

## Studies on Intensity of $f \leftrightarrow f$ Transitions in Sm(III), Ho(III) and Er(III) Complexes with Some Schiff Bases

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The electronic spectral investigations on metal chelates of lanthanon in aqueous media have been made to explain the intensity of  $f \leftrightarrow f$  transition in terms of parameters, viz., oscillator strength ( $P$ ) and Judd-Ofelt parameters ( $T_\lambda$ ). The metal chelates have been derived from the interaction of lanthanon(III) ion, namely, Sm(III), Ho(III) and Er(III) with the six Schiff bases, namely, 2-( $\alpha$ -2-oxopentylideneimino) phenol ( $H_2PAA$ ), 2-( $\alpha$ -2-oxopropylbenzylideneimino) phenol ( $H_2PBA$ ), 2-( $\alpha$ -2-benzoylmethylbenzylideneimino) phenol ( $H_2PDB$ ), *o*-( $N$ - $\alpha$ -pyrroledeneimino) propanoic acid ( $H_2PCA$ ), *o*-( $N$ - $\alpha$ -pyrroledeneimino) isopropyl ethanoic acid ( $H_2PCV$ ) and *o*-( $N$ - $\alpha$ -pyrroledeneimino) ethane sulphonic acid ( $H_2PCT$ ). These ligands were derived by the condensation of *o*-amino phenol with acetyl acetone, benzoyl acetone and dibenzoyl methane and pyrrole-2-carboxaldehyde with  $\beta$ -alanine, L-valine and taurine, respectively.

**Key Words:**  $f \leftrightarrow f$  Transitions, Sm(III), Ho(III), Er(III), Complexes, Schiff Bases.

### INTRODUCTION

The rare earths and their metal chelates have acquired a significant position in various fields like that of biological and medical applications both in diagnostic and remedial purposes where these biological processes seek mechanistic explanations to their activities. Spectrophotometry<sup>1, 2</sup> is an important technique for the determination of structure and bonding in metal chelates. The electronic spectra of lanthanons have earned immense interest in the recent past.

Recently, electronic spectral studies of lanthanon ion complexes have been found to have due significance<sup>3</sup> because of strong validity of the theory given by Judd-Ofelt for explanation of intensity of the Laporte forbidden  $f \leftrightarrow f$  transitions. The various parameters given by Judd-Ofelt have been used to explain the symmetry of ligand around lanthanon ions.

### EXPERIMENTAL

#### Preparation of the ligands

The three ligands, 2-( $\alpha$ -2-oxopentylideneimino) phenol ( $H_2PAA$ ), 2-( $\alpha$ -2-oxo-

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propylbenzylideneimino) phenol (H<sub>2</sub>PBA) and 2-( $\alpha$ -2-benzoylmethylbenzylideneimino) phenol (H<sub>2</sub>PDB) have been synthesized by refluxing the equimolar solutions of *o*-amino phenol with acetyl acetone, benzoyl acetone and dibenzoyl methane, respectively and other three ligands, *o*-(N- $\alpha$ -pyrroledeneimino) propanoic acid (H<sub>2</sub>PCA), *o*-(N- $\alpha$ -pyrroledeneimino) isopropyl ethanoic acid (H<sub>2</sub>PCV) and *o*-(N- $\alpha$ -pyrroledeneimino) ethane sulphonic acid (H<sub>2</sub>PCT) have been synthesized by refluxing the equimolar solutions of pyrrole-2-carboxaldehyde with ( $\beta$ -alanine, L-valine and taurine, respectively), in the presence of piperidine as a catalyst on a water bath for 2–4 h. The resulting solutions were filtered while hot and dried as per the literature procedure<sup>4</sup>.

### Preparation of the metal-ion solution

The lanthanon acetates (Indian Rare Earth Ltd., Udyogmandalam) have been used for the preparation of metal ion solutions in double-distilled water which were duly standardized by conventional methods<sup>5</sup>.

### Preparation of the metal-ligand (sample) solutions

The sample solutions were prepared by taking the metal and the ligand solutions in 1 : 1, 1 : 2, 1 : 4 and 1 : 6 metal-ligand stoichiometries to record spectra. The electronic absorption spectra of the samples have been recorded on a spectrophotometer in the range of 200–900 nm. The Beckman DU-600 spectrophotometer was used. It has been found that the absorbance of the solution 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, *i.e.*, maximum chelation (in the solution) and for this intensity parameters have also been evaluated.

