

Synthesis, spectroscopy and photophysical properties of mixed ligand complexes of europium(III) and terbium(III)

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Abstract

The synthesis and spectroscopic properties of mixed-ligand complexes of Eu^{III} and Tb^{III} with picolinic acid-*N*-oxide (picNO) plus either 2,2':2''-terpyridine (terpy) or 1,10-phenanthroline (*o*-phen) are described. The complexes were characterized by means of chemical analysis, IR, UV absorption and luminescence spectroscopy, excitation spectra and lifetime measurements. A 4f-4f intensity discussion for the Eu^{III} complexes is presented.

1. Introduction

The design of ligands capable of forming stable and highly luminescent Eu^{III} and Tb^{III} compounds is a theme of great interest in view of their potential applications as luminescent materials [1] and luminescent labels in fluoroimmunoassays[2].

In previous papers [3,4], we have studied the synthesis, spectroscopy and photophysical properties of Eu^{III} with 3-aminopyrazine-2-carboxylic acid and 2,2'-bipyridine or 1,10-phenanthroline, which behave as efficient light conversion molecular devices (LCMD) [5].

In order to increase the ligand-to-metal energy transfer efficiency, new compounds containing ligands with *N*-oxide groups like $\text{Eu}(\text{picNO})_3\text{L}$ (where $\text{L} = o\text{-phen}$ or *terpy*) have been synthesized and characterized as part of a study to determine the quantum emission efficiencies in highly luminescent lanthanide(III) compounds. In this paper, spectroscopic properties of these compounds are presented together with a phenomenological 4f-4f intensity discussion focused on the Eu^{III} complexes.

2. Experimental details

2.1. Preparation of the complexes

The complexes were prepared under reflux in aqueous ethanol solution from hydrated europium(III) and terbium(III) perchlorates, picNO and either *terpy* or *o*-phen. The pH of the mixture was controlled at 6.5 by addition of sodium hydroxide solution. Precipitation of the complexes resulted when the volume was reduced and the complexes were then recrystallized from the

ethanol. They consisted of white solids soluble in polar non-aqueous solvents like DMSO and dioxane and highly soluble in water; they decomposed in the temperature range 250–280 °C. C, H, N elemental analyses were performed by the microanalytical Laboratory of the University of São Paulo. The microanalyses indicated that the formulae of the complexes correspond to $\text{Ln}(\text{picNO})_3\text{L}$ ($\text{Ln} = \text{Eu}$ or Tb ; $\text{L} = o\text{-phen}$ or *terpy*) as expected.

2.2. Spectral measurements

IR spectra were recorded using mulls (Nujol and Fluorolube) or KBr pellets on a Beckman 4220 spectrophotometer (4000–650 cm^{-1}). The UV-visible absorption spectra were recorded on a Beckman Acta CV. Excitation was carried out using a 150 W xenon lamp, and a 0.25 m holographic grating monochromator for wavelength selection. The luminescence spectra were obtained using a Jobin-Yvon Ramanor U1000 double monochromator with a slit width of 100 μm . Lifetime measurements were made at 298 K using a pulsed nitrogen laser with excitation at 337 nm and monitoring the signals at 617 nm and 545 nm for the Eu^{III} and Tb^{III} complexes, respectively.

3. Results and discussion

3.1. Spectra and lifetimes

The IR spectrum of the $\text{Ln}(\text{picNO})_3 \cdot \text{terpy}$ complex has a strong band at 1590 cm^{-1} , due to the antisymmetric carbonyl stretch of the carboxylate of the ligand picNO, which is shifted from the 1650 cm^{-1} peak found for the acid form [6]. The spectrum also shows the char-

acteristic “breathing” vibration at approximately 1025 cm⁻¹ indicating a coordinated terpy, whereas the band at 988 cm⁻¹ for the uncomplexed ligand is absent [7,8]. These results suggest that all three nitrogen atoms of the terpy ligand are indeed bound to the Ln^{III} ion [8].

The absorption spectra for both Eu^{III} complexes in DMSO are characterized by the high intensity bands of the aromatic groups of the correspondent ligand.

The similarity between the absorption spectrum (*ca.* 350 nm) of the ligand and the excitation spectra of the Eu^{III} and Tb^{III} complexes shows that energy transfer occurs from the ligand to the encapsulated lanthanide ion. The complexes are stable in DMSO and dioxane solution, and their absorption and luminescence spectra are unaffected by varying the concentration between 4 × 10⁻⁴ and 2 × 10⁻⁵ M.

