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Electronic Spectral Studies on Mixed Ligand Complexes of Some Biologically Active Elements Pr(III) and Nd(III) Involving Histidine as Primary Ligand and Ninhydrin as Secondary Ligand

M.P. GOUTAM‡, ASHOK YADAV and S.N. LIMAYE*
Department of Chemistry
Dr. H.S. Gour University, Sagar-470 003, India

An electronic spectral investigation on some binary and mixed ligand complexes of Pr(III) and Nd(III) in aqueous medium at controlled pH values has been attempted with a view to evaluate the electronic spectral parameters, *viz.*, oscillator strengths, Judd-Ofelt parameters, changes in inter-electronic repulsion (Racah) parameters and the nephelauxetic ratio values in order to examine the variation in these electronic spectral parameters as a result of change in cation environment.

INTRODUCTION

The electronic spectra of lanthanoids have earned immense interest in the past[1-5]. Simultaneously rare earths have acquired a significant position in the field of biological applications[6] both in diagnostic[7] and remedial[8] purposes where these biological processes seek mechanistic explanation to their activities. Thus in continuation with the earlier studies, in the present report an electronic spectral investigation on some binary and mixed ligand complexes of Pr(III) and Nd(III) in aqueous medium at controlled pH-values has been attempted with a view to evaluate the electronic spectral parameters *viz.*, oscillator strengths, Judd-Ofelt parameters, changes in inter-electronic repulsion (Racah) parameters and the nephelauxetic ratio values in order to examine the variation in these electronic spectral parameters as a result of change in cation environment.

EXPERIMENTAL

Standard grade chemicals [Pr(III)/Nd(III)] as nitrate salts (supplied by Indian Rare Earths Ltd), histidine (LOBA Chem) and ninhydrin (Sigma Chemicals Co., USA, product no. 15, 117–3) were used for studies. Ligands were dissolved in double distilled water. Usual sets were prepared by taking requistite amounts of Pr(III) or Nd(III), histidine (hist) and ninhydrin (ninh). The total [Pr(III)/Nd(III).hist], [Pr(III)/Nd(III). ninh], or [Pr(III)/Nd(III).hist.ninh] sets prepared in 1 : 1 and 1 : 1 : 1 proportion keeping total metal-ligand concentrations at *ca.* 0.025 mole dm^{-3}. pH values of the sets were maintained by adding requisite amounts of alkali or HNO_3 solutions where the changes in concentrations as a result of addition of acid or alkali solution have been taken into consideration.

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‡Joint Director (Chemistry), State's Forensic Science Laboratory, Sagar (M.P.), India.

pH of mixing of the solutions (*ca.* 3.5) was recorded on an Orion-940 auto-titrate module with pH precision of ±0.001 pH units. Electronic spectra for the Pr(III) and Nd(III) in different ligand environments were recorded on a Perkin-Elmer Lambda 3B spectrophotometer attached to an RX100 plotter.

Electronic spectra thus obtained (figure not shown) was used to evaluate the oscillator strength values f_{JO} and Judd-Ofelt parameters (τ_λ)[9, 10] using some prominent electronic transitions for Pr(III) and Nd(III) in different ligand environments. The inter-electronic repulsion racah parameters and the nephelauxetic ratio values were evaluated using Wong's[11] approach. Standard equations were used to evaluate these spectral parameters. A PC/AT 486–DX2 computer attached to a TVSE Calligra 24 pin 132 column printer arrangement and self-devised PASCAL compiled computer softwares[12] were used to evaluate the spectral parameters.

RESULTS AND DISCUSSION

Evaluated values of the oscillator strengths, Judd-Ofelt parameters, variations in the inter-electronic requlsion Racah parameters and the nephelauxetic ratio values are recorded in Tables 2–4 respectively.

TABLE-1
SPECTRAL ASSIGNMENTS FOR THE PROMINENT ELECTRONIC TRANSITION FOR Pr(III) and Nd(III) IN LIGAND ENVIRONMENTS

Assignment	E (cm^{-1})								
Pr^{3+}	HOH	hist	ninh	hist. ninh	Nd^{3+}	HOH	hist	ninh	hist.ninh
$^1D_2$	17040	17042	16965	17084	$^3F_{3/2}$	11577	11583	11583	11576
$^3P_0$	20918	20909	20907	21104	$^4F_{5/2}$	12517	12515	12515	12520
$^3P_1$	21521	21506	21476	21726	$^3H_{9/2}$	12625	12611	12617	12611
$^1I_6$	21521	21506	21476	21726	$^4F_{7/2}$	13568	13414	13425	13551
$^3P_2$	23031	22734	22751	23086	$^4S_{3/2}$	13709	13695	13675	13712
					$^4F_{9/2}$	14727	14980	14850	14799
					$^2G_{5/2}$	17468	17465	17335	17474
					$^4G_{7/2}$	17468	17465	17420	17474
					$^2K_{13/2}$	19272	18875	19238	19332
					$^4G_{7/2}$	19272	18895	19238	19332
					$^4G_{9/2}$	19644	19279	19614	19690
					$^2K_{15/2}$	21012	20809	20730	21266
					$^2G_{9/2}$	21279	20905	20995	21531
					$^2D_{3/2}$	21358	21072	21370	21941
					$^4G_{11/2}$	21693	21560	21577	22042
					$^2P_{1/2}$	23358	23402	23057	23193
					$^2I_{11/2}$	28525	28495	28354	28498
					$^4L_{15/2}$	29152	29151	28995	29195

