

## Oscillator Strength and Intensity Parameters of Sm(III), Ho(III) and Er(III) Metal Complexes with Some Schiff Base Ligand

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The absorption spectra of Schiff base ligands, *o*-( $\alpha$ -benzoyl-methylbenzylideneimino) benzoic acid (H<sub>2</sub>AD), *o*-( $\alpha$ -2-oxopropyl-benzylideneimino) benzoic acid (H<sub>2</sub>AB), *o*-( $\alpha$ -2-oxopentylideneimino) benzoic acid (H<sub>2</sub>AA), 2-( $\alpha$ -benzoyl methylbenzylideneimino) propanoic acid (H<sub>2</sub>BD), 2-( $\alpha$ -2-oxopropylbenzylideneimino) propanoic acid (H<sub>2</sub>BB) and 3-( $\alpha$ -2-oxopentylideneimino) propanoic acid (H<sub>2</sub>BA) with Sm(III), Ho(III) and Er(III) ions have been studied in different metal-ligand stoichiometry in 20% dioxane-water medium. The oscillator strengths for the 4*f*-4*f* multiplet to multiplet transitions are empirically determined from the absorption spectra. The intensity parameters  $T_{\lambda}$  ( $\lambda = 2, 4, 6$ ) for all the complexes were evaluated by applying the Judd-Ofelt theorem to the observed oscillator strengths. The values of the intensity parameters are compared and discussed to investigate the sensitivity of the intensity parameters to the ligand environment.

**Key Words:** Oscillator strength, Intensity parameters, Sm(III), Ho(III), Er(III), Complexes, Schiff Base.

### INTRODUCTION

A great deal of work has been done on the electronic spectra of lanthanide(III) complexes, specially on complexes of oxygen donor ligands in order to understand the factors responsible for the narrow line widths in the absorption spectra and nature of chemical bonding in the complexes. The 4*f* orbitals which lie deep inside the core do not generally participate in chemical bonding.<sup>1-3</sup> However, recent studies have provided definite proof for their involvement in bonding as shown by the intensification of the Laporte forbidden 4*f*-4*f* transition as well as the shift observed in the energies of the transition as compared to free aquo ions.

Lanthanide(III) ions show very characteristic 4*f*-4*f* absorption spectra which correspond to transition from the ground multiplet to the excited multiplet. These transitions are forbidden in principle by an electric dipole moment, but are partially allowed by the induced electric dipole moment. Judd<sup>4</sup> and Ofelt<sup>5</sup> individually derived significant theoretical expressions for the oscillator strength

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of the induced electric dipole moment, taking account of the mixing between the 4f orbitals and other orbitals.

A survey of literature<sup>6,7</sup> revealed that no work has been done on absorption spectra of Sm(III), Ho(III) and Er(III) complexes with bioactive ligands, *i.e.*, Schiff base, namely, *o*-( $\alpha$ -benzoylmethylbenzylideneimino) benzoic acid (H<sub>2</sub>AD), *o*-( $\alpha$ -2-oxopropylbenzylideneimino) benzoic acid (H<sub>2</sub>AB), *o*-( $\alpha$ -2-oxopentylideneimino) benzoic acid (H<sub>2</sub>AA), 2-( $\alpha$ -benzoyl methylbenzylideneimino) propanoic acid (H<sub>2</sub>BD), 2-( $\alpha$ -2-oxopropylbenzylideneimino) propanoic acid (H<sub>2</sub>BB) and 3-( $\alpha$ -2-oxopentylideneimino) propanoic acid (H<sub>2</sub>BA). The absorption spectra of the complexes in different metal-ligand stoichiometry and pH range in 20% dioxane-water medium have been recorded. The maximum absorbance has been observed for the sample solution having 1 : 2 metal-ligand stoichiometry in the pH range 7.5-8.5 for all the metal complexes. So, the oscillator strength and Judd-Ofelt parameters have been computed using absorbance for 1 : 2 metal-ligand stoichiometry employing partial regression method.

## EXPERIMENTAL

The Schiff base ligands have been synthesized by condensation of dibenzoylmethane, benzoylacetone and acetyl acetone with  $\beta$ -alanine and anthranilic acid, respectively, as per literature procedure<sup>8</sup>. The ligands thus obtained (H<sub>2</sub>AD, H<sub>2</sub>AB, H<sub>2</sub>AA, H<sub>2</sub>BD, H<sub>2</sub>BB and H<sub>2</sub>BA) were characterized and identified.

The sample solutions for recording absorption spectra of Sm(III), Ho(III) and Er(III) metal ions in the ligand environment having different metal-ligand (M : L) stoichiometry, 1 : 1, 1 : 2, 1 : 4 and 1 : 6 and pH ranges 5.5-6.5, 6.5-7.5, 7.5-8.5, 8.5-9.5 (1 : 2 M : L ratio only) in 20% dioxane-water medium have been prepared.