Both europium complexes are strongly luminescent, emitting in the ⁵D₀ → ⁷F₀₋₄ region. The luminescence spectrum of Eu(picNO)₃·terpy (Fig. 1) shows that the ⁵D₀ → ⁷F₂ transition is approximately twelve times more intense than the ⁵D₀ → ⁷F₁ transition, resulting in a bright red emission, and the ⁵D₀ → ⁷F₄ transition has a considerable intensity. The asymmetry in the weak ⁵D₀ → ⁷F₀ transition may be indicative of the presence of more than one emitting species, although at room temperature, the decay could be fitted with a single term of lifetime equal to 470 μs.

In the Eu(picNO)₃·*o*-phen complex, the ⁵D₀ → ⁷F₂ transition is approximately six times more intense than the ⁵D₀ → ⁷F₁ transition. The ⁵D₀ → ⁷F₄ transition also

has considerable intensity as can be seen in Fig. 2. The luminescence spectrum of this complex in DMSO at 298 K suggests that the Eu^{III} site symmetry is preserved. It is similar to the spectrum obtained from the solid, but with less well-resolved lines of slightly greater widths. The linewidth of the ⁵D₀ → ⁷F₀ transition is 1.16 nm in the solid and 1.59 nm in DMSO, which is still quite small.

Excellent luminescent characteristics and satisfactory stability of the Eu^{III} complexes in water seem to be very promising with respect to its potential applications as a luminescent probe in fluoroimmunoassays. Table 1 lists the luminescence lifetimes of the Eu^{III} and Tb^{III} complexes upon ligand excitation. The values in Table 1 show that the ligands are efficient absorbers. The energy transfer is very effective and the lifetimes of the excited (⁵D₀) europium, although longer than that of the Eu^{III}(aq), is short enough to provide good luminescence intensity. The lifetime of the *o*-phen complex obtained from Fig. 3, is longer than that observed in an oxysulfide matrix [9], which is cited as a strong luminescent system.

The analogous terbium(III) complexes have also been synthesized and characterized but they are only weakly luminescent, most likely due to an unfavorable energy mismatch between the ligand triplet level and the ⁵D₄ level of terbium(III) [10].

3.2. Intensity parameters

From the spectra shown in Figs. 1 and 2, we have determined the Ω₂ and Ω₄ intensity parameters by using

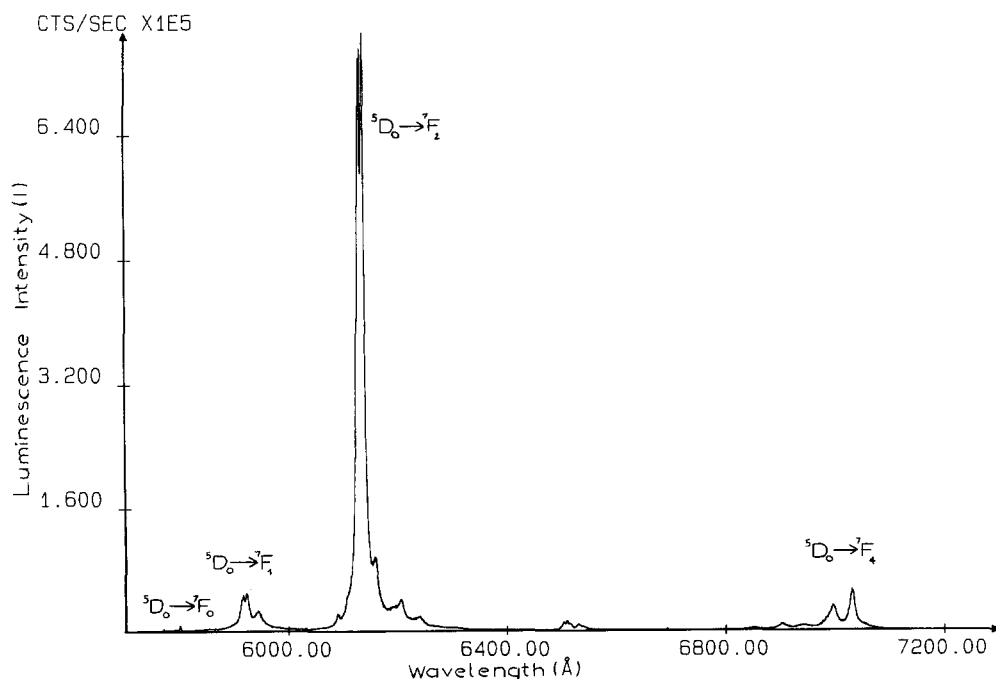


Fig. 1. Room temperature luminescence spectrum of the Eu(picNO)₃·terpy complex excited at 355 nm.

