

Electronic Spectral Studies of Some Schiff Base Chelates of Pr(III) and Nd(III) Metal Ions in Terms of Energy and Intensity Parameters

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Six Schiff bases, namely, H₂PAA, H₂PBA, H₂PDB, H₂PCA, H₂PCV and H₂PCT have been synthesized from *o*-amino phenol with acetyl acetone, benzoyl acetone and dibenzoyl methane, respectively, and pyrrole-2-carboxaldehyde with β-alanine, L-valine and taurine, respectively, by condensation process. Electronic spectral studies of twelve chelates of metal ions, Pr(III) and Nd(III) with these ligands were carried out in different stoichiometric ratios of metal-ligand in solution. The various energy parameters such as Slater-Condon (F_k) Racah (E^k), Lande (ζ_{4f}) and intensity parameters such as oscillator strength (P), Judd Ofelt parameters (T_λ) have been computed using partial and regression statistical method. The bonding parameter ($b^{1/2}$) and nephelauxetic ratio (β) have also been evaluated.

Key Words: Schiff base chelates, Energy and intensity parameters, Bonding parameters, Nephelauxetic ratio.

INTRODUCTION

Lanthanon(III) ions are known to pose interesting bonding interactions with various types of ligands and therefore these are often used as a spectroscopic probe as surrogates for calcium ion in the studies of biological system as well as diagnostic agent in clinical medicine¹. Much work on metal chelates has been carried out with Schiff bases as nitrogen and oxygen donor ligands^{2, 3}.

A survey of literature⁴⁻⁷ has revealed that no spectroscopic studies have been made on trivalent Pr(III) and Nd(III) ions with six tridentate biprotic ligands derived from *o*-amino phenol with acetyl acetone, benzoyl acetone and dibenzoyl methane, respectively, namely, 2-(α -oxopentylideneimino) phenol (H₂PAA), 2-(α -oxopropylideneimino) phenol (H₂PBA) and 2-(α -benzoylmethylbenzylideneimino) phenol (H₂PDB) and pyrrole-2-carboxaldehyde with (3-alanine, L-valine and taurine respectively, namely, *o*-(2-pyrrolideneimino) propanoic acid (H₂PCA), *o*-(N- α -pyrrolideneimino) isopropyl ethanoic acid (H₂PCV), and *o*-(N- α -pyrrolideneimino) ethane sulphonic acid (H₂PCT), in aqueous media.

The values of the various electronic spectral parameters like Judd-Ofelt (T_λ), Slater-Condon (F_k), Racah (E^k), Lande (ζ_{4f}), oscillator strength (P), nephelauxetic ratio (β) and bonding parameter ($b^{1/2}$), which give useful informations regarding spin-orbital interactions, interelectronic repulsion, nephelauxetic effect and bonding in complexes, have been calculated by using partial and multiple regression method involving the theories given by Slater-Condon, Lande and Judd-Ofelt.

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EXPERIMENTAL

Preparation of ligands

The three ligands H₂PAA, H₂PBA and H₂PDB have been synthesized by refluxing the equimolar solution of (0.01 M) *o*-amino phenol with acetyl acetone, benzoyl acetone and dibenzoyl methane, respectively, and the other three ligands, namely, H₂PCA, H₂PCV and H₂PCT were synthesized by refluxing the equimolar solution of (0.01 M) pyrrole-2-carboxaldehyde with (3-alanine, L-valine and taurine, respectively, in the presence of piperidine as a catalyst on water bath for 2–4 h. The resulting solutions were filtered while hot and dried as per literature procedure⁸.

Preparation of metal-ion solution

Lanthanum acetates have been used for the preparation of metal-ion solution in double-distilled water which were duly standardized by the conventional methods⁹.

Preparation of metal-ligand (sample) solution

The sample solutions were prepared by taking metal and ligand solutions in stoichiometric ratio (M : L) of 1 : 1, 1 : 2, 1 : 4 and 1 : 6 to record the spectra. The electronic absorption spectra of these sample solutions have been recorded on a spectrophotometer in the range of 200–1200 nm. A Beckman D-600 spectrophotometer has been used with a scan speed 600 nm/min. It has been found that the absorbance of the sample solutions having 1 : 2 metal-ligand stoichiometry is maximum and hence for this metal-ligand stoichiometry, pH variation was made in the range of 5–10, to ascertain pH range of maximum molecular stacking that is complexation (in the solution).

