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Synthesis and Spectroscopic Properties of Europium(III) and Terbium(III) Complexes with a Pyrano[2,3-b]pyridine Ligand

Carla Bisi Castellani, Oliviero Carugo*, and **Menico Rizzi**

Dipartimento di Chimica Generale, Università di Pavia, I-27100 Pavia, Italy

Summary. Novel Eu^{3+} and Tb^{3+} complexes with a pyrano[2,3-b]pyridine ligand have been synthesized and characterized. The stability constants in 1 : 1 *DMF*-water were determined. In solution, various tautomeric forms of the free ligand are present, and their equilibrium is influenced by complexation to Ln^{3+} cations. Both the Eu^{3+} and Tb^{3+} complexes present an intense cation luminescence following the ligand excitation in the UV region. The cation emission quantum yields and life-times are discussed with regard to the mechanism of the ligand-to-metal energy transfer process.

Keywords. Europium; Terbium; Pyrano[2,3-b]pyridine; Complexes of rare earth elements; f-f spectra of Eu^{3+} and Tb^{3+} complexes.

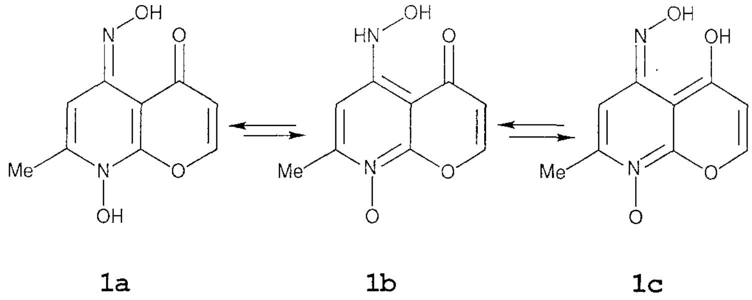
Synthese und spektroskopische Eigenschaften von Europium(III) und Terbium(III) Komplexen mit einem Pyrano[2,3-b]pyridin als Ligand

Zusammenfassung. Es wurden neue Eu^{3+}- und Tb^{3+}-Komplexe mit einem Pyrano[2,3-b]pyridin-Derivat hergestellt und charakterisiert. Die Stabilitätskonstanten in 1 : 1 *DMF*-Wasser wurden festgestellt. In Lösung liegen verschiedene tautomere Formen der freien Liganden vor, wobei die entsprechenden Gleichgewichte von der Komplexierung beeinflußt werden. Sowohl die Eu^{3+}- als auch die Tb^{3+}-Komplexe zeigen eine intensive Kationen-Lumineszenz, die auf die Liganden-Anregung im UV folgt. Die Kationen-Emissionsquantenausbeuten und die Lebenszeiten werden im Hinblick auf den Mechanismus des Prozesses beim Ligand-zu-Metall-Energietransfer diskutiert.

Introduction

The interest in the spectroscopic properties of lanthanoid(III) compounds is steadily increasing, because of their potential use in a variety of chemical and biological appliances [1, 7]. In the last few years, many efforts have been devoted to the synthesis and the photophysical characterization of europium(III) and terbium(III) complexes. Most of these studies are concerned with β-diketonato and polypyridine ligands, which behave as good chromophores towards lanthanoid(III) cations [4, 8–14]. These ligands have high molecular extinction coefficients in the UV region and effectively transfer the absorbed (UV) energy to Ln^{3+} cations (generally Eu^{3+} and Tb^{3+}), which eventually decay by emitting in the visible region with quite high quantum yields and long life-times.

Recently we observed that also ligands derived from 2- and 4-pyrone often sensitize the europium(III) and terbium(III) luminescence [15–18]. Therefore, as an extension of our previous works, in the present paper we report the synthesis and some photophysical properties of europium(III) and terbium(III) complexes with 4-oxo-5-hydroxylamino-7-methyl-4*H*-pyrano[2,3-b]pyridine 8-oxide [referred to as H_2*ppyox* if neutral, and H*ppyox* if monodeprotonated], whose tautomeric formulae are reported in Scheme 1. This ligand is interesting because it contains a pyrone and a pyridine moiety, which separately can behave as good sensitizers of the Eu^{3+} and Tb^{3+} luminescence.



