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NOTE

Studies of Luminescence Spectral Properties of Praseodymium(III) and Samarium(III) Complexes with N,N′,N″-Tri-(2,4-dihydroxylbenzophenone)-triaminotriethylamine

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Pr(III) and Sm(III) complexes with schiff base ligand N,N′,N″-tri-(2,4-dihydroxylbenzophenone)triamino-triethylamine have been prepared. Their luminescence properties in DMSO and THF have been investigated. The solvent factors influencing the luminescence intensity are also discussed.

Key Words: Luminescence properties, Solvent factor, N,N′,N″-Tri-(2,4-dihydroxylbenzophenone)triaminotriethylamine, Tripodal strucutre, Antenna effect.

Trivalent lanthanide chelates have been used in the development of luminescent labels in clinical chemistry. Schiff base lanthanide luminescence complex have also been recently reported[1,2]. To prepare such complex, it is essential to design the appropriate ligand which could readily and maximum enhance the luminescence properties of lanthanides by facilitating the well known light conversion process showing efficient ligand to metal energy transfer process (antenna effect)[3]. Ligand prepared here for complexation is doubly functionalized *i.e.*, having both selective ability to coordinated lanthanide ion and enhancing luminescence in them too. This ligand is synonyms of N,N′,N″-tri-(2,4-dihydroxylacetophenone)triaminotriethylamine[4] having tripodal structure.

Complexes with N,N′,N″-tri-(2,4-dihydroxylbenzophenone)triaminotriethylamine (H_6L) have been prepared as reported earlier[5].

Luminescence measurements were made on a Shimadzu R_f 540 spectrafluorometer equipped with quartz cuvettes of 1 cm path length with courtsey of Center of Advanced Study in Marine-Biology Annamalai University, India. The excitation and emission slit widths were maintained on 10 nm.

Since the ligand has multiple aromatic rings with a rigid planar strucutre, it can be predicted that Ln(III) complexes have strong luminescence due to antenna effect. Under similar conditions, the luminescence properties of two complexes were observed in DMSO, THF, DMF and CH_3OH solutions (1.0×10^{-4} mol L^{-1} each). These are listed in Table-1.

TABLE-1

Complex [conc. (mol lit^{-1})]	Solvent	λex (nm)	λem (nm)	R_f	Assignment
$Pr.H_3L \cdot 3H_2O$ [1.0 × 10^{-4}]	DMSO	365	592	723	$^5Do \rightarrow {}^7F_1$
			616	2426	$^5Do \rightarrow {}^7F_2$
	THF	365	592	436	$^5Do \rightarrow {}^7F_1$
			616	1638	$^5Do \rightarrow {}^7F_2$
	DMF	365	592	317	$^5Do \rightarrow {}^7F_1$
			616	724	$^5Do \rightarrow {}^7F_2$
	CH_3OH	365	592	192	$^5Do \rightarrow {}^7F_1$
			616	216	$^5Do \rightarrow {}^7F_2$
$Sm.H_3L \cdot 3H_2O$ [1.0 × 10^{-4}]	DMSO	350	492	156	$^5D_4 \rightarrow {}^7F_6$
			545	102	$^5D_4 \rightarrow {}^7F_5$
			585	17	$^5D_4 \rightarrow {}^7F_4$
	THF	350	490	126	$^5D_4 \rightarrow {}^7F_6$
			545	88	$^5D_4 \rightarrow {}^7F_5$
			585	16	$^5D_4 \rightarrow {}^7F_4$
	DMF	350	491	80	$^5D_4 \rightarrow {}^7F_6$
			544	46	$^5D_4 \rightarrow {}^7F_5$
			585	9	$^5D_4 \rightarrow {}^7F_4$
	CH_3OH	350	490	41	$^5D_4 \rightarrow {}^7F_6$
			545	17	$^5D_4 \rightarrow {}^7F_5$
			586	8	$^5D_4 \rightarrow {}^7F_4$

As evident from Table-1 in DMSO solution, the Pr(III) and Sm(III) complexes have the strongest luminescence. The order of luminscence is DMSO > THF > DMF > CH_3OH.

Due to presence of a scattering signal near 490 nm, the peak height at 545 nm for Pr was used to measure the luminescence intensities.

It is found that luminescence intensities of Pr(III) complex at 616 nm are stronger than those of Sm(III) complex at 545 nm in all the solutions.

The luminescence of Ln(III) complexes is related to the efficiency of the intra molecular energy transfer between the triplet level of ligand and the emitting levels of the ions, which depends on the energy gap between the two levels. In organic solvent-medium this gap is in favour of the energy transfer process.

Order of luminescence intensities is due to the coordinating effects of solvent[6]. Evidently, luminescence enhancement towards Ln(III) → H_6L from organic solvents is due to not only by removal of inner sphere coordinating water molecules but also energy transfer from organic solvents to the ligand. It may be that after absorbing radiation organic solvents transfer energy to the ligand which is subsequently transferred to emission levels of Ln(III) ion causing a sharp increase in luminescence intensity.

It is clear that ligand acts both as the energy donor and energy acceptor. The luminescence quantum yield (ϕ) of the Pr-H_6L-DMSO system was found to be 0.176 with quinine-bisulfate (0.55) in 1 M H_2SO_4 as reference[7].

UV-Vis spectra of the Pr-H_6L system in DMSO medium shows peak at 367 nm. It corresponds to π-π^* transition of the ligand. Its molar extinction coefficient is 6.34×10^{-4} L mol^{-1} cm^{-1}. Since energy transfer processes in Ln(III) complexes occur *via* absorption of light by the ligand followed by intra molecular energy transfer from the ligand to the metal ion. This strong absorption offers an efficient excitation mechanism for the Pr(III) ion.

Weaker intensity value of both complexes in CH_3OH solvent may be due to O-H oscillators of CH_3OH molecules. It is well known that the excited state of the lanthanide ions is efficiently quenched by interactions with high energy vibrations like O-H groups.

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