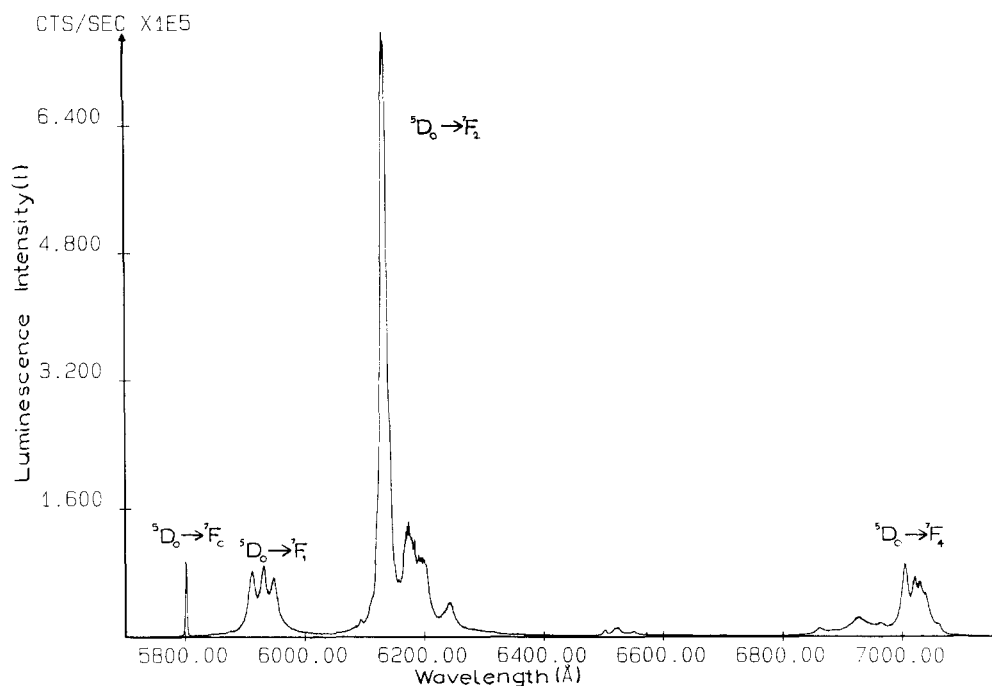


Fig. 2. Room temperature luminescence spectrum of the Eu(picNO)₃o-phen complex excited at 350 nm.

TABLE 1. Spectroscopic data^a of the Eu^{III} and Tb^{III} complexes at 298 K; the absorption data correspond to the complexes in solution while the luminescence and lifetime data correspond to the solid phase

Complex	Absorption		Luminescence		Life-times
	λ_{\max}^b	ϵ_{\max}^c	λ_{exc}^b	λ_{em}^b	
Eu(picNO) ₃ terpy	275	28	355	613	470
Eu(picNO) ₃ o-phen	280	16	350	613	740
Tb(picNO) ₃ terpy	275	26	310	583	286.2

^aExperimental errors $\pm 10\%$ on lifetimes.

^bnm.

^cMolar extinction coefficient in $M^{-1} \text{ cm}^{-1} 10^4$

^d 10^{-6} s.

the $^5D_0 \rightarrow ^7F_2$ and $^5D_0 \rightarrow ^7F_4$ transitions. As usual, the procedure is to express the emission intensity

$$I = \hbar\omega AN$$

where $\hbar\omega$ is the transition energy, A is the corresponding coefficient of spontaneous emission and N is the population of the emitting level, in terms of the surface under the emission curve. In practice, relative intensities are measured and in the case of the Eu^{III} ion, the common practice is to take as the reference the magnetic dipole $^5D_0 \rightarrow ^7F_1$ transition. In this procedure, J -mixing has been neglected and the appropriate reduced matrix elements were taken from ref. 11. An average index of refraction equal to 1.53 has been used in the Lorentz

local field correction which is present in the expressions for the coefficients of spontaneous emission. The results are presented in Table 2.

