

## Electronic Spectra of Lanthanoid(III) Ions in Aminopolycarboxylate Environments. Part-III. [Pr<sup>III</sup>/Nd<sup>III</sup>/Sm<sup>III</sup>/Eu<sup>III</sup>/Dy<sup>III</sup>/Er<sup>III</sup>/Tm<sup>III</sup>-DTPA] Complexes

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Sensitivity and susceptibility of specific intensities of the *f-f* electronic transitions to changes in the immediate environment and the mode of metal ion involvements with ligand have been reported earlier<sup>1-4</sup>. Some efforts have been made to utilise the oscillator strength values for specific electronic transitions of lanthanoid(III) (Ln(III)) ions and their complexes to determine the stability constants<sup>5</sup> and their thermodynamic parameters<sup>6</sup>. In continuation with our earlier studies on the electronic spectra of Ln(III) ions in different aminopolycarboxylate environments<sup>7</sup> and their pH and *J* quantum number profiles<sup>8</sup>, the present work has been undertaken with a view to study the dependence of the oscillator strength values on pH and the degree of complexation. This has been studied in the light of the variations in the spectral parameters, viz. oscillator strength values ( $f_{JO}$ ), Judd-Ofeld parameters ( $\tau_\lambda$ ), interelectronic repulsion (Racah) parameters ( $\partial E^k$ ) and the nephelauxetic ratios ( $\partial E^3/\partial E^1$ ) as a result of complexation, throughout the series.

### Results and Discussion

The values of electronic transitions,  $E$  ( $\text{cm}^{-1}$ , Table 1) exhibit an increase in the energy of absorption with a general increase in pH values, showing a maximum at pH ~4.5. This indicates the susceptibility of the intensity of specific electronic transition to the degree of complexation. The oscillator strength values (Table omitted for simplicity) evaluated using the energy values for specific electronic transitions, also exhibit similar variation with pH values. Fig. 1 exhibits a pH profile of the oscillator strength values for [Pr<sup>III</sup>-DTPA] complex as a representative case. Deviations beyond pH ~6.0 may be on account of formation of hydroxo-complexes. An increase in the degree of complexation is also indicated by the variations in the  $^2P_{1/2}$  and  $^2D_{5/2}$  assignments for Nd<sup>III</sup>. Assignments sensi-

tive to the [Nd<sup>III</sup>-DTPA] interaction and the Ln(III) donor atom bond distance<sup>9</sup> show a decrease in the energy with increase in pH values (viz. pH 2.00,  $E$  ( $\text{cm}^{-1}$ ) 23 240, 23 900; pH 3.00,  $E$  ( $\text{cm}^{-1}$ ) 23 235, 23 478; pH 3.50,  $E$  ( $\text{cm}^{-1}$ ) 23 275, 23 437; pH 4.00,  $E$  ( $\text{cm}^{-1}$ ) 23 169, 23 412; pH 4.50,  $E$  ( $\text{cm}^{-1}$ ) 23 230, 23 414; pH 5.00,  $E$  ( $\text{cm}^{-1}$ ) 23 247, 23 443; pH 5.50,  $E$  ( $\text{cm}^{-1}$ ) 23 255, 23 504). This constitutes further evidence for the above observation that the intensity of specific electronic transition increases with increased degree of complexation, which may be on account of greater release of inter-electronic repulsion with increased degree of complexation.

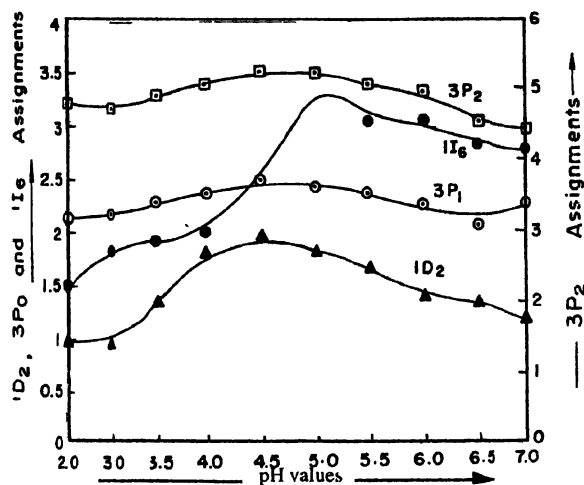


Fig. 1. pH profile of  $f_{JO}$  for [Ln(III)-DTPA] complexes.

