Electronic spectral studies of Pr (III) with thenoyltrifluoroacetone and their complexes

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ABSTRACT

Electronic spectroscopy has been used as tool to understand the coordination of mixed ligand complexes of praseodymium (III) $[PrCl_3(H_2O)_7]$, with Thenoyltrifluorolacetone $[C_8H_5O_2F_3S]$ and their complexes with pyridine [C5H6N], chloropyridine [C5H6NCl] & bromopyridine [C5H6NBr]. Using comparative absorption spectroscopy involving 4f-4f transitions in various solvents, like methanol (CH_3OH), acetonitrile (CH_3CN) and dimethylformamide $[(CH_3)_2NCOH]$. 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 the Judd-Oflet intensity parameters of 4f-4f transition have been computed on computer using partial multiple regression analysis. The intensity of hypersensitive transitions has been used to distinguish between outer and inner sphere coordination, in identifying the coordinating sites of ligands. These parameters oscillator strengths electronic dipole parameter gives information about nature of binding between lanthanide metal and ligands complexes in different solvents.

Keywords: Electronic spectra, Nephelauxetic effects, Thenoyltrifluoroacetone
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INTRODUCTION

Tremendous upsurge in the lanthanide spectral and magnetic characteristics has resulted because of the fact that these lanthanides ions have useful physical and chemical property and closely resemble with divalent calcium and magnesium in their chemical behavior. 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. The coordination chemistry of lanthanides has become most significance in last three decades. The magnetic resonance imaging (MRI) technique has become very useful tool of diagnostic medicine. The lanthanides paramagnetic metal complexes used as image enhancement agents..[1, 2]

Lanthanides β-diketones are used as light converting optical materials, light emitting diodes. The lanthanide chelating ligands possessing oxygen and nitrogen donor atom find new application as bactericides and fungicides. In lanthanides the electrons are successively added to inner lying *4f* sub shell is filled up, by strongly positive and large sized ion undergoes shrinkage in ionic size known as lanthanide contraction. This shrinkage influences the coordination chemistry of lanthanide and affects both coordination number and coordination geometry. The *4f-4f* transition spectra are used to assess the effect of the strength of Lanthanide (III) ligand interaction, the geometry of octacoordination structure and chelate-solvent interaction. These characteristic features are exhibited by hypersensitive transition in the absorption spectra of trivalent lanthanide. [3, 4]

S. N. Misra et al [5, 6] studies the solid complexes of Pr(III) and Nd(III) from mononucleotide and mononucleosides were dissolved in 80:20 organic solvents(DMF:H_2O, MeOH:H_2O, MeCN:H_2O) 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 determined from the observed *4f-4f* transition indicate minor coordination changes around Pr (III) & Nd(III) as a result of slight differences in the binding capabilities of these structurally related ligands. This change depends on the nature of solvents mixture and varying affinities of ligands.

In the present research work, I have prepared the $[Pr(ttfa)_3(H_2O)_2]$ complex and their adducts with structurally related nitrogen donor ligands like pyridine, chloropyridine and bromopyridine, 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 and Judd Oflet intensity parameters have been computed on computer using partial multiple regression analysis, which gives information about the nature of bonding between lanthanide metal and ligands complexes.

MATERIALS AND METHODS

Pr(III) chloride heptahydrated of 99.9% purity from M/s Rare Earths India Ltd. Thenoyltrifluoroacetone of AR grade from Sigma chemicals, nitrogen donor ligands viz., pyridine, chloropyridine and bromopyridine 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 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} Molar.

Synthesis of [Pr (TTFA)$_3$(H$_2$O)$_2$]
Pr(III) chloride heptahydrate 3.74gm was dissolved in distilled water, the methanolic solution of Thenoyltrifluoroacetone 6.67gm 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)$_3$ (py)$_2$]
The [Pr (TTFA)$_3$ (H$_2$O)$_2$] of 6.67gm added into methanolic solution of **1.6** 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 microcrystalline solid obtained was purified by recrystallization form methanol, the chloropyridine and bromopyridine 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 Table2. 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 $4f^n$ 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 [10, 11] (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,

$$\mathbf{Ej[F_k\ \xi_{4F}] = E_{oj}\ [F_k{}^o\xi_{4f}] + \sum \left[\frac{\delta E_j}{\delta F_k}\right]\Delta F_k + \left[\frac{\delta E_j}{\delta\xi_{4f}}\right]\Delta\xi_{4f}}$$
$$\mathbf{k= 2, 4, 6}$$

