Absorption Spectral Studies on Pr(III) and Nd(III) Metal Complexes with Schiff Base Ligand in Dioxane-water Media

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The interaction of Schiff base ligands, H_2AD, H_2AB, H_2BD, H_2BB and H_2BA with Pr(III) and Nd(III) ion have been studied in different metal-ligand stoichiometry and pH in 20% dioxane-water medium. The absorption spectra have been recorded in visible range. The sharp bands in the spectra have been individually analysed by Gaussian curve analysis and various energy and intensity parameters such as Racah (E^k), Slator-Condon (F_k), Landé (ζ_{4f}), oscillator strength (P) and Judd-Ofelt parameter (T_λ) etc. have been computed using partial and multiple regression methods. The bonding parameter ($b^{1/2}$) and nephalauxetic ratio (β) have been evaluated.

Key Words: Absorption spectra, Pr(III), Nd(III), Complexes, Schiff base.

INTRODUCTION

The sharp line like bonds arising from transitions among different levels of $4f^n$ configuration exhibit red shifts as well as some broadening when lanthanide ion undergoes complexation. The 4f orbitals which lie deep in the core do not generally participate in chemical bonding. However, recent studies have provided definite proof for their involvement in bonding as shown by the intensification of the laporate forbidden 4f-4f transition as well as the shift observed in the energies of the transitions.

A search through literature[4-6] reveals that very little work has been done on electronic spectra of metal ions, Pr(III) and Nd(III) complexes with Schiff base ligands, namely, *o*-(α-benzoylmethylbenzylideneimino) benzoic acid (H_2AD), *o*-(α-2-oxopropyl benzylideneimino) benzoic acid (H_2BD), *o*-(α-2-oxopentylideneimino) benzoic acid (H_2AA), 2-(α-benzoylmethylbenzylideneimino) propanoic acid (H_2BD), 2-(α-2-oxopropyl benzylideneimino) propanoic acid (H_2BB), 3-(α-2-oxopentylideneimino) propanoic acid (H_2BA), in 20% dioxane-water medium. The electronic spectra of the complexes in different metal - ligand stoichiometry (1 : 1, 1 : 2 , 1 : 4 and 1 : 6) have been recorded and various energy and intensity parameters, *viz.*, Slator-Condon, Racah, Landé, oscillator strength, Judd-Ofelt and nephelauxetic ratio have been computed.

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EXPERIMENTAL

The Schiff base ligands have been synthesized by condensation of dibenzoyl methane, benzoyl acetone and acetyl acetone with β-alanine and anthranilic acid, respectively, as per literature procedure[7]. The ligands were characterized by various physico-chemical methods. The sample solutions for recording electronic spectra of Pr(III) and Nd(III) metal ions in the ligand's environment having different metal-ligand (M-L) stoichiometry (1 : 1, 1 : 2, 1 : 4 and 1 : 6) in 20% dioxane-water medium were prepared.

The absorbance measurement of the solutions of different stoichiometry shows maximum absorbance for 1 : 2 metal-ligand ratio in the pH range of 7.5–8.5. Hence, all the different parameters were calculated for this metal-ligand stoichiometry.

All the spectra were recorded in solution in the range of 200–900 nm on a Beckman DU 600 spectrophotometer.

All chemicals and reagents used were of AnalaR or AR grade. The lanthanide acetates were obtained from Indian Rare Earth Ltd., Udyogmandalam, India.

RESULTS AND DISCUSSION

Energy parameters: The energy level structures of 4f configurations arise as a result of coulombic and spin-orbit interactions, which are expressed as electronic repulsion (F_k, E^k) and Landé parameter (ζ_{4f}) respectively. These parameters can be evaluated by solving Taylor series expansion equations[8, 9].

$$E_j(F_k, \zeta_{4f}) = E_{0j}(F_k^\circ, \zeta_{4f}^\circ) + \sum_{k=2,4,6} \frac{\partial E_j}{\partial F_k} \Delta F_k + \frac{\partial E_j}{\partial \zeta_{4f}} \Delta \zeta_{4f}$$

where E_{0j} = the zero order energy of level j.

$$F_k = F_k^\circ + \Delta F_k$$
$$\zeta_{4f} = \zeta_{4f}^\circ + \Delta \zeta_{4f}$$
$$\Delta F_k \ll F_k^\circ, \Delta \zeta_{4f} \ll \zeta_{4f}^\circ$$

The difference between the observed E_j values and zero-order ones, ΔE_j, can be expressed as

$$\Delta E_j = \sum_{k=2,4,6} \frac{\partial E_j}{\partial F_k} \Delta F_k + \frac{\partial E_j}{\partial \zeta_{4f}} \Delta \zeta_{4f}$$

The magnitude of parameters F_2, F_4, F_6 and ζ_{4f} were computed using regression analysis and refined by the least squares techniques.