RESULTS AND DISCUSSION

Energy parameters

The Slater-Condon (F_k) and Lande (ζ_{4f}) parameters have been calculated using the following equations (1–3) as suggested by Wong^{10, 11}:

$$\Delta E_j = \sum_{(k=2,4,6)} \frac{\partial E_j}{\partial F_k} \Delta F_k + \frac{\partial E_j}{\partial \zeta_{4f}} \Delta \zeta_{4f} \quad (1)$$

$$F_4 = 0.1381F_2 \quad (2)$$

$$F_6 = 0.151F_2 \quad (3)$$

The values of energies for different peaks of various transitions have been summarized in Tables 1 and 2 for Pr(III) and Nd(III) chelates, respectively, and the values of various energy parameters have been shown in Table-3 for both metal chelates.

On the basis of these data it has been found that the values of F_2 parameter (Slater-Condon) decrease from free-ion value, indicating decrease in interelectronic repulsion due to complexation and the values range from 310.495 to 323.961 and 319.133 to 323.447 for Pr(III) and Nd(III) metal chelates, respectively. The order of Slater-Condon parameters has been found to be $F_2 > F_4 > F_6$ and the observed values of F_6/F_2 (0.0151 and 0.0146 to 0.0151) are less than F_4/F_2 (0.1381 and 0.1585 to 0.1675) for Pr(III) and Nd(III) metal chelates, respectively. The decrease in the value of ζ_{4f} (as compared with free ion) clearly suggests the decrease in spin-orbit interactions indicating a general red shift and the value

TABLE-1
 COMPUTED VALUES OF OSCILLATOR STRENGTH, ENERGIES AND INTENSITY PARAMETERS
 OF THE VARIOUS BANDS OBSERVED FOR THE Pr(III) CHELATES WITH DIFFERENT
 LIGANDS FOR 1 : 2 METAL-LIGAND STOICHIOMETRIES

Metal chelates	Oscillator strength and energy	Energy level				r.m.s. deviation $\sigma_{r.m.s.}$	Intensity parameters ($T_{\lambda} \times 10^9$)			
		1D_2	3P_0	3P_1	3P_2		T_2	T_4	T_6	T_4/T_6
Pr(III)-H ₂ PAA	$P_{\text{expt}} \times 10^6$	3.950	3.840	3.990	12.480	$\pm 0.664 \times 10^{-6}$	-11.61	0.615	3.33	0.1842
	$P_{\text{cal}} \times 10^6$	3.907	2.946	3.008	12.435					
	$E_{\text{expt}} (\text{cm}^{-1})$	16972	20730	21290	22558	± 110.684				
	$E_{\text{cal}} (\text{cm}^{-1})$	17115	20725	21225	22402					
Pr(III)-H ₂ PBA	$P_{\text{expt}} \times 10^6$	3.820	3.780	3.940	12.010	$\pm 0.581 \times 10^{-6}$	-11.19	0.604	3.19	0.1891
	$P_{\text{cal}} \times 10^6$	3.786	2.980	3.098	11.990					
	$E_{\text{expt}} (\text{cm}^{-1})$	16966	20738	21351	22548	± 117.459				
	$E_{\text{cal}} (\text{cm}^{-1})$	17125	20737	21240	22418					
Pr(III)-H ₂ PDB	$P_{\text{expt}} \times 10^6$	3.790	3.670	3.820	11.840	$\pm 0.654 \times 10^{-6}$	-10.89	0.569	3.14	0.1810
	$P_{\text{cal}} \times 10^6$	3.695	2.775	2.868	11.828					
	$E_{\text{expt}} (\text{cm}^{-1})$	16958	10738	21336	22533	± 116.492				
	$E_{\text{cal}} (\text{cm}^{-1})$	11711	20736	21228	22399					

TABLE-1 (contd.)

Metal chelates	Oscillator strength and energy	Energy level				r.m.s. deviation $\sigma_{r.m.s.}$	Intensity parameters ($T_\lambda \times 10^9$)			
		1D_2	3P_0	3P_1	3P_2		T_2	T_4	T_6	T_4/T_6
Pr(III)-H ₂ PCA	$P_{expt} \times 10^6$	3.620	3.550	3.780	11.650	$\pm 0.411 \times 10^{-6}$	-10.69	0.603	3.15	0.1911
	$P_{cal} \times 10^6$	3.565	3.004	3.168	11.604					
	$E_{expt} (cm^{-1})$	16963	20751	21354	22563	± 122.061				
	$E_{cal} (cm^{-1})$	17127	20749	21245	22419					
Pr(III)-H ₂ PCV	$P_{expt} \times 10^6$	3.500	3.490	3.710	11.410	$\pm 0.886 \times 10^{-6}$	-10.65	0.616	3.11	0.1981
	$P_{cal} \times 10^6$	3.455	2.343	2.415	11.310					
	$E_{expt} (cm^{-1})$	16972	20751	21313	22563	± 114.108				
	$E_{cal} (cm^{-1})$	17121	20747	21237	22408					
Pr(III)-H ₂ PCT	$P_{expt} \times 10^6$	3.470	3.420	3.630	11.240	$\pm 0.973 \times 10^{-6}$	-10.46	0.592	3.06	0.1933
	$P_{cal} \times 10^6$	3.427	2.063	2.239	11.240					
	$E_{expt} (cm^{-1})$	16952	20743	21336	22520	± 117.352				
	$E_{cal} (cm^{-1})$	17111	20742	21223	22389					

