J. Indian Chem. Soc.,
Vol. 81, October 2004, pp. 879-880

NOTE

Trends in spectral parameters and nephelauxetic ratio values for some lanthanoid(III) tyrosine complexes. Part-III

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Electronic spectral studies of [Ln(III).L] complexes, where, Ln = Pr, Nd and Er with tyrosine (tyr) have been undertaken with a view to evaluate the oscillator strengths (f_{JO}), Judd-Ofelt parameters (τ_λ), inter-electronic repulsion Racah parameters (δE^K) and nephelauxetic ratios ($\delta E^3/\delta E^1$). Studies have been performed at five different pH values to examine the pH dependence of the spectral parameters. The metal-ligand bonding pattern has been studied in the light of changes in τ_λ and nephelauxetic ratio values. The [Ln(III). tyr] interaction shows a drift from ionic to partial covalent nature.

The spectral properties of lanthanoids have been studied with great interest[1] in view of their intense sharp peaks, cation solvato dynamics, cation-symmetry and coordination polyhedra, f-shell behaviour and their nephelauxetic consequences. In persuation with the earlier studies on the electronic spectra of Ln^{III}-cations in different complex environments[2,3], the present study reports our observation on the electronic spectral parameters of Pr^{III}, Nd^{III} and Er^{III} on complexation with tryrosine.

Results and discussion

Table 1 records the oscillator strength values (f_{JO}) for Pr^{III}, Nd^{III} and Er^{III} [Pr^{III} as representative case at five pH values] alongwith other spectral parameters. A pH profile of the oscillator strength values (figure omitted for simplicity) exhibited a maximum at pH 5.5-6.0. SCOGS-NR studies on determination and refinement of formation constants of [Ln(III).tyr] and evaluating their distribution of species (figure omitted for brevity) showed[2] good agreement with the above observations. An increase in the degree of complexation may also be visualized by the variations in the $^2P_{1/2}$ assignments for Nd^{III}. The $^2P_{1/2}$ assignment sensitive to the metal-ligand interactions and the Ln^{III} to donor atom bond distance[3] show a decrease in the energy [viz. pH 2.04 E (cm^{-1}) 24530; pH 4.0 E (cm^{-1}) 24517; pH 5.0 E (cm^{-1}) 24426; pH 5.5 E (cm^{-1}) 24372 and pH 6.0 E (cm^{-1}) 24468] with increased pH values which is in agreement with the observation indicating increased susceptibility of the electronic spectral parameters with increased degree of complexation.

The oscillator strength values (f_{JO}) composed of τ_λ parameters[1,6] where τ_2 represent the [Ln(III).tyr] interactions

and τ_6 the symmetry around Ln^{III} metal ion (Table 1). These τ_λ exhibit a sequence $\tau_2 < \tau_4 < \tau_6$, based on their responses towards the [Ln(III).tyr] interactions. The τ_λ parameters are also found to be higher for Pr^{III} and Nd^{III} than for Er^{III} which may be expected on account of higher symmetry produced with Pr^{III} and Nd^{III} due to larger cation sizes. The difference in τ_2 parameters for configurationally identical Nd^{III} and Er^{III} may be on account of involvement of covalence for pre-Gd^{III} cations than for post-Gd^{III} cations. The change

Table 1. Representative values of f_{JO}, τ_λ and δE^k values for [Ln(III). tyr] complexes at pH of complexation [Pr^{III} as representative case for f_{JO} at different pH values]

pH	$^1D_2$	$^3P_0$	$^3P_1$; $^1I_6$	$^3P_2$
E (cm^{-1})	16850	20800	21400–21700	22600
2.00	3.010	2.236	4.012	11.015
(Std.)	(3.171)	(2.341)	(4.910)	(12.861)
4.00	5.512	6.957	9.342	22.130
5.00	5.438	7.752	9.875	21.935
5.50	5.304	8.213	10.553	21.945
6.00	5.065	7.735	9.937	23.769

[Nd^{III}.tyr] :

	$^1F_{3/2}$	$^4F_{5/2}$; $^2H_{9/2}$	$^4F_{7/2}$	$^4G_{5/2}$	$^3K_{3/2}$	$^4D_{3/2}$
Assignment						
E (cm^{-1})	11450	12500; 12600	13500	17300	19000	28300
f_{JO}	3.964	14.442	10.078	17.272	14.265	14.487

[Er^{III}.tyr]

	$^4F_{9/2}$	$^4S_{3/2}$	$^2H_{11/2}$	$^4F_{7/2}$	$^4F_{5/2}$	$^2G_{9/2}$	$^4G_{11/2}$	$^4D_{9/2}$
Assignment								
E (cm^{-1})	15300	18400	19200	20500	22200	24600	26400	27400
f_{JO}	2.662	1.263	3.644	4.296	1.059	1.140	6.615	1.519

N.B. : τ_λ for Pr^{III}, Nd^{III} and Er^{III}; τ_2 17.69; 0.01; 1.24; τ_6 1; 16.45, 5.20; $\delta E^3/\delta E^1$: 0.0202, 0.0464, 0.0356.

in IERP-Racah (δE^k) parameters and the nephelauxetic ratio ($\delta E^3/\delta E^1$) values (cf. foot-note Table 1) are in good agreement with the above observation. Smaller values of $\delta E^3/\delta E^1$ for Er^{III} than for Nd^{III} indicate a predominantly ionic pattern of bonding.

The studies overall reveal that oscillator values are susceptible towards the Ln^{III} environment and the degree of complexation. The trends in τ_2 smaller than τ_4 and τ_6 and $\delta E^3/\delta E^1$ (negative and smaller) values indicate a change in the [Ln(III).tyr] interactions predominantly ionic to partial covalent from Nd^{III} to Er^{III}.

Experimental

Standard solutions of Ln^{III} nitrates (99.99% purity, Indian Rare Earths Ltd.) and tyrosine (Merck, G.R.) were prepared in double-distilled water. The solutions of Ln^{III} metal ions blank (~0.025 mol dm^{-3}) and [Ln(III).tyr] complexes (1 : 2) with total concentration of ~0.025 mol dm^{-3} were prepared. Carbonate free-NaOH solution (0.2 mol dm^{-3}) was used to maintain the pH, which were recorded on an Orion-940 extended ion analyzer system. Electronic spectra were recorded on a Perkin-Elmer lambda 3B spectrophotometer. Spectral parameter were calculated using Judd-Ofelt approach[6]. Inter-electronic repulsion Racah parameters (IERP-Racah; δE^k) for Pr^{III}, Nd^{III} and Er^{III} were evaluated using Wong's[7] equations. Self devised, Pascal compiled computer softwares were used to evaluate[4] these aforesaid parameters.

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