Scheme 1

Experimental

Physicochemical Measurements

IR spectra were obtained with a 1130 Perkin-Elmer spectrophotometer as mujol mulls or KBr pellets. Electronic absorption spectra were recorded with a Varian Cary spectrophotometer; the solid state spectra were obtained by pasting the samples with nujol and spreading them on stripes of filter paper. Excitation and emission spectra were recorded with a LS50 Perkin-Elmer spectrophotofluorimeter; the excitation spectra were automatically corrected, and the emission ones were corrected according to Ref. [19]; the emission quantum yields were determined as the average of three measurements by using quinine sulphate solutions in 0.1 *N* H_2SO_4 as standard (estimated error = ±10%) [20, 21]. Although the decay curves of the examined samples were multiexponential, the life-times were evaluated assuming a monoexponential decay since only a sampling technique was available with our instrumental facilities. Conductometric measurements were carried out on $1 \cdot 10^{-5} - 5 \cdot 10^{-5} M$ solutions in *DMF*, by using a Radiometer CDM 80 conductometer, equipped with a Radiometer CDC 104 conductivity cell. Proton-ligand and metal-ligand stability constants were determined by the Calvin-Wilson *pH*-titration technique [22] in 1 : 1 *DMF*– water; an E366 Metrohm *pH*-meter equipped with a Metrohm glass electrode was used for *pH* measurements; the concentrations of the various species were in the range $1 \cdot 10^{-4} - 5 \cdot 10^{-4} M$, temperature 25±0.1°C and $I = 0.1\,M$ $NaClO_4$.

Syntheses

The H_2*ppyox* ligand was synthesized by literature methods [23]. The lanthanoid chlorides were prepared as previously described [24].

Complexes. 0.33 mmol of hydrated $LnCl_3$ ($Ln^{3+} = Eu^{3+}$ or Tb^{3+}), KOH (1 mmol) and H_2*ppyox* (1 mmol) were boiled for 90 min in 50 ml of ethanol. By slowly concentrating the obtained yellowish solution, the complexes *Ln*(H*ppyox*)$_2$Cl · H_2*ppyox* · H_2O precipitated as white powder. They were centrifugated, washed with ethanol and dried for 1 h at room temperature and 0.5 mm Hg. Dec.

points 205–210°C ($Ln^{3+}=Eu^{3+}$) and 210–215°C ($Ln^{3+}=Tb^{3+}$). Found ($Ln^{3+}=Eu^{3+}$): C 39.1, H 3.0, N 9.9; calc. for $C_{27}H_{24}ClEuN_6O_{13}$: C 39.2, H 3.0, N 10.1%. Found ($Ln^{3+}=Tb^{3+}$): C 38.9, H 2.8, N 10.0; calc. for $C_{27}H_{24}ClN_6O_{13}Tb$: C 38.8, H 2.9, N 10.1%.

Results and Discussion

Syntheses and Characterization of the Complexes

H_2*ppyox* can exist in three tautomeric forms (see Scheme 1) [23]. On the basis of the IR, ^{1}H-NMR and mass spectra it is impossible to assign unambiguously a structure to it, both in the solid state and in solution, and insofar it has been impossible to grow H_2*ppyox* crystals suitable for single crystal X-ray analysis.

The europium(III) and terbium(III) complexes of H_2*ppyox* have been formulated as *Ln*(H_2*ppyox*)$_2$Cl · H_2*ppyox* · H_2O on the basis of the elemental analyses. Their IR spectra are superimposable, and slightly different from that of H_2*ppyox*. While this one presents signals at 1 500, 1 570, and 1 630 cm^{-1}, the spectra of the complexes show bands at 1 545, 1 585, and 1 620 cm^{-1}, besides a wide band centered at 3 380 cm^{-1} assignable to the ν(OH). Nevertheless, since the assignment of the IR signals of the free ligand is ambiguous [23], the vibrational spectra do not allow to evaluate if the ligand is representable by the same tautomeric forms (see Scheme 1) when it is free and when it is complexed.

The complexes *Ln*(H*ppyox*)$_2$Cl · H_2*ppyox* · H_2O ($Ln^{3+}=Eu^{3+}$ or Tb^{3+}) are very slightly soluble in the most common solvents, with the exception of methanol, *DMF*, and ethanol. Their *DMF* solutions show ionic conductivities of 135.7 ($Ln^{3+}=Eu^{3+}$) and 141.3 $\Omega^{-1}cm^2mol^{-1}$ ($Ln^{3+}=Tb^{3+}$). These values indicate a 2 : 1 electrolyte behaviour [27] and therefore a quite low stability in solution.