TABLE-2
 COMPUTED VALUES OF OSCILLATOR STRENGTH, ENERGIES AND INTENSITY PARAMETERS OF THE VARIOUS BANDS OBSERVED
 FOR THE Nd(III) CHELATES WITH DIFFERENT LIGANDS FOR 1 : 2 METAL-LIGAND STOICHIOMETRIES

Metal chelates	Oscillator strength and energy	Energy level										r.m.s. deviation $\sigma_{r.m.s.}$	Intensity parameters ($T_\lambda \times 10^9$)				
		$^4F_{3/2}$	$^4F_{5/2}$	$^4F_{7/2}$	$^4F_{9/2}$	$^4F_{9/2}$	$^4G_{5/2}$	$^4G_{7/2}$	$^4G_{9/2}$	$^2K_{1/2}$	$^2G_{9/2}$		$^4G_{11/2}$	T_2	T_4	T_6	T_4/T_6
Nd(III)- H ₂ PAA	$P_{\text{expt}} \times 10^6$	1.076	7.535	6.560	0.554	13.73	6.045	6.041	0.508	1.650	0.503	$\pm 1.099 \times 10^{-6}$	0.3142	0.6292	0.6771	0.9292	
	$P_{\text{cal}} \times 10^6$	2.079	6.715	6.392	0.504	12.97	5.070	5.268	0.271	0.656	0.753						
	$E_{\text{expt}} (\text{cm}^{-1})$	11461	12494	13448	14702	17316	19142	19493	20986	20920	21191	21612	± 81.80	0.3509	0.5640	0.6751	0.8354
	$E_{\text{cal}} (\text{cm}^{-1})$	11459	12518	13342	14776	17288	19239	19632	20920	21191	21649						
Nd(III)- H ₂ PBA	$P_{\text{expt}} \times 10^6$	1.062	7.001	6.500	0.502	13.50	5.473	5.470	0.471	1.602	0.468	$\pm 1.050 \times 10^{-6}$	0.3509	0.5640	0.6751	0.8354	
	$P_{\text{cal}} \times 10^6$	1.907	9.058	6.335	0.495	12.91	4.678	4.528	0.264	0.614	0.699						
	$E_{\text{expt}} (\text{cm}^{-1})$	11461	12492	13450	14648	17319	19128	19459	20907	21286	21608	± 80.30	0.3509	0.5640	0.6751	0.8354	
	$E_{\text{cal}} (\text{cm}^{-1})$	11440	12499	13320	14754	17266	19227	19617	20891	21183	21618						
Nd(III)- H ₂ PDB	$P_{\text{expt}} \times 10^6$	1.058	6.902	6.021	0.453	12.91	5.012	5.010	0.402	1.541	0.421	$\pm 1.098 \times 10^{-6}$	0.3351	0.5475	0.6499	0.8423	
	$P_{\text{cal}} \times 10^6$	0.008	5.880	6.102	0.476	12.43	4.226	4.079	0.255	0.595	0.672						
	$E_{\text{expt}} (\text{cm}^{-1})$	11461	12492	13450	14684	17319	19412	19478	20986	21322	21622	± 89.60	0.3351	0.5475	0.6499	0.8423	
	$E_{\text{cal}} (\text{cm}^{-1})$	11502	12534	13337	14739	17383	19317	19676	20912	21216	21629						

TABLE-2 (contd.)