For all the complexes of both the metal ions the order of Slator-Condon parameter is found to be $F_2 > F_4 > F_6$ and values are summarized in Table-3.

On complexation, contraction or expansion of wave function occurs, which is reflected by changes in values of F_k and ζ_{4f} parameters with respect to the corresponding free ion values. This phenomenon is known as nephelauxetic effect, and can be expressed by the nephelauxetic ratio[10]

$$\beta = \frac{F_k^C}{F_k^f}$$

where C and f refer to the complex and free ion respectively.

The values of nephelauxetic ratio for all the metal complexes were found less than one. The values of this parameter were summarized in Table-3. This indicates that metal-ligand interaction is not merely ionic but there is mixing of metal and ligand orbitals, and hence covalent nature of metal-ligand bond may be concluded.

The bonding parameter ($b^{1/2}$) is also related to nephelauxetic ratio (β) by the relation

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

The values of energies (E) for peaks of various transitions of all metal-ligand complexes are summarized in Tables 1 and 2.

The change in values of all these parameters in all the complexes and also in the various metal and ligand (M-L) ratios (1 : 1, 1 : 2, 1 : 4 and 1 : 6) is not much appreciable. Further, this shows that ligands have little effect on the spectral pattern thereby indicating largely outer sphere (high spin) complexation[11] and also metal-ligand interaction is not merely ionic.

The decrease in the value of the Landé parameter (ζ_{4f}) is more than Slator-Condon (F_k) parameter indicating that the ligands affect the spin-orbit coupling more than the electrostatic repulsion.

Intensity parameter

The intensity of absorption bands was measured in terms of oscillator strength (P), calculated by performing a Gaussian curve analysis of the curve. The oscillator strength (P) of a transition between the ground state $\langle f^N \psi_j |$ to excited state $| f^N \psi_j \rangle$ of the lanthanide ion in solution is given by

$$P_{obs} = \sum_{\lambda = 2, 4, 6} T_\lambda \bar{\nu} \langle f^N \psi_j | | U^{(\lambda)} | | f^N \psi_j \rangle^2 / (2J + 1)$$

where the unit tensor operator $U^{(\lambda)}$ connects the initial and final states through three phenomenological parameters, T_λ ($\lambda = 2, 4, 6$). These parameters are related to the radial part of $4f^N$ wave function, wave function of perturbing configuration and ligand field parameters that characterize them and the immediate environment around the metal ion. These parameters and oscillator strength of all the bands observed in Pr(III)-metal ion complexes and Nd(III)-metal ion complexes are given in Tables 1 and 2.

The Judd-Ofelt parameter (T_2) is found negative in the present case as expected for Pr(III) metal-ion complexes and this may be due to overlapping of f-d transition in the region of f-f transition. The presence of this tail enhances the intensity of $^3P_2$ in the visible region. For the present case the values of T_λ parameters are too low, thereby indicating outer sphere (high spin) complexation.[12] But in Nd(III) metal ion, the T_2 parameter has been considered to be an indication of the immediate coordination environment.

The ratio of Judd-Ofelt parameter T_4/T_6 of Pr(III) complexes and Nd(III) complexes has been found in the range 0.16–0.29 and 0.62–0.97 respectively, suggesting that coordination is through the oxygen and nitrogen donor atoms.

The highest values of oscillator strength have been found for 1 : 2 metal-ligand

TABLE-1

OSCILLATOR STRENGTH AND ENERGY (cm^{-1}) AND JUDD-OFELT PARAMETERS OF Pr(III) IONS WITH DIFFERENT LIGANDS IN 1 : 2 METAL-LIGAND STOICHIOMETRY