The absorbance measurements of the sample solutions in different stoichiometry show maximum absorbance for the sample solution having 1 : 2 metal-ligand ratio in the pH range of 7.5 to 8.5.

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

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

## RESULTS AND DISCUSSION

The absorption spectra of Sm(III), Ho(III) and Er(III) complexes were measured in near UV-Vis wavelength range. The intensity of absorption band 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  $\langle f^N \psi_j |$  excited state  $| f^N \psi'_j \rangle$  of the lanthanide ion solution is given by<sup>4,5</sup>

$$P_{\text{obs}} = \sum T_{\lambda} \bar{\nu} \langle f^N \psi_j | U^{(\lambda)} | \psi'_j \rangle^2 / (2j + 1) \quad (\lambda = 2, 4, 6)$$

where  $\bar{\nu}$  is the transition energy (expressed in wavenumbers),  $\langle f^N \psi_j | U^{(\lambda)} | f^N \psi'_j \rangle$  are the reduced matrix elements of the unit tensor operator

$U^{(\lambda)}$ , connecting the initial and final states of transition and  $T_\lambda$  parameters are generally called Judd-Ofelt intensity parameters. These parameters are related to the radial part of  $4f^n$  wave function, wave function of perturbing configuration and ligand field parameters that characterised them and the immediate environment around the metal ion.

The three Judd-Ofelt intensity parameters ( $T_2$ ,  $T_4$  and  $T_6$ ) were obtained from the empirically determined oscillator strength by the partial and multiple regression method. The values of oscillator strengths have been computed by the relation

$$P_{\text{obs}} = 4.6 \times 10^{-9} \times \varepsilon_m \times \Delta\bar{\nu}_{1/2}$$

where  $\varepsilon_m$  = molar extinction coefficient and  $\Delta\bar{\nu}_{1/2}$  = half band width

The value of oscillator strength of each band is recalculated from the values of  $T_2$ ,  $T_4$  and  $T_6$  computed by using the relation<sup>4,5</sup>

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

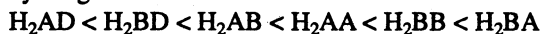
The computed values of oscillator strengths ( $P_{\text{obs}}$  and  $P_{\text{cal}}$ ) and Judd-Ofelt parameters of all the bands observed in Sm(III), Ho(III) and Er(III) metal ion complexes have been summarised in Tables 1–3.

The r.m.s. deviation ( $\sigma$ ) between  $P_{\text{obs}}$  and  $P_{\text{cal}}$  of Sm(III), Ho(III) and Er(III) have been found to be 0.054–0.148, 0.209–0.302 and 0.340–0.706, respectively. The low values of r.m.s. deviations for all the complexes support the applicability of Judd-Ofelt theory of f-f transition for lanthanides.

The Judd-Ofelt intensity parameters  $T_\lambda$  ( $\lambda = 2, 4, 6$ ) for Sm(III), Ho(III) and Er(III) complexes with Schiff base ligands have been determined to demonstrate the sensitivity of these parameters to the coordination environment. Among the three ( $T_2$ ,  $T_4$  and  $T_6$ ) parameters,  $T_2$  is the most sensitive to co-ordination environment. The sensitivity of  $T_2$  to the coordination environment appears from the matrix element of  $U^{(2)}$  which is only determined from the electronic states in the ground and excited states of free ion.

The ratios of Judd-Ofelt parameters  $T_4/T_6$  for Sm(III), Ho(III) and Er(III) complexes have been found in the range 0.978–1.180, 0.808–0.917 and 0.845–1.183, respectively suggesting the co-ordination is through the oxygen and nitrogen donor atoms<sup>9</sup>.

The highest values of oscillator strength have been found for 1 : 2 metal-ligand stoichiometry in the pH range 7.5–8.5 in all the complexes; so it can be inferred that 1 : 2 metal-ligand stoichiometry in the pH range 7.5–8.5 has more molecular staking and molecular association, thereby indicating favourable stereoenvironment around metal ions for complexation. Hence, it may be concluded that interactions of Sm(III), Ho(III) and Er(III) ion with the Schiff base ligands have not been merely ionic but covalent and on the basis of oscillator strength the order of covalency may be given as



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 oscillator strength, higher will be complexation and covalency. This is in agreement to earlier findings<sup>10</sup>.