Where, E_{oj} is the zero order energy of the jth level is given by Wong [12, 13]. The zero order energy values of E_{oj}, partial derivative $\left[\frac{\delta E_j}{\delta F_k}\right]$ and $\left[\frac{\delta E_j}{\delta\xi 4f}\right]$, 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, $$\beta = \frac{F_k^c}{F_k^f}$$

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 [14-16],

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

S. P. Sinha [17, 18] introduced another parameter, percentage covalency parameter (δ) as, $\delta = \left[\dfrac{1-\bar{\beta}}{\bar{\beta}}\right] \times 100$

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

$$P_{exp} = 4.6 \times 10^{-9} \, \text{€m}(\bar{v}) \, d\bar{v}$$

Where, €_m is the molar extinction coefficient of corresponding energy $(\bar{v})$.

RESULTS AND DISCUSSION

The Fig. 1 shows comparative absorption spectra of Pr(III) complexes in acetonitrile. There is marginal red shift of $4f$-$4f$ transition and most intensification observed in [Pr(hfaa)$_3$ (H$_2$O)$_2$]. The enhancement is more in case of chloropyridine (Clpy) indicating a better ligand than bromopyridine (Brpy) when recorded in methanol. The intensity of $^3H_4 \rightarrow {}^3P_2$, $> {}^3H_4 \rightarrow {}^3P_1 > {}^3H_4 \rightarrow {}^3P_0 > {}^3H_4 \rightarrow {}^1D_2$ [19, 26].
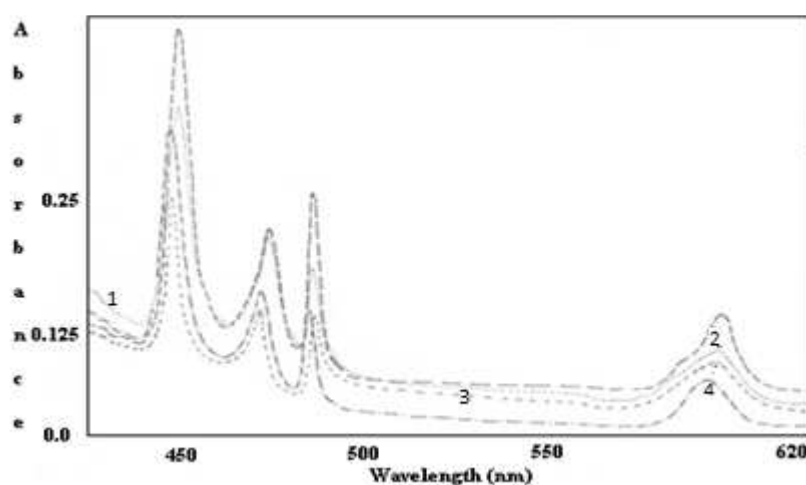
Fig. 1 Comparative absorption spectra of 1)[Pr(ttfa)$_3$(H$_2$O)$_2$] 2) [Pr(ttfa)$_3$(py)$_2$] 3) [Pr(ttfa)$_3$(Clpy)$_2$] and 4) [Pr(ttfa)$_3$(Brpy)$_2$], complexes in acetonitrile

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

Table 1 show the obs. and cal. values of M. W. of Pr (III) complexes

Complexes	Cal. MW	Obs. MW
Pr (ttfa)$_3$(H$_2$O)$_2$	861.477	860.566
Pr (ttfa)$_3$(py)$_2$	1019.657	1017.563
Pr (ttfa)$_3$(clpy)$_2$	1088.578	1087.110
Pr (ttfa)$_3$(brpy)$_2$	1177.484	1075.889

Table 2 shows the observed and calculated values of analytical data where as 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 120.30 to 155.97, clearly shows that accuracy in the various energy interaction parameters,

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

Complexes	% metal		%Carbon		% Hydrogen		% Nitrogen	
	Obs	Cal	Obs	Cal	Obs	Cal	Obs	Cal
Pr (ttfa)$_3$(H$_2$O)$_2$	17.03	16.24	34.01	32.81	2.24	1.85	-	-
Pr (ttfa)$_3$(py)2	14.90	13.06	42.15	40.97	2.58	2.22	2.89	2.31
Pr (ttfa)$_3$(clpy)2	13.89	12.40	39.31	37.60	2.41	1.81	2.69	2.16
Pr (ttfa)$_3$(brpy)2	12.80	11.09	34.20	34.18	2.22	2.10	2.48	2.08