The first point to be noted is the rather unusual high values of Ω_2 and Ω_4 for the Eu^{III} compounds and their considerable variation, particularly Ω_2 , from one compound to the other. The $^5D_0 \rightarrow ^7F_2$ transition shows clearly its hypersensitive behavior to the chemical environment. These facts suggest that the dynamic coupling mechanism is very operative and it is possibly dominant with respect to the forced electric dipole mechanism [12]. This may be explained by the fact that the atoms, or groups of atoms, to which the Eu^{III} ion is coordinated are expected to be highly polarizable. Also, it is possible that the coordination geometry in both compounds is such that it provides high values of the odd rank sums-over-ligands which appear in the dynamic coupling as well as in the forced electric dipole Hamiltonians.

The Eu(picNO)₃o-phen complex, in which the coordination number of the Eu^{III} ion is 8, appears to have a first coordination sphere of very low symmetry. This is particularly indicated by the total splitting of the $^5D_0 \rightarrow ^7F_0$ transition. This point is further corroborated by X-ray structural determinations of similar compounds, with β -diketonates as ligands in place of picNO, in which the Eu^{III} ion occupies a site of very low symmetry [13].

In the Eu(picNO)₃terpy complex, the Eu^{III} ion is ninefold-coordinated. The intensity of the $^5D_0 \rightarrow ^7F_0$ transition is very low and the 7F_1 manifold shows practically only two components. These facts together

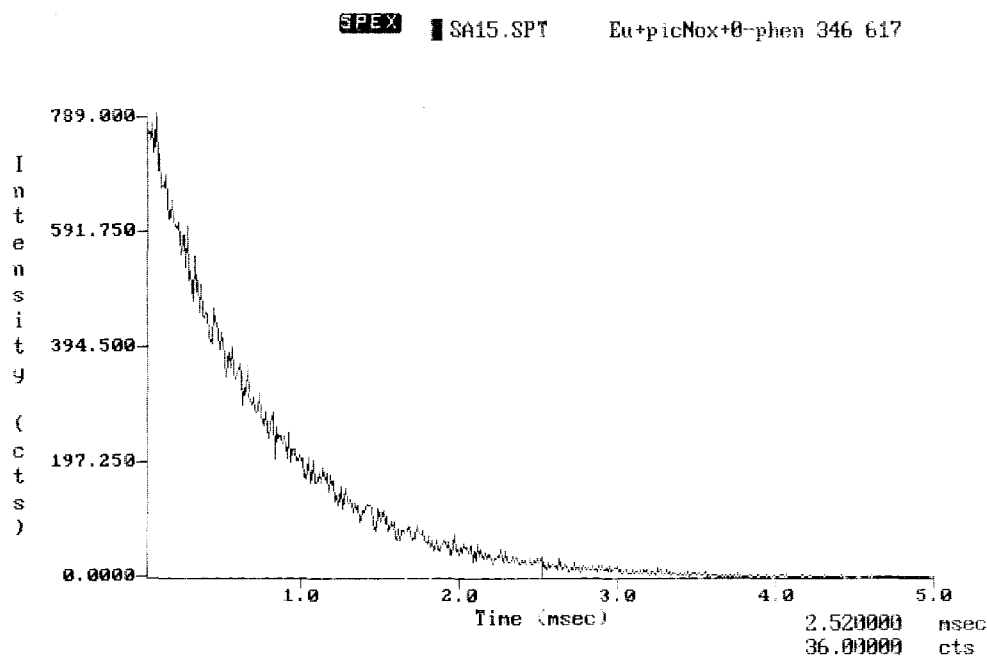


Fig. 3. Decay curve, at 298 K, of the ⁵D₀ level in the Eu(picNO)₃o-phen complex monitored at 613 nm.

TABLE 2. Experimental intensity parameters, Ω_2 and Ω_4 (in cm²), for the Eu(picNO)₃o-phen and Eu(picNO)₃Terpy complexes

	Eu(picNO) ₃ o-phen	Eu(picNO) ₃ Terpy
Ω_2	8.7×10^{-20}	22.8×10^{-20}
Ω_4	5×10^{-20}	8.3×10^{-20}

with the high value measured for Ω_2 suggest a site symmetry for the Eu^{III} ion close to D_{3h} . As mentioned previously, in this compound an asymmetry in the ⁵D₀ → ⁷F₀ transition is observed, indicating the presence of more than one site symmetry for the Eu^{III} ion.

In both spectra, from the observed splittings of the ⁷F₁ manifold, there is no evidence of high values of the second rank (B_2^2) ligand field parameters, although they are certainly the most relevant to account for the J -mixing effects on the ⁵D₀ → ⁷F₀ transition.

Provided that structural data are available, a theoretical calculation of these parameters is certainly of worth for a deeper elucidation of these points. This is currently under investigation in our laboratory.

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