Ligand	Oscillator strength and energy	Energy levels				$\pm\sigma_{r.m.s}$	Judd-Ofelt parameter			
		$^1D_2$	$^3P_0$	$3P_1$	$^3P_2$		$T_2\times10^{10}$	$T_4\times10^{10}$	$T_6\times10^{10}$	T_4/T_6
H$_2$BD	$P_{exp}\times10^6$	4.580	3.961	5.300	13.450	0.45×10^{-6}	-48.28	12.87	44.59	0.29
	$P_{cal}\times10^6$	4.851	4.581	4.670	13.450					
	E_{exp}	16960	20730	21242	22537	111.107				
	E_{cal}	17096	20724	21204	22366					
H$_2$BB	$P_{exp}\times10^6$	5.375	4.312	6.818	18.292	1.09×10^{-6}	-64.9	8.96	53.95	0.16
	$P_{cal}\times10^6$	4.472	3.209	5.687	17.203					
	E_{exp}	16960	20721	21240	22534	109.59				
	E_{cal}	17095	20715	21198	22366					
H$_2$BA	$P_{exp}\times10^6$	6.618	5.537	10.737	19.027	1.57×10^{-6}	-59.41	10.99	53.67	0.20
	$P_{cal}\times10^6$	5.311	3.939	9.096	17.290					
	E_{exp}	16954	20724	21236	22530	117.55				
	E_{cal}	17113	20723	21222	23399					

TABLE-1 (*contd.*)

Ligand	Oscillator strength and energy	¹D₂	³P₀	³P₁	³P₂	±σ$_{r.m.s}$	T₂ × 10¹⁰	T₄ × 10¹⁰	T₆ × 10¹⁰	T₄/T₆
H₂AD	P$_{exp}$ × 10⁶	2.908	1.473	4.204	13.042	0.94 × 10⁻⁶				
	P$_{cal}$ × 10⁶	2.908	2.792	2.853	13.042		−1.17	7.82	44.35	0.18
	E$_{exp}$	16960	20732	21244	22543	111.23				
	E$_{cal}$	17098	20726	21204	22368					
H₂AB	P$_{exp}$ × 10⁶	4.812	4.098	6.878	15.432	0.84 × 10⁻⁶				
	P$_{cal}$ × 10⁶	4.108	3.238	5.996	14.496		−28.40	9.03	45.04	0.20
	E$_{exp}$	16956	20729	21267	22540	113.65				
	E$_{cal}$	17101	20724	21207	22375					
H₂AA	P$_{exp}$ × 10⁶	4.818	4.098	6.870	16.285	0.48 × 10⁻⁶				
	P$_{cal}$ × 10⁶	4.407	3.603	6371	15.747		−59.41	10.99	53.67	0.20
	E$_{exp}$	16954	20722	21238	22530	111.57				
	E$_{cal}$	17092	20716	21194	22360					

The ¹D₂, ³P₀, ³P₁, ³P₂ columns fall under the heading **Energy levels**; the T₂, T₄, T₆, T₄/T₆ columns fall under the heading **Judd-Ofelt parameter**.

TABLE-2
OSCILLATOR STRENGTH AND ENERGY (cm⁻¹) AND JUDD-OFELT PARAMETERS OF Nd(III) IONS WITH DIFFERENT LIGANDS IN 1 : 2 METAL-LIGAND STOICHIOMETRY

Ligand	Oscillator strength and energy	$^2P_{1/2}$	$^4G_{11/2}$	$^2G_{9/2}$	$^4G_{9/2}$	$^4G_{7/2}$	$^4G_{5/2}$	$^4F_{9/2}$	$^4F_{7/2}$	$^4F_{5/2}$	$^4F_{3/2}$	$\pm\sigma_{r.m.s}$	$T_2 \times 10^{10}$	$T_4 \times 10^{10}$	$T_6 \times 10^{10}$	T_4/T_6
H₂BD	$P_{exp} \times 10^6$	1.422	1.348	1.386	1.700	4.412	20.872	0.468	5.372	6.522	2.706	0.61×10^{-6}	9.63	7.02	8.09	0.86
	$P_{cal} \times 10^6$	0.662	0.230	1.790	0.470	4.200	20.660	0.620	5.120	6.230	0.230					
	E_{exp}	23148	21570	21349	19486	19128	17283	14719	13423	12484	11455	75.538				
	E_{cal}	23157	21570	21282	19603	19250	17221	14782	13300	12468	11430					
H₂BB	$P_{exp} \times 10^6$	1.642	1.248	1.971	2.210	5.028	23.290	0.571	7.451	8.901	2.702	0.71×10^{-6}	10.90	7.71	12.30	0.62
	$P_{cal} \times 10^6$	0.661	0.302	2.154	0.582	4.771	23.120	0.872	7.412	8.301	2.812					
	E_{exp}	23148	21617	21310	19520	19120	17300	14670	13300	12484	11450	66.734				
	E_{cal}	23144	21519	21253	19581	19248	17234	14744	13277	12453	11435					
H₂BA	$P_{exp} \times 10^6$	1.418	1.252	1.078	1.702	4.742	24.013	0.429	5.680	8.152	2.178	0.73×10^{-6}	11.33	8.61	10.41	0.83
	$P_{cal} \times 10^6$	0.732	0.283	2.112	0.560	4.908	24.302	0.772	6.412	7.661	2.930					
	E_{exp}	23148	21617	21322	19531	19120	17301	14662	13315	12496	11455	69.380				
	E_{cal}	23143	21524	21261	19589	19258	17243	14745	13280	12456	11440					