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 (ttfa)$_3$(H$_2$O)$_2$	22482	22303	21312	21168	20746	20743	16857	17068	155.97
Pr (ttfa)$_3$(py)$_2$	22461	22290	21294	21156	20733	20731	16854	17057	149.75
Pr (ttfa)$_3$(clpy)$_2$	22456	22285	21285	21151	20733	20734	16857	17055	146.97
Pr(ttfa)$_3$(brpy)$_2$	22471	22300	21299	21165	20742	20739	16866	17065	147.32
DMF									
Pr (ttfa)$_3$(H$_2$O)$_2$	22441	22264	21272	21113	20712	20710	16832	17022	152.24
Pr (ttfa)$_3$(py)$_2$	22431	22254	21272	21151	20712	20708	16823	17016	144.25
Pr (ttfa)$_3$(clpy)$_2$	22426	22243	21253	21112	20703	20700	16818	17016	150.20
Pr(ttfa)$_3$(brpy)$_2$	22421	22230	21258	21151	20669	20708	16815	17033	120.30
CH$_3$CN									
Pr (ttfa)$_3$(H$_2$O)$_2$	22527	22333	21344	21188	20755	20734	16949	17084	141.39
Pr (ttfa)$_3$(py)$_2$	22492	22371	21326	21183	20738	20736	16880	17079	150.56
Pr (ttfa)$_3$(clpy)$_2$	22476	22314	21317	21170	20738	20737	16866	17069	149.21
Pr(ttfa)$_3$(brpy)$_2$	22497	22331	21317	21186	20745	20744	16891	17084	148.73

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) of Pr (III) complexes were less than unity. The value of bonding parameters ($b^{1/2}$) were varies from 0.123 to 0.131 and which is positive indicate covalent bonding between Pr (III) metal and ligands.

S. N. Misra et al [27-31] 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 ,hfaa, acac, ttfa, dbm) and nitrogen donor ligand aniline, bromo aniline 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.

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 (ttfa)$_3$(H$_2$O)$_2$	311.73	43.02	4.71	656.69	0.921	0.128	3.156
Pr (ttfa)$_3$(py)$_2$	311.57	42.99	4.70	656.14	0.925	0.130	3.125
Pr (ttfa)$_3$(clpy)$_2$	311.73	43.00	4.71	654.84	0.933	0.123	3.190
Pr (ttfa)$_3$(brpy)$_2$	311.67	43.00	4.71	653.87	0.925	0.123	3.124
DMF							
Pr (ttfa)$_3$(H$_2$O)$_2$	311.32	42.96	4.70	654.68	0.939	0.123	3.145
Pr (ttfa)$_3$(py)$_2$	311.36	42.97	4.70	654.54	0.941	0.125	3.177
Pr (ttfa)$_3$(clpy)$_2$	311.28	42.98	4.70	650.79	0.940	0.124	3.178
Pr (ttfa)$_3$(brpy)$_2$	311.29	42.96	4.70	650.40	0.939	0.123	3.156
CH$_3$CN							
Pr (ttfa)$_3$(H$_2$O)$_2$	311.32	42.96	4.70	668.12	0.933	0.131	3.562
Pr (ttfa)$_3$(py)$_2$	311.88	42.94	4.69	680.82	0.932	0.132	3.519
Pr (ttfa)$_3$(clpy)$_2$	311.51	42.99	4.71	665.90	0.929	0.128	3.423
Pr (ttfa)$_3$(brpy)$_2$	311.49	42.98	4.71	665.90	0.923	0.128	3.423

Karraker showed that the symmetry coordination number of lanthanide ion could be predicted from the shape, intensity and wavelength of hypersensitive transition in visible region. The energy and oscillator strength of hypersensitive and pseudo hypersensitive transition can be correlated with coordination number [32, 34].All these four transitions of Pr(III) $^3H_4 \rightarrow {}^3P_2$, $^3H_4 \rightarrow {}^3P_1$, $^3H_4 \rightarrow {}^3P_0$ and $^3H_4 \rightarrow {}^1D_2$ are showing substantial variation of oscillator strength which conform the ligand mediated pseudo hypersensitivity of these pseudo hypersensitive transitions. These transitions also show variation in intensification and wavelength which is observed by values of energies at various transitions [35-38].