## RESULTS AND DISCUSSION

### Intensity parameters

The oscillator strength of a band is proportional to the area under the band, which is calculated by resolving a composite band into one or more constituent of Gaussian curves. The Judd-Ofelt equation for experimentally observed oscillator strength is given as

$$P_{\text{obs}} = T_2\nu[U^{(2)}]^2 + T_4\nu[U^{(4)}]^2 + T_6\nu[U^{(6)}]^2 \quad (1)$$

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

The observed values of oscillator strength have been compared with those of calculated ones. The values of r.m.s. deviation range from  $\pm 0.26$  to  $0.34 \times 10^{-6}$ ,  $\pm 0.23$  to  $0.26 \times 10^{-6}$  and  $\pm 0.22$  to  $0.32 \times 10^{-6}$  for Sm(III), Ho(III) and Er(III) metal chelates, respectively. The small deviation between observed and calculated values of oscillator strength for different  $f \leftrightarrow f$  transitions show the validity of Judd-Ofelt theory. The values of oscillator strength and r.m.s. deviation have been

TABLE-1  
 COMPUTED VALUES OF OSCILLATOR STRENGTHS OF VARIOUS ABSORPTION BANDS FOR THE Sm(III), Ho(III) AND Er(III)  
 METAL-CHELATES WITH DIFFERENT LIGANDS IN SOLUTION FOR 1 : 2 METAL-LIGAND STOICHIOMETRY

Metal ion	Levels	H <sub>2</sub> PAA		H <sub>2</sub> PBA		H <sub>2</sub> PDB		H <sub>2</sub> PCA		H <sub>2</sub> PCV		H <sub>2</sub> PCT	
		P <sub>expt</sub> × 10 <sup>6</sup>	P <sub>cal</sub> × 10 <sup>6</sup>	P <sub>expt</sub> × 10 <sup>6</sup>	P <sub>cal</sub> × 10 <sup>6</sup>	P <sub>expt</sub> × 10 <sup>6</sup>	P <sub>cal</sub> × 10 <sup>6</sup>	P <sub>expt</sub> × 10 <sup>6</sup>	P <sub>cal</sub> × 10 <sup>6</sup>	P <sub>expt</sub> × 10 <sup>6</sup>	P <sub>cal</sub> × 10 <sup>6</sup>	P <sub>expt</sub> × 10 <sup>6</sup>	P <sub>cal</sub> × 10 <sup>6</sup>
Sm(III)	<sup>4</sup> I <sub>9/2</sub> , <sup>4</sup> M <sub>15/2</sub> , <sup>4</sup> I <sub>11/2</sub>	1.754	1.622	1.744	1.605	1.739	1.625	1.721	1.803	1.710	1.800	1.700	1.805
		0.904	0.495	0.894	0.487	0.877	0.489	0.861	0.530	0.850	0.529	0.837	0.534
	<sup>4</sup> M <sub>17/2</sub> , <sup>4</sup> G <sub>9/2</sub> , <sup>4</sup> I <sub>15/2</sub>	0.526	0.228	0.509	0.225	0.497	0.226	0.479	0.246	0.459	0.247	0.441	0.246
		1.020	0.970	1.011	0.948	1.004	0.944	0.999	0.967	0.981	0.962	0.970	0.957
	<sup>4</sup> F <sub>7/2</sub> , <sup>6</sup> P <sub>3/2</sub> , <sup>4</sup> K <sub>11/2</sub>	4.390	4.074	4.300	0.397	4.242	3.949	4.195	4.000	4.144	3.963	4.101	3.937
		0.464	0.161	0.452	0.140	0.439	0.159	0.421	0.174	0.410	0.174	0.401	0.174
	<sup>4</sup> D <sub>1/2</sub> , <sup>6</sup> P <sub>7/2</sub> , <sup>4</sup> L <sub>17/2</sub> , <sup>4</sup> K <sub>13/2</sub> , <sup>4</sup> F <sub>9/2</sub>	2.090	1.919	2.079	1.890	2.060	1.898	2.051	2.073	2.041	2.073	2.029	2.073
		1.130	1.123	1.121	1.096	1.111	1.089	1.100	1.094	1.091	1.094	1.072	1.086
	<sup>4</sup> H <sub>7/2</sub> , <sup>4</sup> K <sub>15/2</sub> , <sup>4</sup> H <sub>9/2</sub> , <sup>4</sup> D <sub>7/2</sub>	2.810	2.411	2.800	2.377	2.794	2.395	2.779	2.595	2.751	2.595	2.742	2.596
		±0.27	±0.28	±0.26	±0.34	±0.33	±0.33	±0.33	±0.33	±0.33	±0.33	±0.33	±0.33
Ho(III)	<sup>5</sup> I <sub>5</sub>	0.459	0.711	0.440	0.844	0.410	0.115	0.397	0.099	0.381	0.084	0.365	0.661
	<sup>4</sup> I <sub>4</sub>	0.027	0.082	0.010	0.092	0.009	0.099	0.008	0.090	0.006	0.087	0.005	0.076
	<sup>5</sup> F <sub>5</sub>	3.891	4.295	3.870	3.566	3.851	3.743	3.840	3.949	3.820	3.639	3.805	3.597
	<sup>5</sup> F <sub>4</sub>	4.872	4.545	4.842	4.973	4.821	4.691	4.810	4.942	4.795	4.687	4.780	4.644
	<sup>5</sup> F <sub>3</sub>	1.832	1.871	1.810	2.081	1.774	2.040	1.754	1.487	1.731	1.862	1.700	1.435