The formation constants of the europium(III) and terbium(III) complexes with H_2*ppyox* were potentiometrically determined in 1 : 1 *DMF*–water. *DMF* was chosen because it is the only solvent able to dissolve quite well the free ligand. H_2*ppyox* shows a monoprotic acid behaviour, with $pK_a=7.43$ (±0.03), and the metal-ligand stability constants have the following values: $\log(\beta_1)=3.83\,(\pm0.03)$ and $\log(\beta_2)=6.88\,(\pm0.03)$ for $Ln^{3+}=Eu^{3+}$, and $\log(\beta_1)=3.76\,(\pm0.03)$ and $\log(\beta_2)=6.75\,(\pm0.03)$ for $Ln^{3+}=Tb^{3+}$[1]. The very small differences between the stability constants of europium(III) and terbium(III) complexes agree with the well known trend of variation of the stability constants along the lanthanoids series [28, 29]. No evidence of formation in solution of species containing more than two H_2*ppyox* ligands and/or more than one Ln^{3+} cation emerged. The stability constants of the lanthanoid(III) complexes with H_2*ppyox* are quite small with respect to those of the complexes with pyrone ligands reported in Table 1. This presumably can be ascribed to the H_2*ppyox* geometry which hinders its ability of binding a lanthanoid(III) cation. In fact, while all the other ligands reported in Table 1 can behave as bidentate forming stable five and hexaatomic chelated rings, this is not the case for H_2*ppyox*. A chelating behaviour of H_2*ppyox* would involve the pyrone carbonyl and the oxime oxygen atoms[2], giving a heptaatomic chelated ring, which is very unlikely and poorly stable in the case of lanthanoid(III) complexes [36].

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[1] β_1 refers to the reaction: $Ln^{3+}+H_2ppyox = Ln(Hppyox)^{2+}+H^+$; β_2 refers to $Ln^{3+}+2\,H_2ppyox = Ln(Hppyox)_2^{+}+2\,H^+$

[2] Lanthanoid(III) cations form more stable bonds with the oxygen than with the nitrogen oxime donor atoms (compare Ref. [35])

Table 1. Stability constants of europium(III) and terbium(III) complexes with pyrone ligands

Ligand	Eu^{3+}		Tb^{3+}		Solvent	Reference
	log (β_1)	log (β_2)	log (β_1)	log (β_2)		
H_2*ppyox*	3.84	6.88	3.76	6.75	1:1 *DMF* water	This work
Dehydroacetic acid	4.62	8.44	4.63	8.45	1:1 Dioxane – water	[30]
Maltol	6.72	12.03	–	–	Water	[31]
Kojic acid	5.35	10.45	–	–	Water	[32]
Kojic acid	6.15	11.25	–	–	Water	[33]
Kojic acid	6.12	–	6.25	–	Water	[34]
3-Acetyl-4-hydroxycoumarin	3.92	6.89	3.88	6.81	1:1 Dioxane – water	[30]
4-Methylesculetin	4.99	–	4.99	–	1:1 Ethanol – water	[17]
Coumarin-3-carboxylic acid	–	–	5.60	10.20	Methanol	[16]

Eventually, our data suggest that in $Ln(\mathrm{H}ppyox)_2\mathrm{Cl}\cdot \mathrm{H}_2ppyox\cdot \mathrm{H_2O}$ ($Ln^{3+} = \mathrm{Eu}^{3+}$ or Tb^{3+}) the anionic H*ppyox* ligands behave as non-chelating. Therefore, in the solid state they presumably bridge adjacent Ln^{3+} cations, in order to fulfill the coordinative requirements of the cations; it is probable that also the Cl^- anions act as bridging ligands in the solid state, as it happens in several other lanthanoid complexes [37]. In diluted solution (1 : 1 *DMF*—water) the solvated species $Ln(\mathrm{H}ppyox)^{2+}$ and $Ln(\mathrm{H}_2ppyox)_2{}^{+}$ are present, and the coordination of Cl^- anions is quite unlikely [38]. No experimental evidence on the involvement of the neutral H_2ppyox and of the water molecules in the coordination to Ln^{3+} arises from our data.