Table no 5 shows experimental and computed values of Oscillator strength the σ   r m s deviation varies from 0.018 to 3.01.

Table 5 Experimental and computed values of Oscillator strength (Px10^6) in CH3OH, DMF, CH3CN

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 (ttfa)$_3$(H$_2$O)$_2$	19.69	19.91	6.68	3.87	3.82	3.81	7.33	6.00	1.55
Pr (ttfa)$_3$(py)$_2$	49.34	46.87	12.02	10.99	10.83	10.83	15.98	15.86	1.33
Pr (ttfa)$_3$(clpy)$_2$	37.35	37.33	10.33	7.34	7.25	7.25	11.03	11.02	1.49
Pr (ttfa)$_3$(brpy)$_2$	29.69	29.68	10.12	7.35	4.73	7.25	10.85	11.04	1.87
DMF									
Pr (ttfa)$_3$(H$_2$O)$_2$	32.89	32.89	8.44	6.91	6.81	6.81	10.75	10.86	0.77
Pr (ttfa)$_3$(py) $_2$	49.94	49.93	12.08	12.10	11.94	11.94	13.37	13.39	0.018
Pr (ttfa)$_3$(clpy) $_2$	36.21	36.19	10.03	6.78	6.70	6.70	11.32	11.32	1.62
Pr (ttfa)$_3$(brpy)$_2$	30.30	30.29	10.55	6.02	5.93	5.93	10.53	10.53	2.27
CH3CN									
Pr (ttfa)$_3$(H$_2$O)$_2$	15.53	15.52	4.62	2.64	2.61	2.59	4.63	5.62	0.94
Pr (ttfa)$_3$(py) $_2$	41.69	40.47	8.05	5.43	7.35	5.35	11.10	11.10	1.44
Pr (ttfa)$_3$(clpy) $_2$	28.65	28.65	12.18	6.16	6.07	6.07	10.96	10.96	3.01
Pr (ttfa)$_3$(brpy)$_2$	23.24	23.24	6.39	4.06	4.01	4.01	8.85	8.85	1.16

Table no 6 shows Judd Ofelt intensity parameters are derived from the observed oscillator strength and T_4/T_6 varies between 0.112 to 0.219 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 Judd Ofelt parameters (Tx10^{10}) for Pr(III) Complexes in different solvents

Complexes and Solvent	T_2	T_4	T_6	T_4/T_6
CH$_3$OH				
Pr (ttfa)$_3$(H$_2$O)$_2$	66.23	10.63	61.52	0.172
Pr (ttfa)$_3$(py)$_2$	343.8	30.24	153.99	0.196
Pr (ttfa)$_3$(clpy)$_2$	37.69	20.21	117.39	0.172
Pr (ttfa)$_3$ (brpy)$_2$	543.80	20.21	92.09	0.219
DMF				
Pr (ttfa)$_3$(H$_2$O)$_2$	296.23	19.02	103.10	0.184
Pr (ttfa)$_3$(py)$_2$	-265.00	33.35	155.37	0.214
Pr (ttfa)$_3$(clpy)$_2$	184.00	18.74	114.10	0.164
Pr (ttfa)$_3$ (brpy)$_2$	393.80	16.58	95.27	0.174
CH$_3$CN				
Pr (ttfa)$_3$(H$_2$O)$_2$	223.07	7.23	48.92	0.147
Pr (ttfa)$_3$(py)$_2$	-221.90	14.93	132.79	0.112
Pr (ttfa)$_3$(clpy)$_2$	597.69	16.94	89.57	0.189
Pr (ttfa)$_3$ (brpy)$_2$	476.10	11.18	73.27	0.152

CONCLUSION

In our studies the intensity of $^3H_4 \rightarrow {}^3P_2$ is higher than $^3H_4 \rightarrow {}^1D_2$, $^3H_4 \rightarrow {}^3P_1$, $^3H_4 \rightarrow {}^3P_0$ transitions. The comparative absorption spectra of Pr(III) clearly show that all the complexes consist of identical chromophore (LnO$_6$N$_2$) and six oxygen atoms from β–diketone from a strong bond to lanthanide metal, while two lanthanide nitrogen are much weaker. The Pr(III) complexes with thenoyltrifluoroacetone and their adducts with nitrogen donor ligands like pyridine, chloropyridine and bromopyridine complexes shows high degree of intensification to pseudo hypersensitive transitions, in different immediate coordination environment around Pr(III). 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.

