94	462.73	0.924	0.130	3.626
Pr (bzac) <sub>3</sub> (Py) <sub>2</sub>	311.60	43.00	4.71	676.24	4574.84	23.93	462.54	0.928	0.132	3.519
Pr (bzac) <sub>3</sub> (2-acpy) <sub>2</sub>	311.70	43.03	4.71	671.53	4576.32	23.94	462.68	0.921	0.128	3.350
Pr (bzac) <sub>3</sub> (3-acpy) <sub>2</sub>	311.53	43.00	4.68	678.24	4573.82	23.93	462.45	0.925	0.130	3.498
Pr (bzac) <sub>3</sub> (4-acpy) <sub>2</sub>	311.68	43.03	4.71	672.81	4576.02	23.94	462.65	0.922	0.130	3.766
Pr (bzac) <sub>3</sub> (2-clpy) <sub>2</sub>	311.69	43.00	4.71	676.69	4574.84	23.93	462.54	0.922	0.132	3.626
Pr (bzac) <sub>3</sub> (2-brpy) <sub>2</sub>	311.73	43.01	4.71	673.37	4576.75	23.94	462.73	0.922	0.130	3.626
Pr (bzac) <sub>3</sub> (Phen)	311.73	43.01	4.71	669.64	4576.46	23.94	462.60	0.928	0.128	3.413
Pr (bzac) <sub>3</sub> (bipy)	311.28	42.95	4.70	671.31	4570.15	23.91	462.06	0.927	0.128	3.413
Acetonitrile										
Pr (bzac) <sub>3</sub> (H <sub>2</sub> O) <sub>2</sub>	311.06	42.96	4.70	656.58	4566.92	23.88	461.74	0.925	0.130	3.521
Pr (bzac) <sub>3</sub> (Py) <sub>2</sub>	311.32	42.96	4.68	677.38	4570.73	23.91	462.12	0.931	0.144	3.521
Pr (bzac) <sub>3</sub> (2-acpy) <sub>2</sub>	311.34	42.95	4.70	671.50	4571.03	23.91	462.15	0.935	0.136	3.521

Pr (bzac) <sub>3</sub> (3-acpy) <sub>2</sub>	311.33	42.96	4.70	669.87	4570.88	23.91	462.13	0.935	0.130	3.521
Pr (bzac) <sub>3</sub> (4-acpy) <sub>2</sub>	311.39	42.97	4.70	665.38	4571.76	23.91	462.23	0.932	0.130	3.521
Pr (bzac) <sub>3</sub> (2-clpy) <sub>2</sub>	311.32	42.96	4.70	664.59	4570.73	23.91	462.13	0.931	0.130	3.521
Pr (bzac) <sub>3</sub> (2-brpy) <sub>2</sub>	311.45	42.98	4.71	665.12	4572.65	23.92	462.32	0.931	0.128	3.521
Pr (bzac) <sub>3</sub> (Phen)	311.45	42.98	4.71	656.26	4572.65	23.92	462.32	0.927	0.128	3.487
Pr (bzac) <sub>3</sub> (bipy)	311.40	42.97	4.71	660.21	4571.91	23.91	462.32	0.928	0.128	3.487

**Table 4 Experimental and computed values of oscillator strength ( $P \times 10^6$ ) for pr(III) complexes in methanol, isopropanol and acetonitrile solvents.**