TABLE-2 (*contd.*)

| Ligand	Oscillator strength and energy	Energy levels										±σ_r.m.s	Judd-Ofelt parameter			
		$^2P_{1/2}$	$^4G_{11/2}$	$^2G_{9/2}$	$^4G_{9/2}$	$^4G_{7/2}$	$^4G_{5/2}$	$^4F_{9/2}$	$^4F_{7/2}$	$^4F_{5/2}$	$^4F_{3/2}$		$T_2 \times 10^{10}$	$T_4 \times 10^{10}$	$T_6 \times 10^{10}$	T_4/T_6
H$_2$AD	$P_{exp} \times 10^6$	1.828	1.387	0.658	0.936	4.032	18.921	0.899	5.422	3.392	1.972	1.78×10^{-6}				
	$P_{cal} \times 10^6$	0.592	0.246	1.812	0.470	4.132	21.200	0.658	0.952	6.790	2.380		2.22	10.2	13.8	0.73
	E_{exp}	23148	21626	21331	19501	19128	17295	14693	13441	12484	11468	78.296				
	E_{cal}	23152	21581	21262	19607	19253	17245	14780	13310	12480	11445					
H$_2$AB	$P_{exp} \times 10^6$	0.978	0.372	2.302	0.818	5.762	21.412	0.952	7.012	9.301	3.352	0.21×10^{-6}				
	$P_{cal} \times 10^6$	0.992	0.333	2.546	0.646	5.452	21.432	0.826	7.212	9.024	3.674		8.34	11.19	11.77	0.95
	E_{exp}	23148	21600	21349	19520	19140	17280	14693	13420	12484	11468	72.328				
	E_{cal}	23152	21567	21283	19610	19265	17242	14775	13301	12472	11442					
H$_2$AA	$P_{exp} \times 10^6$	1.012	0.418	2.352	0.881	5.928	21.860	0.952	7.168	9.580	3.482	0.21×10^{-6}				
	$P_{cal} \times 10^6$	1.032	0.339	2.632	0.662	5.640	21.886	0.842	7.392	9.291	3.812		8.37	11.66	12.04	0.97
	E_{exp}	23148	21617	21310	19520	19120	17300	14670	13300	12484	11452	66.759				
	E_{cal}	23144	21519	21253	19582	19249	17235	14743	13277	12453	11435					

TABLE-3

RACAH, SLATOR-CONDON AND AVERAGE BONDING PARAMETERS OF Pr(III) AND Nd(III) IONS WITH DIFFERENT LIGANDS IN 1 : 2 METAL–LIGAND STOICHIOMETRY