Metal chelates	Oscillator strength and energy	Energy level										r.m.s. deviation $\sigma_{r.m.s.}$	Intensity parameters ($T_\lambda \times 10^9$)			
		$4F_{3/2}$	$4F_{5/2}$	$4F_{7/2}$	$4F_{9/2}$	$4G_{5/2}$	$4G_{7/2}$	$4G_{9/2}$	$2K_{15/2}$	$2G_{9/2}$	$4G_{11/2}$		T_2	T_4	T_6	T_4/T_6
Nd(III)- H ₂ PCA	$P_{expt} \times 10^6$	1.052	6.853	5.941	0.402	12.54	4.953	4.950	0.374	1.441	0.394	$\pm 0.853 \times 10^{-6}$	0.3121	0.5539	0.6434	0.8610
	$P_{cal} \times 10^6$	0.357	5.858	6.053	0.471	12.10	4.422	4.575	0.253	0.596	0.675					
	$E_{expt} (cm^{-1})$	11455	12492	13462	14691	17325	19128	19459	20907	21266	21608	± 83.59				
	$E_{cal} (cm^{-1})$	11447	12493	13309	14733	17279	19231	19608	20893	21169	21591					
Nd(III)- H ₂ PCV	$P_{expt} \times 10^6$	1.047	6.800	5.513	0.371	12.00	4.902	4.900	0.321	1.402	0.354	$\pm 0.877 \times 10^{-6}$	0.2317	0.4780	0.5966	0.8021
	$P_{cal} \times 10^6$	0.054	5.836	5.685	0.455	11.62	4.695	4.437	0.250	0.649	0.750					
	$E_{expt} (cm^{-1})$	11468	12494	13441	14663	17301	19139	19478	20955	21313	21621	± 81.68				
	$E_{cal} (cm^{-1})$	11455	12501	13326	14752	17289	19239	19623	20902	21180	21620					
Nd(III)- H ₂ PCT	$P_{expt} \times 10^6$	1.040	6.212	5.001	0.302	11.71	4.511	4.499	0.297	1.001	0.310	$\pm 0.828 \times 10^{-6}$	0.2407	0.4812	0.5409	0.8896
	$P_{cal} \times 10^6$	1.077	5.398	5.174	0.419	11.41	3.961	3.821	0.230	0.613	0.712					
	$E_{expt} (cm^{-1})$	11461	12489	13439	14695	17310	19139	19493	20950	21313	21612	± 76.94				
	$E_{cal} (cm^{-1})$	11453	12512	13335	14766	17282	19233	19626	20900	21181	21638					

TABLE-3
 COMPUTED VALUES OF SLATER-CONDON (F_k), LANDE (ζ_{4f}) RACAHA (E^k) (ALL IN cm^{-1}), NEPHELAUXETIC RATIO (β) AND BONDING PARAMETERS ($b^{1/2}$) FOR Pr(III) AND Nd(III) CHELATES WITH DIFFERENT LIGANDS FOR 1 : 2 METAL-LIGAND STOICHIOMETRIES

Metal ion	Ligand	Slater-Condon parameters					Lande Parameter (ζ_{4f})	Racah Parameters					Nephelauxetic ratio	Bonding parameters
		F_2	F_4	F_6	F_4/F_2	F_6/F_2		E^1	E^2	E^3	E^1/E^3	E^2/E^3		
Pr(III)	H ₂ PAA	310.495	42.864	4.692	0.1381	0.0151	692.889	4558.632	23.846	460.899	9.891	0.0517	0.9640	0.1341
	H ₂ PBA	310.609	42.880	4.693	0.1381	0.0151	694.586	4560.290	23.855	461.067	9.891	0.0517	0.9643	0.1335
	H ₂ PDB	310.757	42.900	4.696	0.1381	0.0151	688.913	4562.470	23.866	461.288	9.891	0.0517	0.9648	0.1326
	H ₂ PCA	310.873	42.916	4.697	0.1381	0.0151	691.244	4564.170	23.875	461.459	9.891	0.0517	0.9651	0.1319
	H ₂ PCV	310.925	42.923	4.698	0.1381	0.0151	688.344	4564.942	23.879	461.537	9.891	0.0517	0.9653	0.1316
	H ₂ PCT	310.961	42.923	4.699	0.1381	0.0151	684.073	4565.510	23.882	461.595	9.891	0.0517	0.9654	0.1314
Nd(III)	H ₂ PAA	323.447	50.294	4.899	0.1585	0.0151	880.729	4922.012	22.650	493.064	9.983	0.0459	0.9710	0.1387
	H ₂ PBA	321.333	50.701	4.827	0.1609	0.0151	878.056	4900.682	22.217	492.559	9.949	0.0451	0.9703	0.1368
	H ₂ PDB	319.133	53.455	4.668	0.1675	0.0146	855.527	4892.568	21.271	497.198	9.840	0.0428	0.9636	0.1347
	H ₂ PCA	319.153	52.108	4.818	0.1623	0.0150	869.791	4906.969	22.062	493.332	9.947	0.0447	0.9697	0.1229
	H ₂ PCV	319.981	51.803	4.840	0.1609	0.0150	874.151	4910.639	22.273	493.413	9.952	0.0451	0.9722	0.1177
	H ₂ PCT	319.931	51.412	4.865	0.1594	0.0151	879.530	4911.137	22.495	491.968	9.962	0.0456	0.9714	0.1134

ranges from 684.073 to 694.586 and 855.527 to 880.729 for Pr(III) and Nd(III) metal chelates, respectively.