A strong interaction in solution between Ln^{3+} and neutral H_2ppyox seems unlikely, since the absorption spectrum (*DMF* and methanol solutions) of the free ligand is not affected by the addition of lanthanoid(III) salts. However, it is possible that neutral H_2ppyox coordinates the Ln^{3+} cation in the solid state, which is also the case for the water molecule.

Photophysical Studies

Figure 1 reports the absorption spectra of H_2ppyox in the solid state (λ_{max} at 314 and 290 nm), in 1 : 1 *DMF*—water solution (λ_{max} at 314 nm with log ε 3.91) and in methanol solution (λ_{max} at 314 nm and shoulders at 274 and 282 nm with log ε 3.92, 3.64 and 3.66 respectively). Although the lowest-energy band does not show solvatochromism by changing the solvent polarity (ranging from $\mathrm{CCl_4}$ to $\mathrm{CHCl_3}$, $\mathrm{CH_2Cl_2}$, dioxan, ethyl ether, *THF*, acetonitrile, benzene, toluene, *DMF*, 1 : 1

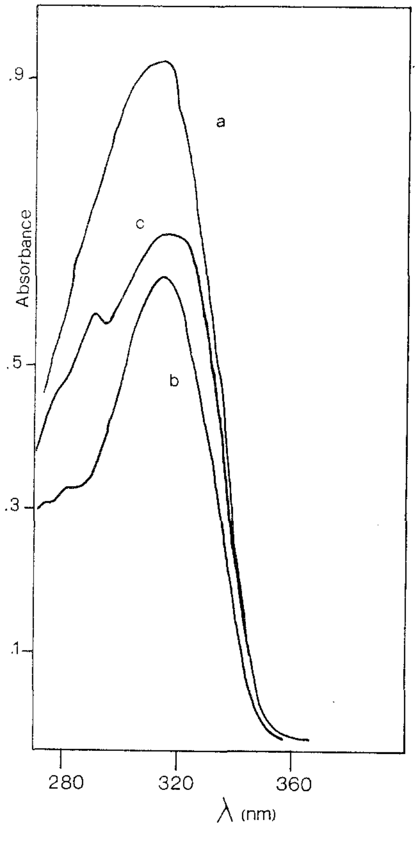

Fig. 1. Absorption spectra of H_2ppyox in 1 : 1 *DMF*—water (*a*), in methanol (*b*) and in the solid state (*c*)

DMF−water, ethanol and methanol), it has probably a prevalent π*-π character because of its high intensity [20, 39]; nevertheless, the quite low singlet-triplet splitting (about 35 kJ mol^{-1}, see below) suggests that this band has a certain π*-n character too [39]. The spectra of Fig. 1 are clearly different. Consequently, also the emission spectra depend on the solvent; by exciting in the 280–340 region, a structureless band with maximum at 425 nm (in methanol) or at 440 nm (in 1 : 1 *DMF*−water) appears, in spite of the fact that the quantum yields are not significantly different: 25% in methanol and 30% in 1 : 1 *DMF*−water (λ_{ex} 314 nm).

The dependences of the absorption and emission spectra on the solvent can depend either on the effects of the surrounding and/or on different equilibria between the tautomeric forms (reported in Scheme 1) in the various cases. The second hypothesis seems to be preferred on the basis of the H_2*ppyox* excitation spectra shown in Fig. 2, which present maxima at 280 and 330 nm (in methanol) and at 282 and 330 nm (in 1 : 1 *DMF*−water). Both the excitation spectra do not match the absorption spectra, indicating that the species emitting at 425–440 nm is/are only some of those absorbing UV light. Therefore, the differences between the spectra obtained in different solvents depend also (or only) on the differences in the equilibria between the tautomeric forms reported in Scheme 1.