Ligand	Metal	Racah parameters (E^k) (cm^{-1})					Slator-Condon parameters (cm^{-1})					Landé parameter (ζ_{4f})	Nephelauxetic ratio (β)	Bonding parameter ($b^{1/2}$)
		E_1	E_2	E_3	E_1/E_3	E_2/E_3	F_2	F_4	F_6	F_4/F_2	F_6/F_2			
H$_2$BD	Pr(III)	4562.544	23.866	461.295	9.891	5.123×10^{-2}	310.762	42.900	4.696	0.1380	0.0151	682.216	0.9648	0.1326
	Nd(III)	5044.686	23.216	491.141	10.141	4.727×10^{-2}	327.790	51.832	5.236	0.1581	0.0159	876.790	0.9898	0.0713
H$_2$BB	Pr(III)	4559.616	23.851	460.999	9.891	5.173×10^{-2}	310.562	47.873	4.692	0.1380	0.0151	684.932	0.9642	0.1337
	Nd(III)	5053.175	22.960	492.100	10.268	4.665×10^{-2}	327.375	52.424	5.220	0.1601	0.0159	863.565	0.9895	0.0755
H$_2$BA	Pr(III)	4558.001	23.843	460.836	9.891	5.173×10^{-2}	310.452	42.858	4.691	0.1380	0.0151	692.954	0.9638	0.1344
	Nd(III)	5052.869	22.884	492.453	10.260	4.647×10^{-2}	327.199	52.567	5.209	0.1606	0.0159	862.423	0.9890	0.0773
H$_2$AD	Pr(III)	4562.865	23.868	461.327	9.891	5.173×10^{-2}	310.784	42.904	4.696	0.1380	0.0151	682.394	0.9648	0.1324
	Nd(III)	5041.511	23.310	491.951	10.248	4.730×10^{-2}	328.246	51.675	5.224	0.1574	0.0159	874.794	0.9912	0.0663
H$_2$AB	Pr(III)	4561.418	23.860	461.181	9.891	5.173×10^{-2}	310.685	42.890	4.694	0.1380	0.0151	685.066	0.9645	0.1330
	Nd(III)	5045.603	23.057	492.028	10.254	4.686×10^{-2}	327.502	52.159	5.213	0.1592	0.0159	871.587	0.9889	0.0743
H$_2$AA	Pr(III)	4560.747	23.857	461.112	9.891	5.173×10^{-2}	310.639	42.884	4.693	0.1380	0.0151	682.619	0.9644	0.1331
	Nd(III)	5053.303	22.958	492.144	10.268	4.665×10^{-2}	327.381	52.431	5.220	0.1601	0.0159	863.388	0.9885	0.1116

stoichiometry in the pH range of 7.5–8.5 in both the complexes; so it can be inferred that 1 : 2 metal-ligand stoichiometry in the pH range of 7.5–8.5 has more molecular stacking and molecular association, thereby indicating favourable stereo-environment around the metal ion for complexation.

Hence, at large it may be concluded that interaction of Pr(III) and Nd(III) ions with the Schiff base ligands has not been ionic but covalent and on the basis of oscillator strength the order of covalency may be given as

$$H_2AD < H_2BD < H_2AB < H_2AA < H_2BB < H_2BA$$
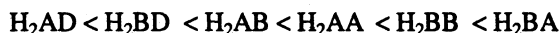
The complexation and covalency have been found related to spectral intensity (*i.e.*, oscillator strength). The metal-ligand stoichiometry affects the oscillator strength. Higher the value of oscillator strength, higher will be the complexation and covalency. This is in agreement with earlier findings[4,9].

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REFERENCES

1. C.K. Jorgensen, *Structure and Bonding*, 1, 3 (1996).
2. W.T. Carnall, P.R. Field and K. Ranjak, *J. Chem. Phy.*, **49**, 4412, 4424, 4443, 4447, 4500 (1968).
3. S.P. Tandon, and P.C. Mehta, *J. Chem. Phys.*, **52**, 4313 (1970).
4. U. Shekhawat, K. Mathur and R.P. Mathur, *Asian Chem. Letter*, 3, 300 (1990).
5. S. Giroux, P. Rubine, B. Henry and S. Aury, *Polyhedron*, **19**, 1567 (2000).
6. P. Raut, R. Singhal, S. Limaye and M.C. Saxena, *Proc. Indian Acad. Sci. (Chem. Sci.)*, **108**, 361 (1996).
7. C.P. Gupta, N.K. Sankhla and R.K. Mehta, *J. Inorg. Nucl. Chem.*, **41**, 1392 (1979).
8. R.C. Mathur, S.S.L. Surana and S.P. Tandon, *Indian J. Pure Appl. Phys.*, **17**, 452 (1979).
9. S.S.L. Surana, M. Singh and S.N. Misra, *J. Inorg. Nucl. Chem.*, **42**, 61 (1980).
10. S.N. Misra, N. Kiran and G.G. Talale, *Indian J. Chem.*, **26A**, 309 (1987).
11. G. Joseph, K. Anjaiah, V. Subramanian, H.C. Bajaj and S.N. Mishra, *Indian J. Chem.*, **29A**, 346 (1990).
12. D.E. Henrie, and G.R. Chopping, *J. Chem. Phys.*, **49**, 477 (1968).