Nephelauxetic ratio (β) and Bonding parameter ($b^{1/2}$)

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

$$b^{1/2} = [(1 - \beta)/2]^{1/2} \quad (4)$$

and the values of these have been listed in Table-3. From these values it has been found that the nephelauxetic ratios (β) for all the systems are less than one indicating that the metal-ligand interaction is not ionic but there is a mixing of metal and ligand orbitals, *i.e.*, the metal-ligand bonding in these chelates is not mere ionic but there is covalency in them.

Intensity parameters

The oscillator strength of each band has been computed using the following equation:

$$P_{\text{obs}} = 4.6 \times 10^{-9} \times \epsilon_{\text{max}} \times \Delta\nu_{1/2} \quad (5)$$

where $\Delta\nu_{1/2}$ is half band width and ϵ_{max} is molar extinction coefficient.

The solution spectra have been analyzed by resolving each band into Gaussian curve shape to enable evaluation of oscillator strength. The bands for different transitions have been identified by comparing the values of energies with corresponding energy level in free metal ion. The small r.m.s. deviation ($\sigma_{\text{r.m.s.}}$) for Pr(III) and Nd(III) metal-chelates between experimental and calculated values of oscillator strength (± 0.411 to 0.97×10^{-6} and ± 110.684 to 122.061), respectively, are listed in Tables 1 and 2 indicating the suitability of relation used.

The oscillator strength values which are a measure of intensities of specific electronic transitions or degree to which a specific transition is allowed, show marked dependence on the cation environment¹². The oscillator strength values besides several minor interactions are composed of prominently three main parameters known as Judd-Ofelt parameters (T_2 , T_4 and T_6). The values of these parameters are listed in Tables 1 and 2 for Pr(III) and Nd(III) metal chelates, respectively.

The Judd-Ofelt equation for experimentally observed oscillator strength is given by

$$P_{\text{obs}} = T_2\nu[U^{(2)}]^2 + T_4\nu[U^{(4)}]^2 + T_6\nu[U^{(6)}]^2 \quad (6)$$

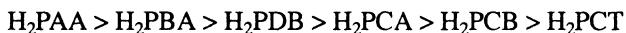
where ν is energy of the band (cm^{-1}), T_2 , T_4 and T_6 are Judd-Ofelt parameters.

There is much variation in Judd-Ofelt parameters (T_2 , T_4 and T_6) and these values follow the order $T_2 < T_4 < T_6$ which is in good agreement with the lanthanon metal ion characteristics¹³. These parameters show a marked difference in the values of Pr(III) and Nd(III) metal chelates. Higher values of T_6 for Pr(III) metal chelates than Nd(III) metal chelates is due to the large cation size of Pr(III) metal ion than that of Nd(III) metal ion, which may experience a greater disturbance of hydration sphere as a result of intimate Pr(III) and Nd(III)-ligand contact on chelation. Similarly the smaller values of T_2 parameters of Pr(III) than that of Nd(III) may be due to the increased covalent interaction with decreased cationic size due to lanthanon contraction^{12, 14}. In lanthanons the 4f-orbitals are deep seated and thus are less available for bonding and ligand field stabilization energy effects are also negligible. Under these conditions the Pr(III) and

Nd(III)-ligand interaction are expected to be predominantly ionic. A change from ionic to ionic-covalent bonding is due to lanthanide contraction. The ratio T_4/T_6 indicates the symmetry around the cation and are from 0.1810–0.1981 and 0.8021–0.9292 for Pr(III) and Nd(III) metal chelates respectively. This indicates that there is a very slight change in symmetry around Pr(III) and Nd(III) in the present case.

Conclusion

In all the cases metal-ligand bonding is not merely ionic but the data suggest covalency in them. From the values of various parameters, the order of covalency of Pr(III) and Nd(III) metal-chelates with these ligands are as follows:



On the basis of the above observations it has been found that in all the cases the absorbance values were highest in the solution having 1 : 2 metal-ligand stoichiometry and at pH range 7.5–8.5. Thus it may be concluded that in this condition there is greatest molecular stacking and favourable stereo-environment for complexation and this is also confirmed by using Job's¹⁵ method.

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