The absorption spectra of the Eu^{3+} and Tb^{3+} complexes with H_2*ppyox* are superimposable and present (see Fig. 3) maxima at 282, 297, and 330 nm (in the solid state), at 282 and 318 nm with a shoulder at 296 nm (in 1 : 1 *DMF*−water) and at 282 and 320 nm with a shoulder at 296 (in methanol). The difference between the solid state and the solution spectra accounts for the instability of the complexes in solution. Moreover, the absorption spectra of the complexes (both in the solid state and in solution) are markedly different from those of the free ligand (see Fig. 1). This fact can be due either to the complexation itself and/or to a tautomeric rearrangement of the ligands following the complexation. The latter hypothesis seems preferable on the basis of the similarity between the absorption spectra of the complexes and the excitation spectra of the free ligand (see Fig. 2). In fact, as

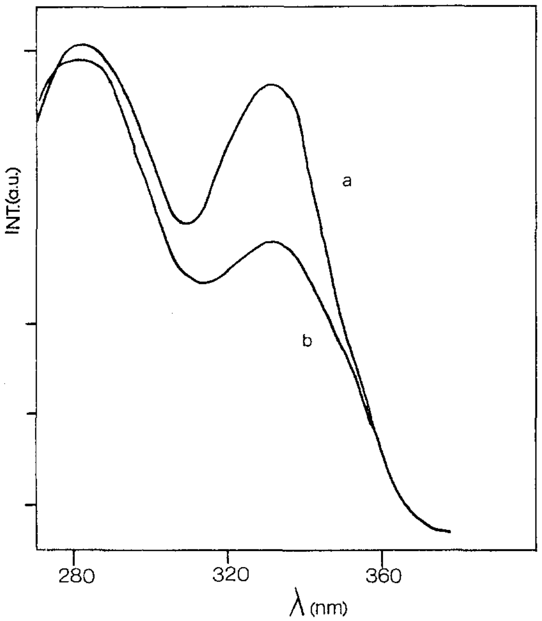

Fig. 2. Excitation spectra of H_2*ppyox* in 1 : 1 *DMF*−water (*a*) (λ_{em} = 440 nm), in methanol (*b*) (λ_{em} = 425 nm)

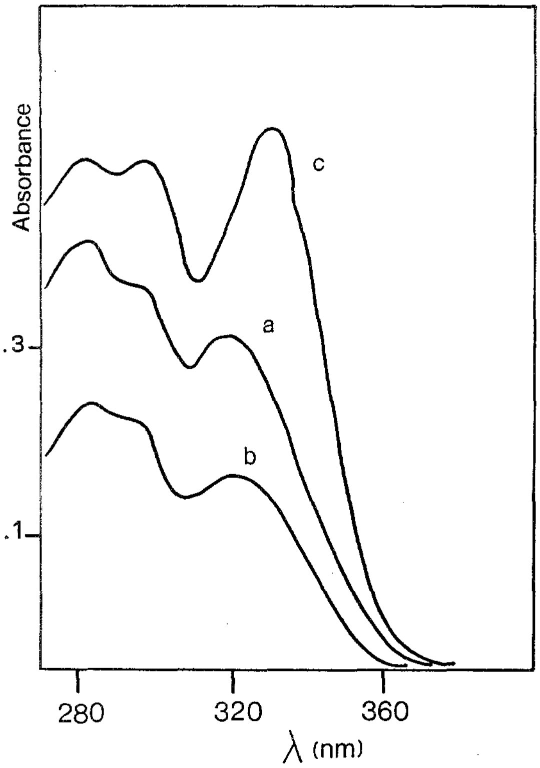

Fig. 3. Absorption spectra of Tb $(Hppyox)_2Cl \cdot H_2ppyox \cdot H_2O$ in 1 : 1 *DMF*-water (*a*), in methanol (*b*) and in the solid state (*c*)

we previously pointed out, the difference between the absorption and excitation spectra of the free ligand indicates that H_2*ppyox* is actually a mixture of more than one of the tautomeric forms shown in Scheme 1.

Excitation of the complexes in the ligand-centered bands results in the well known strucured luminescence of the lanthanoid ions. The observed transitions were the $^5D_0-{}^7F_j$ (j = 0, 1, 2, 3) in the case of the europium(III) complex, and the $^5D_4-{}^7F_j$ (j = 3, 4, 5, 6) in the case of the terbium(III) one. No emissions from upper excited states were detected. The emission quantum yield values do not depend on the excitation wavelength with the 270–340 nm region. Table 2 reports pertinent data on the luminescence properties of these complexes. These data show that, as a consequence of the instability of the complexes in solution, the emission quantum yields (Φ) markedly depend on the concentration of the sample. Moreover, while the Tb^{3+} complex has similar Φ and life-time (τ) values in methanol and in 1 : 1 *DMF*–water, the Eu^{3+} one shows Φ and τ values significantly higher in methanol than in 1 : 1 *DMF*–water. This is probably due to the non-radiative decay via multiphonon-like processes induced by the water molecules complexed to the metal[3], which affect the Eu^{3+} luminescence much more than the Tb^{3+} one [41–43].