The oscillator strength values ( $f_{JO}$ ) are composed of  $\tau_\lambda$  parameters (Table 2) where  $\tau_2$  represents mode of [Ln(III)-DTPA] interactions and  $\tau_4$ ,  $\tau_6$  reflect the symmetry around

TABLE 1—REPRESENTATIVE VALUES OF ELECTRONIC TRANSITIONS OBTAINED FOR [Pr(III)-DTPA] AT DIFFERENT pH VALUES

Assign-ment	2.0	3.0	3.5	4.0	4.5	5.0	5.5	6.0	6.5	7.0
$^1D_2$	17 032	17 037	17 048	17 068	17 080	17 084	17 078	17 064	17 057	17 053
$^3P_1$	20 507	20 693	20 789	20 893	20 821	20 793	20 704	20 709	20 604	20 607
$^1I_6$	21 245	21 316	21 486	21 550	21 686	21 516	21 493	21 391	21 293	21 545
$^3P_2$	22 468	22 654	22 874	22 922	22 913	22 892	22 862	22 622	22 700	22 868

Ln(III) metal ion. The  $\tau_\lambda$  parameters are found to exhibit a general sequence  $\tau_2 < \tau_4 < \tau_6$ , based on the relative responses of these parameters towards the [Ln(III)-DTPA] interactions. These parameters show a marked difference in the values for pre- and post-Gd elements. Higher values of  $\tau_6$  for Pr<sup>III</sup>, Nd<sup>III</sup>, Sm<sup>III</sup> and Eu<sup>III</sup> than the corresponding values for Dy<sup>III</sup>, Er<sup>III</sup> and Tm<sup>III</sup> may be expected on account of larger cationic sizes of Pr<sup>III</sup>, Nd<sup>III</sup>, Sm<sup>III</sup> and Eu<sup>III</sup> which experience a greater disturbance in the hydration sphere as a result of complexation. This may also be partly on account of change in coordination number<sup>9</sup> from 9 to 8 at around Gd<sup>III</sup>. Similarly, smaller value of  $\tau_2$  parameters for pre-Gd elements than those for the post-Gd elements may be due to increased covalent interaction<sup>10</sup> with decreased cationic size of Ln(III) ions. In lanthanoids, the 4*f*-orbitals are deep lying and are less available for bonding, and the ligand field stabilisation energy effects are also negligible. Under these conditions the [Ln(III)-DTPA] interactions are expected to be predominantly ionic. A change in the bonding pattern from ionic to ionocovalent type is, however, expected<sup>11</sup> on account of lanthanoid contraction. A gradual change in the bonding pattern in lanthanoids on account of decreased ionic sizes has been reported from our laboratories<sup>11</sup> for Ln(III) ions in silicates and silicate like hosts. In the present case also a change in the bonding pattern from ionic to ionocovalent is indicated as above while traversing the Ln(III) series. The variations in the IERP-Racah values ( $\partial E^k$ ) and the nephelauxetic ratio ( $\partial E^3/\partial E^1$ ) evaluated for [Pr<sup>III</sup>/Nd<sup>III</sup>/Er<sup>III</sup>-DTPA] complexes in the present case (Table 2) lend further support to the above observations. An agreement in the  $\partial E^k$  and  $\partial E^3/\partial E^1$  values

values of spin-quantum number  $S = 3/2$  and orbital angular momentum number  $L = 6$ ) show higher values of  $\partial E^k$  and  $\partial E^3/\partial E^1$  for Er<sup>III</sup>. This may be expected on account of greater deformation in the *f*-electron wave functions in the case of Er<sup>III</sup> than in Nd<sup>III</sup>, due to intimate approach and involvement of greater covalency in the [Ln(III)-DTPA] interaction.