TABLE-1  
 OSCILLATOR STRENGTH AND JUDD-OFFELT PARAMETERS OF Sm(III) IONS WITH DIFFERENT LIGANDS  
 IN 1 : 2 METAL-LIGAND STOICHIOMETRY

Ligand	Oscillator strength	Energy Level										Judd-Ofelt parameters				$\pm\sigma_{rms}$
		${}^6P_{7/2}$	${}^4L_{15/2}, {}^4K_{11/2}$	${}^6P_{3/2}$	$({}^6P, {}^4P_{5/2})$	${}^4G_{9/2}$	${}^4I_{13/2}$	${}^4M_{15/2}, {}^4P_{11/2}$	${}^4G_{7/2}$	${}^4G_{5/2}$	$T_2 \times 10^9$	$T_4 \times 10^9$	$T_6 \times 10^9$	$T_4/T_6$		
H <sub>2</sub> AD	$P_{exp} \times 10^6$	1.667	0.155	6.122	1.509	0.223	0.369	0.947	0.171	0.138	4.662	0.745	0.762	0.978	$0.071 \times 10^{-6}$	
	$P_{cal} \times 10^6$	1.590	0.141	6.108	1.351	0.186	0.467	0.919	0.128	0.093						
H <sub>2</sub> AB	$P_{exp} \times 10^6$	1.786	0.145	7.410	1.681	0.304	0.416	0.999	0.164	0.129	4.841	0.904	0.829	1.091	$0.056 \times 10^{-6}$	
	$P_{cal} \times 10^6$	1.729	0.154	7.397	1.620	0.205	0.518	0.987	0.144	0.105						
H <sub>2</sub> AA	$P_{exp} \times 10^6$	2.019	0.155	8.047	1.819	0.400	0.429	1.018	0.175	0.163	3.210	0.965	0.923	1.046	$0.090 \times 10^{-6}$	
	$P_{cal} \times 10^6$	1.919	0.171	8.010	1.762	0.222	0.573	0.996	0.140	0.104						
H <sub>2</sub> BD	$P_{exp} \times 10^6$	1.686	0.168	6.979	1.597	0.263	0.395	0.986	0.171	0.141	5.433	0.856	0.774	1.106	$0.054 \times 10^{-6}$	
	$P_{cal} \times 10^6$	1.619	0.144	6.957	1.522	0.194	0.485	0.965	0.142	0.104						
H <sub>2</sub> BB	$P_{exp} \times 10^6$	2.038	0.154	9.681	1.894	0.435	0.451	1.071	0.175	0.142	4.923	1.084	0.952	1.138	$0.109 \times 10^{-6}$	
	$P_{cal} \times 10^6$	1.989	0.176	9.658	2.088	0.240	0.612	1.103	0.170	0.126						
H <sub>2</sub> BA	$P_{exp} \times 10^6$	2.197	0.177	10.667	1.949	0.472	0.505	1.140	0.187	0.172	5.334	1.220	1.030	1.184	$0.148 \times 10^{-6}$	
	$P_{cal} \times 10^6$	2.148	0.190	10.628	2.294	0.260	0.663	1.192	0.185	0.138						

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

Ligand	Oscillator strength	Energy Level										Judd-Ofelt parameters				$\pm\sigma_{rms}$
		$^5G_4$	$(^5G, ^3G)_5$	$^5G_6$	$^3K_8$	$^5F_2$	$^5F_3$	$^5F_4$	$^5F_5$	$5I_4$	$^5I_6$	$T_2 \times 10^9$	$T_4 \times 10^9$	$T_6 \times 10^9$	$T_4/T_6$	
H <sub>2</sub> AD	$P_{exp} \times 10^6$	0.930	2.572	12.033	0.886	1.004	1.325	4.557	3.868	0.042	0.397	0.212	0.219	0.264	0.829	$0.217 \times 10^{-6}$
	$P_{cal} \times 10^6$	0.425	2.838	12.061	1.139	1.073	1.881	4.444	3.783	0.027	0.302					
H <sub>2</sub> AB	$P_{exp} \times 10^6$	1.029	3.167	14.617	1.080	1.273	1.958	5.008	4.063	0.021	0.486	0.273	0.235	0.280	0.839	$0.224 \times 10^{-6}$
	$P_{cal} \times 10^6$	0.453	3.046	14.482	1.233	1.137	1.996	4.750	4.036	0.029	0.321					
H <sub>2</sub> AA	$P_{exp} \times 10^6$	1.071	3.112	15.247	1.417	1.324	1.869	5.066	4.054	0.040	0.489	0.297	0.227	0.281	0.808	$0.265 \times 10^{-6}$
	$P_{cal} \times 10^6$	0.446	2.938	15.046	1.239	1.137	1.998	4.713	3.982	0.029	0.320					
H <sub>2</sub> BD	$P_{exp} \times 10^6$	1.000	2.999	13.977	1.107	1.203	1.810	4.920	4.004	0.044	0.426	0.260	0.228	0.277	0.824	$0.209 \times 10^{-6}$
	$P_{cal} \times 10^6$	0.446	2.963	13.876	1.213	1.126	1.977	4.680	3.965	0.029	0.317					
H <sub>2</sub> BB	$P_{exp} \times 10^6$	1.053	3.217	16.408	1.456	1.321	2.020	5.116	4.115	0.049	0.514	0.329	0.232	0.284	0.815	$0.264 \times 10^{-6}$
	$P_{cal} \times 10^6$	0.452	2.986	16.180	1.265	1.148	2.017	4.769	4.032	0.029	0.324					
H <sub>2</sub> BA	$P_{exp} \times 10^6$	1.085	3.561	17.298	1.484	1.324	2.028	5.135	4.146	0.040	0.554	0.344	0.252	0.274	0.917	$0.302 \times 10^{-6}$
	$P_{cal} \times 10^6$	0.459	3.238	17.024	1.252	1.108	1.945	4.724	4.074	0.028	0.314					