TABLE-1 (Contd.)

Metal ion	Levels	H <sub>2</sub> PAA		H <sub>2</sub> PBA		H <sub>2</sub> PDB		H <sub>2</sub> PCA		H <sub>2</sub> PCV		H <sub>2</sub> PCT	
		P <sub>expt</sub> × 10 <sup>6</sup>	P <sub>cal</sub> × 10 <sup>6</sup>	P <sub>expt</sub> × 10 <sup>6</sup>	P <sub>cal</sub> × 10 <sup>6</sup>	P <sub>expt</sub> × 10 <sup>6</sup>	P <sub>cal</sub> × 10 <sup>6</sup>	P <sub>expt</sub> × 10 <sup>6</sup>	P <sub>cal</sub> × 10 <sup>6</sup>	P <sub>expt</sub> × 10 <sup>6</sup>	P <sub>cal</sub> × 10 <sup>6</sup>	P <sub>expt</sub> × 10 <sup>6</sup>	P <sub>cal</sub> × 10 <sup>6</sup>
	<sup>5</sup> F <sub>2</sub>	1.153	0.942	1.141	1.365	1.321	1.642	1.302	0.980	1.279	0.913	1.250	0.930
	<sup>3</sup> K <sub>8</sub>	1.018	1.243	1.004	0.679	0.991	1.313	0.872	1.195	0.861	1.181	0.852	1.174
	<sup>5</sup> G <sub>6</sub>	11.571	11.182	11.502	11.739	11.482	11.717	11.450	11.686	11.393	11.158	11.350	11.570
	( <sup>2</sup> G, <sup>3</sup> G) <sub>5</sub>	3.015	2.755	3.002	2.697	2.957	2.703	2.942	2.684	2.930	3.183	2.900	2.543
	<sup>5</sup> G <sub>4</sub>	0.998	0.766	0.975	0.853	0.964	0.843	0.942	0.820	0.931	0.810	0.902	0.776
	σ <sub>r.m.s. deviation</sub> × 10 <sup>6</sup>	±0.25		±0.26		±0.23		±0.23		±0.23		±0.26	
	<sup>4</sup> F <sub>9/2</sub>	1.549	1.500	1.502	1.455	1.491	1.454	1.480	1.461	1.452	1.444	1.439	1.429
	<sup>4</sup> S <sub>3/2</sub>	0.400	0.741	0.397	7.255	0.380	0.725	0.366	0.719	0.354	7.187	0.340	0.706
	<sup>2</sup> H <sub>11/2</sub>	3.820	4.184	0.380	4.165	3.794	4.169	3.742	4.160	3.734	4.027	3.721	3.838
	<sup>4</sup> F <sub>7/2</sub>	2.560	2.419	2.510	2.362	2.495	2.360	2.465	2.351	2.452	2.339	2.441	2.302
	<sup>4</sup> F <sub>5/2</sub>	0.899	0.903	0.869	0.883	0.842	0.882	0.804	0.877	0.795	0.874	0.780	0.859
	<sup>4</sup> F <sub>3/2</sub>	0.368	0.523	0.351	0.512	0.342	0.511	0.305	0.508	0.297	0.507	0.281	0.498
	<sup>2</sup> H <sub>9/2</sub>	0.996	1.027	0.979	1.003	0.961	1.003	0.943	0.996	0.921	0.929	0.911	0.977
	<sup>4</sup> G <sub>11/2</sub>	7.984	7.424	7.969	7.400	7.942	7.397	7.932	7.738	7.542	7.157	7.024	6.809
	<sup>4</sup> G <sub>9/2</sub>	2.154	1.593	2.140	1.522	2.129	1.522	2.112	1.726	1.517	1.517	1.991	1.512
	<sup>2</sup> G <sub>7/2</sub>	0.810	0.533	0.794	0.643	0.764	0.671	0.752	0.638	0.668	0.668	0.072	0.664
	σ <sub>r.m.s. deviation</sub> × 10 <sup>6</sup>	±0.32		±0.31		±0.32		±0.26		±0.26		±0.22	