Table-1 records the E (in cm^{-1}) values for Pr(III) and Nd(III) in different environments. The E values in Table-1 clearly indicate a general red shift indicating a release in inter-electronic repulsion due to change in environment. The $\Delta\nu$ ($\Delta\nu = \nu_{aqua} - \nu_{compl}$) values evaluated for Pr(III) and Nd(III) in various binary and mixed ligand complexes are also positive showing an increased electron release on complexation. The $\Delta\nu$ values for the ternary complexes are relatively higher than their corresponding binary complexes which is indicative of enhanced metal-ligand interaction in the mixed ligand complexes. The ν and $\Delta\nu$ values for aqua and binary and mixed ligand environments exhibit a red shift *i.e.*, ($\Delta\nu$) is positive ($\Delta\nu$ = [Pr(III). hist] = 66.8; [Nd(III).hist] = 36.92; [Pr(III).ninh] = 91.2; [Nd(III).ninh] = 93.8; [Pr(III).hist.ninh] = 139; [Nd(III).hist.ninh] = 137.2) showing involvement of partial covalency in the [Ln(III)-L] bonds.

The oscillator strength values (Table-2, for binary and mixed ligand environments of Pr(III)/Nd(III) respectively) which is a measure of intensities of specific electronic transitions or degree to which a specific transition is allowed, show marked dependence on the cation environment[4, 13].

TABLE-2
THE OSCILLATOR STRENGTHS ($P \times 10^{-5}$) for Pr(III) AND Nd(III) IN AQUEOUS AND VARIOUS LIGAND ENVIRONMENTS

$E\ cm^{-1}$ Assign	16589 $^1D_2$	20800 $^3P_0$	21400, 21700 $^3P_1 : {}^1I_6$	22600 $^3P_2$
		[Pr(III).aqua]		
P	3.555	7.125	8.661	22.693
		[Pr(III).hist]		
P	3.433	6.308	8.695	23.196
		[Pr(III).ninh]		
P	3.497	7.394	8.251	22.926
		[Pr(III).hist.ninh]		
P	3.434	7.125	8.661	22.693

$E\ cm^{-1}$ Assign	11450 $^4F_{3/2}$	12500 $^4F_{5/2}$	13500–600 $^4F_{7/2}$	17300–400 $^4G_{5/2}$	19000–500 $^2K_{13/2}$	28300 $^4D_{3/2}$
			[Nd(III).aqua]			
P	1.047	8.591	6.957	9.730	9.011	9.713
			[Nd(III).hist]			
P	7.741	4.804	4.636	5.942	4.472	5.559
			[Nd(III).ninh]			
P	1.573	9.043	11.418	8.688	—	—
			[Nd(III).hist.ninh]			
P	2.276	9.197	7.939	11.129	10.259	—

The oscillator strength values besides several minor interactions are composed of[14] prominently three main parameters known as Judd-Ofelt parameters. These parameters are indicative of (i) the degree of metal ligand (M–L) interactions, (τ_2), (ii) the refractive index of the medium (τ_4) and (iii) the changes in symmetry around the cation (τ_6). Table-3 records the T_λ values for Pr(III) and Nd(III) in binary and mixed ligand environments. A perusal of these values shows a general sequence of $\tau_2 < \tau_4 < \tau_6$ which is in good agreement with the lanthanoid metal ions characteristics. The deep lying 4f-shells experiencing intense shielding make these orbitals less available for bonding thereby leading to a lesser degree of metal-ligand interactions, *i.e.*, predominantly an ionic nature of the M-L bond with probable covalency, the τ_2 parameter being small, but the larger cation sizes of lanthanoids associated with three concentric hydration zones may lead to greater changes in symmetry around metal ion during viscinal M–L approach.