TABLE-3  
 OSCILLATOR STRENGTH AND JUDD-OFFELT PARAMETERS OF Er(III) IONS WITH DIFFERENT LIGANDS  
 IN 1 : 2 METAL-LIGAND STOICHIOMETRY

Ligand	Oscillator strength	Energy Level										Judd-Ofelt parameters				$\pm\sigma_{rms}$
		$^4F_{9/2}$	$^4S_{3/2}$	$^2H_{11/2}$	$^4F_{7/2}$	$4F_{5/2}$	$4F_{3/2}$	$^2H_{9/2}$	$^4G_{11/2}$	$^4G_{9/2}$	$^2G_{7/2}$	$T_2 \times 10^9$	$T_4 \times 10^9$	$T_6 \times 10^9$	$T_4/T_6$	
H <sub>2</sub> AD	$P_{exp} \times 10^6$	1.460	0.440	3.088	1.764	0.663	0.382	0.709	9.458	1.740	0.550	0.258	0.095	0.107	0.887	$0.706 \times 10^{-6}$
	$P_{cal} \times 10^6$	1.543	0.438	4.465	1.671	0.533	0.309	1.043	7.921	0.998	0.398					
H <sub>2</sub> AB	$P_{exp} \times 10^6$	1.499	0.343	4.935	1.783	0.648	0.352	0.734	10.154	1.876	0.667	0.316	0.107	0.090	1.183	$0.414 \times 10^{-6}$
	$P_{cal} \times 10^6$	1.514	0.368	5.322	1.484	0.449	0.260	1.002	9.439	1.015	0.348					
H <sub>2</sub> AA	$P_{exp} \times 10^6$	1.457	0.565	5.157	1.850	0.675	0.382	0.731	11.982	1.920	0.630	0.376	0.092	0.103	0.895	$0.594 \times 10^{-6}$
	$P_{cal} \times 10^6$	1.485	0.420	6.050	1.605	0.512	0.297	1.005	10.733	0.962	0.382					
H <sub>2</sub> BD	$P_{exp} \times 10^6$	1.493	0.324	4.915	1.794	0.617	0.311	0.714	9.875	1.858	0.590	0.309	0.108	0.093	1.161	$0.370 \times 10^{-6}$
	$P_{cal} \times 10^6$	1.540	0.379	5.240	1.520	0.461	0.267	1.020	9.307	1.031	0.356					
H <sub>2</sub> BB	$P_{exp} \times 10^6$	1.534	0.580	6.099	1.989	0.698	0.428	0.777	12.086	1.950	0.680	0.401	0.093	0.107	0.874	$0.340 \times 10^{-6}$
	$P_{cal} \times 10^6$	1.519	0.435	6.403	1.651	0.529	0.307	1.029	11.362	0.981	0.394					
H <sub>2</sub> BA	$P_{exp} \times 10^6$	1.509	0.686	7.108	1.983	0.734	0.413	0.776	14.075	2.090	0.720	0.479	0.089	0.105	0.845	$0.509 \times 10^{-6}$
	$P_{cal} \times 10^6$	6.147	0.430	7.435	1.594	0.523	0.303	1.002	13.210	0.948	0.388					

### ACKNOWLEDGEMENTS

Thanks are due to the Principal and to Dr. K.P. Soni, Head, Deptt of Chemistry, Dungan College, Bikaner; to Dr. I.G. Gulati, Senior Scientist, Agriculture Research Centre (RAU), Bikaner for experimental facility and to Prof. R.K. Mehta for valuable suggestions and discussion.

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(Received: 20 November 2002; Accepted: 22 January 2003)

AJC-2976

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