On the basis of the above observation it may be concluded that the intensities of specific *f-f* electronic transitions show a marked dependence on pH due to variation in the degree of complexation with pH. The variation in the intensity of electronic transition changing partly due to the extent of [Ln(III)-DTPA] interaction and/or the changes in symmetry around metal ions also show a marked dependence on the size of Ln(III) cation. Pre-Gd elements being larger in size exhibit a more closer [Ln(III)-DTPA] interaction. The variations in the IERP-Racah values on going across the Ln(III) series indicate increased covalency in [Ln(III)-DTPA] interaction due to decreased cationic size suggesting a gradual change in the mode of interaction from ionic to covalent as we traverse the Ln(III) series.

### Experimental

Stock solutions of metal ions and ligands (AnalaR) were prepared in double-distilled water. Ln(III) nitrates (99.99% purity; Indian Rare Earths Ltd.) were used. Pentaacid form of DTPA was dissolved in double-distilled water using 0.5 mol dm<sup>-3</sup> NaOH solution. A 0.1 mol dm<sup>-3</sup> HNO<sub>3</sub> solution was used as reference acid. A 0.2 mol dm<sup>-3</sup> carbonate-free NaOH solution was used to maintain pH, which was recorded on an Orion-940 extended ion analyser system. Measured quantities of alkali were added to adjust the pH of the observation sets. The variation in concentration due to addition of alkali was taken into consideration while calculating the oscillator strength values. Electronic spectra for metal ion blank (0.025 mol dm<sup>-3</sup>) and [Ln(III)-DTPA] complexes in 1 : 1 ratio with total Ln(III) concentration ~0.025 mol dm<sup>-3</sup> were recorded on a Perkin-Elmer Lambda-3B spectrophotometer.

The values of the oscillator strength and Judd-Ofelt parameters were evaluated using Judd-Ofelt<sup>12,13</sup> approach, whereas the variations in inter-electronic repulsion Racah parameters [IERP-Racah] for Pr<sup>III</sup>, Nd<sup>III</sup> and Er<sup>III</sup> were evaluated using Wong's equations<sup>14</sup>. Pascal compiled self-devised<sup>15</sup> computer softwares were used to evaluate these spectral parameters using standard equations<sup>11</sup>.

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TABLE 2—CALCULATED VALUES OF JUDD-OFELT PARAMETERS ( $\tau_\lambda$ ), RACAH (IERP) PARAMETERS ( $\partial E^k$ ) AND NEPHELAUXETIC RATIO ( $\partial E^3/\partial E^1$ ) FOR LN(III) IONS IN DTPA LIGAND ENVIRONMENT AT pH  $\approx$  4.5

Ligand environment	$\tau_2$	$\tau_4$	$\tau_6$
[Pr <sup>III</sup> -DTPA]	0.99	3.28	29.90
[Nd <sup>III</sup> -DTPA]	-0.641	2.047	35.50
[Sm <sup>III</sup> -DTPA]	0.00	4.35	25.30
[Eu <sup>III</sup> -DTPA]	0.00	-3.39	38.47
[Dy <sup>III</sup> -DTPA]	0.72	5.19	23.90
[Er <sup>III</sup> -DTPA]	0.76	-0.84	23.40
[Tm <sup>III</sup> -DTPA]	1.21	1.40	5.66
	$\partial E^3$	$\partial E^1$	$\partial E^3/\partial E^1$
[Pr <sup>III</sup> -DTPA]	-104	11.00	-0.0010
[Nd <sup>III</sup> -DTPA]	118.87	3.44	0.0290
[Er <sup>III</sup> -DTPA]	119.03	2.52	0.0211

with the theoretically calculated<sup>1</sup> ranges for these parameters justifies the validity of the calculations. A comparison of the IERP values for Nd<sup>III</sup> with Er<sup>III</sup> (having similar

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