TABLE-3
JUDD-OFELT (T_λ) PARAMETERS FOR Pr(III) AND Nd(III) IN AQUEOUS AND DIFFERENT LIGAND ENVIRONMENTS

Systems	τ_2	τ_4	τ_6
[Pr. Aqua]	-2.70	2.10	6.57
[Pr. Hist.]	-2.35	1.91	6.83
[Pr. Ninh]	-3.07	2.17	6.17
[Pr. Hist.Ninh]	-2.89	2.17	6.85
[Nd. Aqua]	1.54	6.12	8.97
[Nd. Hist]	2.52	6.00	9.79
[Nd. Ninh]	2.44	6.14	9.75
[Nd. Hist.Ninh]	2.17	6.36	10.13

Carnall[15] has pointed out that the proportionality of the τ_λ parameters using a crystal field model may be expressed as

$$\Gamma_\lambda \sim \langle r^{t+i} \rangle^2 R^{-2t-2}$$

where for $\lambda = 2$, t is 1 and 3; for $\lambda = 4$, t is 3 and 5; and for $\lambda = 6$, t is 5 and 7. This expects an order of decreasing sensitivity of the τ_λ parameters to the environment giving a sequence $\tau_2 < \tau_4 < \tau_6$. Choppin[16], Judd and Jorgensen[17] and Reisfield[18] have individually observed this sequence for the sensitivity of these parameters towards the intensity of specific electronic transitions.

Authors are of the opinion that the τ_2 parameter which is covalency-denoting parameter is expected to be smaller in magnitude in view of predominantly ionic nature of Ln(III)-L bonding[4, 13]. Deep lying 4f-shells are strongly shielded and are less available for bonding, the Ln(III)-L bonds are thus expected to be predominantly ionic with probable partial covalency. On the other hand the τ_4 and τ_6 which are symmetry denoting parameters are expected to be large on account of large cationic size of Ln(III) with large hydration zones. These factors are expected to cause greater perturbations in the symmetry around the coordination sphere during a closer Ln(IIII)-L interaction thereby increasing the magnitude of these values.

These parameters show a marked difference in the values for Pr(III) and Nd(III) elements. Higher values of τ_6 for Pr(III) than Nd(III) may be expected on account of larger cationic size for Pr(III) than for Nd(III), which may experience a greater disturbance of the hydration sphere as a result of intimate Ln(III) ligand contact on complexation. Similarly smaller value of τ_2 parameters for Pr(III) than for Nd(III) may be due to increased covalent interaction[13] with decreased cationic size due to lanthanoid contraction. In lanthanoids the 4f-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)-L interactions are expected to be predominantly ionic. A change in the bonding pattern from ionic to covalo-ionic type is, however, expected on account of lanthanoid contraction[4, 19]. In the present case a partial change in the bonding pattern from ionic to covalo-ionic associated with cationic sizes is observed.

The variations in the IERP-Racah values (δE^k) and the nephelauxetic ratio ($\delta E^3/\delta E^1$) evaluated[11] for Pr(III) and Nd(III) complexes in the present case (Table-4) lend further support to the above observations. An agreement in the δE^k and $\delta E^3/\delta E^1$ values with the theoretically calculated[20] ranges for these parameters justify the validity of the calculations. A comparison of the IERP values for Pr(III) with Nd(III) (having values of spin-quantum number S = 1/2, 3/2 and orbital angular momentum number L = 5, 6 respectively) show higher values of δE^k and $\delta E^3/\delta E^1$ for Nd(III). This may be expected on account of greater deformation[21] in the f-electron wave functions in the case of Nd(III) than in Pr(III), due to intimate approach and involvement of greater covalency in the Ln(III)-L interaction. It also points at a possible S or L dependency of these spectral parameters[4–6]. The exact dependency needs elaborate studies.

TABLE-4
VARIATIONS IN THE INTER-ELECTRONIC REPULSION (RACAH) PARAMETERS AND THE NEPHELAUXETIC RATIO VALUES FOR Pr(III) AND Nd(III) IN DIFFERENT LIGAND ENVIRONMENTS

Systems	δE^1	δE^2	$\delta E^3/\delta E^1$
[Pr. Aqua]	970.83	16.87	–0.0173
[Pr. Hist]	440.65	61.28	0.1391
[Pr. Ninh]	251.76	34.92	0.1387
[Pr. Hist. Ninh]	184.22	38.58	0.2094
[Nd. Aqua]	45.97	4.87	0.1060
[Nd. Hist]	63.16	5.27	0.0834
[Nd. Ninh]	63.35	5.29	0.0835
[Nd. Hist.Ninh]	39.73	–0.22	0.1108

Conclusions

On the basis of above observations it may be concluded that the intensities of specific f-f electronic transitions show a marked dependence on ligand environments and nature of the donor atoms. The variation in the intensity of electronic transition changing partly due to extent of Ln(III)-L interaction and/or the changes in symmetry around metal ions also show a marked dependence on the size of Ln(III) cation. General positive red shifts, oscillator strengths, covalency and symmetry parameters with a change in cation environments indicate that the electronic spectral parameters are susceptible to the cation environment and its complexation with ligand. Variations in the IERP-Racah parameter values on going across the Ln(III) series indicate increased covalency in Ln(III)-L interaction due to decreased cationic size suggesting a gradual change in the mode of interaction from ionic to covalo-ionic from Pr(III) to Nd(III).

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