Complexes and Solvents	<sup>3</sup> P <sub>2</sub>		<sup>3</sup> P <sub>1</sub>		<sup>3</sup> P <sub>0</sub>		<sup>1</sup> D <sub>2</sub>		$\sigma_{r.m.s.}$
	Obs	Cal	Obs	Cal	Obs	Cal	Obs	Cal	
<b>Methanol</b>									
Pr (bzac) <sub>3</sub> (H <sub>2</sub> O) <sub>2</sub>	14.829	14.829	7.109	3.857	3.808	3.806	6.317	6.322	1.625
Pr (bzac) <sub>3</sub> (Py) <sub>2</sub>	29.965	29.296	13.479	7.489	7.383	7.381	7.457	7.457	2.995
Pr (bzac) <sub>3</sub> (2-acpy) <sub>2</sub>	28.667	28.667	12.108	6.724	6.628	6.627	8.782	8.382	2.701
Pr (bzac) <sub>3</sub> (3-acpy) <sub>2</sub>	24.472	25.386	11.749	5.562	5.482	5.480	8.308	8.307	3.126
Pr (bzac) <sub>3</sub> (4-acpy) <sub>2</sub>	25.539	25.517	11.901	7.817	7.710	7.708	8.703	8.704	2.042
Pr (bzac) <sub>3</sub> (2-clpy) <sub>2</sub>	26.849	26.862	10.349	5.662	5.583	5.580	7.407	6.037	2.466
Pr (bzac) <sub>3</sub> (2-brpy) <sub>2</sub>	22.388	22.386	10.584	5.233	5.162	5.158	5.716	5.717	2.675
Pr (bzac) <sub>3</sub> (Phen)	24.214	24.202	9.133	6.186	6.112	6.099	5.957	6.461	1.495
Pr (bzac) <sub>3</sub> (bipy)	18.319	18.350	8.042	5.303	5.037	5.224	5.037	5.038	1.369
<b>Isopropanol</b>									
Pr (bzac) <sub>3</sub> (H <sub>2</sub> O) <sub>2</sub>	13.166	13.165	4.945	3.712	3.657	3.654	3.914	4.466	0.675
Pr (bzac) <sub>3</sub> (Py) <sub>2</sub>	44.174	44.176	18.068	15.508	15.279	15.265	15.699	15.699	1.560
Pr (bzac) <sub>3</sub> (2-acpy) <sub>2</sub>	31.354	31.361	11.798	8.871	9.158	8.736	13.044	12.703	1.488
Pr (bzac) <sub>3</sub> (3-acpy) <sub>2</sub>	24.271	23.424	8.277	3.784	3.726	3.725	6.942	6.941	2.285
Pr (bzac) <sub>3</sub> (4-acpy) <sub>2</sub>	27.559	27.557	10.569	8.108	8.210	7.983	10.329	10.320	1.250
Pr (bzac) <sub>3</sub> (2-clpy) <sub>2</sub>	44.049	44.070	19.899	10.691	10.527	10.526	15.709	15.703	1.488
Pr (bzac) <sub>3</sub> (2-brpy) <sub>2</sub>	35.033	35.034	14.782	8.316	8.192	8.189	11.109	11.101	3.233
Pr (bzac) <sub>3</sub> (Phen)	19.147	19.146	8.951	4.445	4.380	4.381	5.647	5.199	2.277
Pr (bzac) <sub>3</sub> (bipy)	18.457	17.457	7.203	4.483	4.416	4.414	6.456	6.391	1.370
<b>Acetonitrile</b>									
Pr (bzac) <sub>3</sub> (H <sub>2</sub> O) <sub>2</sub>	9.434	10.431	4.355	3.149	3.105	3.105	3.786	3.786	0.781
Pr (bzac) <sub>3</sub> (Py) <sub>2</sub>	35.659	35.624	10.973	7.959	7.833	7.834	11.223	9.754	1.676
Pr (bzac) <sub>3</sub> (2-acpy) <sub>2</sub>	32.568	32.552	9.730	6.865	6.728	6.738	9.487	9.328	1.450
Pr (bzac) <sub>3</sub> (3-acpy) <sub>2</sub>	30.116	30.109	9.546	5.001	4.918	4.925	11.299	9.390	2.461
Pr (bzac) <sub>3</sub> (4-acpy) <sub>2</sub>	30.210	30.199	10.782	7.003	6.900	6.878	9.422	9.286	1.889
Pr (bzac) <sub>3</sub> (2-clpy) <sub>2</sub>	29.449	29.434	9.720	7.080	6.969	6.971	10.661	10.662	1.320
Pr (bzac) <sub>3</sub> (2-brpy) <sub>2</sub>	26.938	26.936	10.558	6.117	6.027	6.025	9.953	9.946	2.221
Pr (bzac) <sub>3</sub> (Phen)	15.438	15.438	5.486	3.492	3.442	3.442	5.704	5.676	0.997
Pr (bzac) <sub>3</sub> (bipy)	10.453	10.449	4.144	3.349	3.300	3.298	3.864	3.865	0.400