REFERENCES

[1] S N Misra, M A Gagnani, I Devi, R S Shukla, *Bio Inorg.Chem. Appl.,* **2004**, 2, 155-192.
[2] C H Evans, *Biochemistry of lanthanides. New York, Plenum.,* **1990,** 120-121.
[3] A A Khan, H A Hussein, K Iftikhar, *Spectrochima Acta Part A Molecular and Bimolecular Spectroscopy.*, **2003**, 59(5), 1051-1059.
[4] H A Huuain, A A Ansari, K Iftikhar, *Spectrochima Acta.* **2004,** A60,873.
[5] S N Misra, S B Mehta, K Venkatasubramaniyan, *Asian J. of Chem. Rev.,* **1991**, 2(2), 100-125.
[6] S N Misra, *J. Indian Chem. Soc*., **1982**, 59, 99-101.
[7] B R Judd, *Phys. Rev*. **1962**,127, 750-761.
[8] G S Oflet, *J. of Chem. Phys*., **1962**, 37,511-521.

[9] B R Judd, *J. of Luminescence*., **1966**, 18 (19), 604-608.
[10] G Racha, *Physics Rev*., **1949**, 76, 1352-1365.
[11] G Racha, *Physics Rev*., **1942**, 62,438-462.
[12] E Y Wong, *J. of Chem. Phys*., **1958**, 29,754-761.
[13] E Y Wong, *J. of Chem. Phys*., **1961**, 35, 544-557.
[14] K G Chaudhari, P A Savale, Int. *Research J.Research Analysis and Evolution.,* **2009**,1(3) 4,132-138.
[15] Th David, Ch Sumitra, G C Bag, M Indira Devi, N R Singh, *Spectrochim Acta*., **2006,** 63A,154-160.
[16] N Yaiphaba, Th Devid Singh, M Indira Devi, N R Singh, *Asian J. of Chem*., **2008**, 20(2), 901-914.
[17] S P Sinha, H H Schmidtke, *Mol. Phys*., **1965**, 38, 2190-2198.
[18] S P Sinha, *Spectrochim. Acta*., **1966**, 22A, 57-64.
[19] D E Henrie, G R Choppin, *J. Chem. Phys*., **1968,** 49, 477-481.
[20] S N Misra, S O Sommerer, *Can. J. Chem*., **1992**, 70,46-54.
[21] G R Choppin*, J. of Alloy and Compounds*., **2002**, 344, 55-59.
[22] W T Carnall, P R Field, B G Wybourne, *J. Chem. Phys.,***1968**, 49 ,4424 – 4442.
[23] K G Chaudhari, P A Savale, *Advances In Applided Science Research.,* **2012**, 3(5), 1169-1174.
[24] K G Chaudhari, P A Savale, *Science Research Link*.,**2010, 9** (2), 9-11.
[25] K G Chaudhari, P A Savale, *Archives of Applied Science Research*.,**2011**, 3(6), 327-332.
[26] K G Chaudhari, P A Savale, *Advances In Applided Science Research*. 2012, 3(2), 1895-1899.
[27] S N Misra, W.N. Cabalfin, *Chemica Scripta,*, 1989,29,75-80.
[28] S N Misra, G Josep, K Anjaiah, SHR Abdi*, Indian J. of Biochem.Biophys.,* **1992,** 29, 70-76.
[29] S N Misra, S B Mehta, Bull*. Chem. Soc., Japan*. **1991**, 64,3653-3658.
[30] S N Misra, S B Mehta, Suma Mathew, Koshy John, Proc.*Indian Nata, Sci. Acad*., **1992**, 58A, 29-36.
[31] S N Misra, S B Mehta, K G Chaudhari, CM. Suveerkumar, *Indian J. of Chem,*. **1994**,33A, 893-897.
[32] D G Karrakar, *Inorg. Chem*., **1968**, 7, 473-479.
[33] D G Karrakar, Inorg*. Chem*., **1967**, 6, 1863-897.
[34] D G Karrakar, *Inorgnucl. Chem*., **1971**, 33, 3713-3719.
[35] K G Chaudhari, *Archives of Applied Science Research.***2013,**5(2).98-103.
[36] K G Chaudhari. *Advances In Applided Science Research*.**2013**, 4(3), 295-301
[37] K GChaudhari, *Archives of Applied Science Research.***2013,** 5(3). 74-80.
[38] K G Chaudhari, *Archives of Applied Science Research.* **2013,** 5(5). 94-99.

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