summarized in Table-1 for Sm(III), Ho(III) and Er(III) metal-chelates, respectively.

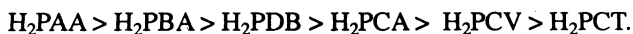
The intensities of the observed bands have been given in terms of oscillator strength (P). The Judd-Ofelt parameters ( $T_2$ ,  $T_4$  and  $T_6$ ) for metal chelates of Sm(III), Ho(III) and Er(III) have been computed by taking values of the oscillator strength and the matrix elements  $U^{(\lambda)}$  as given by Carnall<sup>6</sup>, employing partial and multiple regression method<sup>7,8</sup>. Out of these three parameters,  $T_2$  parameter shows high sensitivity changes while  $T_4$  and  $T_6$  have been found to exhibit more sensitivity towards symmetry changes<sup>9</sup>. The values of intensity parameters have been summarized in Table-2 for Sm(III), Ho(III) and Er(III) metal chelates, respectively.

TABLE-2  
COMPUTED VALUES OF JUDD-OFELT INTENSITY  $T_\lambda$  PARAMETERS FOR Sm(III),  
Ho(III) and Er(III) METAL CHELATES IN SOLUTION FOR 1 : 2 METAL-LIGAND  
STOICHIOMETRY

Ligand	Intensity parameter ( $T_\lambda \times 10^9$ )											
	Sm(III)				Ho(III)				Er(III)			
	$T_2$	$T_4$	$T_6$	$T_4/T_6$	$T_2$	$T_4$	$T_6$	$T_4/T_6$	$T_2$	$T_4$	$T_6$	$T_4/T_6$
H <sub>2</sub> PAA	20.395	0.9257	0.8870	1.0436	0.3069	0.5916	0.8039	0.7359	0.2685	0.0260	0.1818	0.1433
H <sub>2</sub> PBA	20.371	0.9020	0.8738	1.0322	0.3027	0.5879	0.7975	0.7372	0.2671	0.0240	0.1778	0.1355
H <sub>2</sub> PDB	20.320	0.8958	0.8777	1.0206	0.3033	0.5780	0.7900	0.7317	0.2669	0.0241	0.1777	0.1359
H <sub>2</sub> PCA	18.116	0.9036	0.9607	0.9405	0.3027	0.5815	0.7924	0.7339	0.2665	0.0258	0.1766	0.1466
H <sub>2</sub> PCV	17.855	0.8945	0.9606	0.9312	0.3017	0.5817	0.7914	0.7350	0.2582	0.0243	0.1761	0.1376
H <sub>2</sub> PCT	17.760	0.8848	0.9616	0.9243	0.3006	0.5810	0.7901	0.7353	0.2442	0.0248	0.1731	0.1435

In all the metal chelates  $T_6 > T_4$  except for Sm(III) metal-chelates, which may be due to the enhancement of magnetic dipole interaction in Sm(III). The ratio of  $T_4/T_6$  may be used to determine the changes in symmetry of stereo-environment around the Sm(III), Ho(III) and Er(III) ions. The values of  $T_4/T_6$  range from 1.0436 to 0.9243, 0.7372 to 0.7317 and 0.1466 to 0.1355 for Sm(III), Ho(III) and Er(III) metal chelates, respectively, indicating similar symmetry of stereo-environment around these metal ions.  $T_2$  parameter, which is a covalency parameter, is important to explain the hypersensitivity.

From the data it has been found that in all the cases metal-ligand bonding is not merely ionic but covalent. The order of covalency on the basis of oscillator strength in Sm(III), Ho(III) and Er(III) metal chelates with these ligands is as follows:



The absorbance values were highest in the solution having 1 : 2 metal-ligand

stoichiometry and at pH range 7.5 to 8.5. Thus, in this metal-ligand stoichiometry there is the greatest molecular stacking (metal-ligand) and favourable stereo-environment.

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