**Table 5 Judd Ofelt parameters ( $T \times 10^{10}$ ) for Pr(III) complexes in methanol, isopropanol and acetonitrile solvents.**

Complexes and Solvents	T <sub>2</sub>	T <sub>4</sub>	T <sub>6</sub>	T <sub>4</sub> /T <sub>6</sub>
<b>Methanol</b>				
Pr (bzac) <sub>3</sub> (H <sub>2</sub> O) <sub>2</sub>	452.30	10.63	45.94	0.231
Pr (bzac) <sub>3</sub> (Py) <sub>2</sub>	-288.50	20.59	92.86	0.221

Pr (bzac) <sub>3</sub> (2-acpy) <sub>2</sub>	10.23	18.29	89.90	0.207
Pr (bzac) <sub>3</sub> (3-acpy) <sub>2</sub>	272.30	15.28	76.16	0.200
Pr (bzac) <sub>3</sub> (4-acpy) <sub>2</sub>	286.50	21.52	78.13	0.275
Pr (bzac) <sub>3</sub> (2-clpy) <sub>2</sub>	8.615	15.52	83.97	0.184
Pr (bzac) <sub>3</sub> (2-brpy) <sub>2</sub>	-181.50	14.39	69.64	0.206
Pr (bzac) <sub>3</sub> (Phen)	-133.50	17.02	74.94	0.227
Pr (bzac) <sub>3</sub> (bipy)	-74.23	14.57	56.32	0.258
Isopropanol				
Pr (bzac) <sub>3</sub> (H <sub>2</sub> O) <sub>2</sub>	140.60	10.18	40.38	0.252
Pr (bzac) <sub>3</sub> (Py) <sub>2</sub>	643.60	29.32	136.35	0.214
Pr (bzac) <sub>3</sub> (2-acpy) <sub>2</sub>	965.00	24.34	96.15	0.253
Pr (bzac) <sub>3</sub> (3-acpy) <sub>2</sub>	-26.54	10.38	76.69	0.135
Pr (bzac) <sub>3</sub> (4-acpy) <sub>2</sub>	514.60	22.24	84.32	0.268
Pr (bzac) <sub>3</sub> (2-clpy) <sub>2</sub>	621.10	42.53	133.30	0.319
Pr (bzac) <sub>3</sub> (2-brpy) <sub>2</sub>	199.23	22.81	108.63	0.209
Pr (bzac) <sub>3</sub> (Phen)	309.20	12.30	53.92	0.228
Pr (bzac) <sub>3</sub> (bipy)	201.9	12.22	59.31	0.206
Acetonitrile				
Pr (bzac) <sub>3</sub> (H <sub>2</sub> O) <sub>2</sub>	168.00	8.68	32.00	0.271
Pr (bzac) <sub>3</sub> (Py) <sub>2</sub>	-145.00	21.84	110.90	0.196
Pr (bzac) <sub>3</sub> (2-acpy) <sub>2</sub>	-34.23	18.77	101.70	0.184
Pr (bzac) <sub>3</sub> (3-acpy) <sub>2</sub>	145.70	13.74	95.08	0.144
Pr (bzac) <sub>3</sub> (4-acpy) <sub>2</sub>	110.30	19.25	93.97	0.204
Pr (bzac) <sub>3</sub> (2-clpy) <sub>2</sub>	473.40	19.45	91.34	0.212
Pr (bzac) <sub>3</sub> (2-brpy) <sub>2</sub>	478.00	16.81	83.89	0.200
Pr (bzac) <sub>3</sub> (Phen)	270.00	9.61	48.60	0.199
Pr (bzac) <sub>3</sub> (bipy)	185.00	9.21	31.85	0.289

**Conclusion** The Pr(III) metal β-diketone complexes with nitrogen donors ligands are octacoordinated. The three β-diketones groups are satisfying six coordination position and two positions are satisfied with nitrogen from the ligand. It is quite

apparent that the stereochemistries possible for octacoordination and are interconvertible. The change in the stereochemistry will change the distance between lanthanide and ligands and hence will change the extent of interactions between metal and ligand.

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