At similar concentration the Φ values of the Tb^{3+} complex (both in 1 : 1 *DMF*–water and in methanol) are much higher than those of the Eu^{3+} complex,

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[3] Although methanol can behave in the same way as water, it can be assumed that the complexed water molecules are more effective than the methanol ones in deactivating the metal excited states; see Ref. [40]

Table 2. Emission quantum yields (Φ) and life-times (τ) of the complexes $Ln(Hppyox)_2Cl \cdot H_2ppyox \cdot H_2O$ ($Ln^{3+} = Eu^{3+}$ or Tb^{3+}) in 1 : 1 *DMF*−water and methanol solutions

Ln	Solvent	Concentration (mol/l)	Φ^a (%)	τ^b (ms)
Tb	1 : 1 *DMF*−water	$2.9 \cdot 10^{-6}$	4.2	0.37
Tb	1 : 1 *DMF*−water	$2.9 \cdot 10^{-4}$	22.3	0.38
Tb	*Me*OH	$3.2 \cdot 10^{-6}$	4.2	0.41
Tb	*Me*OH	$3.2 \cdot 10^{-4}$	20.3	0.43
Eu	1 : 1 *DMF*−water	$2.9 \cdot 10^{-6}$	0.2	0.14
Eu	1 : 1 *DMF*−water	$2.9 \cdot 10^{-4}$	1.0	0.15
Eu	*Me*OH	$3.2 \cdot 10^{-6}$	0.6	0.38
Eu	*Me*OH	$3.2 \cdot 10^{-4}$	2.0	0.38

[a] Quantum yield of the metal emission after exciting the ligands at wavelength with $0.01 < \text{absorbance} < 0.04$

[b] Life-time of the metal emission after exciting the ligands

agreeing with the fact that τ of the Tb^{3+} species are higher than those of the Eu^{3+} one. This can be due either to a different quenching efficiency of the metal excited states by the surrounding and/or to a different efficiency in the ligand-to-metal energy transfer process. The latter hypothesis seems to be preferred since the ratio between the Tb^{3+} and the Eu^{3+} life-times in methanol is much smaller than the ratio between their Φ values.

In order to reach a deeper understanding on the ligand-to-metal energy transfer process, the excitation spectra of the complexes were recorded both in 1 : 1 *DMF*−water and in methanol. They are very similar and reminiscent of those of the free H_2ppyox ligand (see Fig. 2) with the exception of a shoulder at 300 (1 : 1 *DMF*− water solution) and at 296 nm (methanol solution). The quite strict similarity between the excitation spectra of the complexes and that of the free ligand indicates that the ligand excited states which allow the energy transfer to Ln^{3+} are similar to those which allow the radiative decay of the free ligand.

Generally the intramolecular ligand-to-lanthanoid(III) energy transfer proceeds by a Dexter exchange mechanism through the lowest-energy ligand triplet state. Fig. 4 reports the phosphorescence emission spectrum of H_2ppyox at 77 K in glass of *EPA* (ether-pentane-ethanol), which consists in a poorly structured band with maxima at 475 and 510 nm. From this spectrum, the triplet energy is evaluable as about 408 nm (24 500 cm^{-1}). Such a value is about 4 000 cm^{-1} higher than the $^5D_4$ terbium(III) excited state, and therefore a triplet → $^5D_4$ energy transfer is probable and a thermally activated $^5D_4$ → triplet energy transfer (that is the "triplet quenching") is difficult [8]. This interpretation is supported by the excitation spectra of the terbium(III) complex, where the presence of the band corresponding to the lowest-energy singlet excited state of the ligand suggests that the ligand-to-metal energy transfer occurs through the ligand tirplet state. On the contrary, it seem probable that an energy transfer from the ligand triplet state to the europium(III) ion is poorly effective. It has been shown, both in the solid state and in solution, that the excited europium(III) ion levels $^5D_1$ and $^5D_0$, which are in general the metal levels accepting energy from the triplet state, are poor energy acceptor from the triplet state when the energy difference between the triplet and the $^5D_1$ ($^5D_0$)

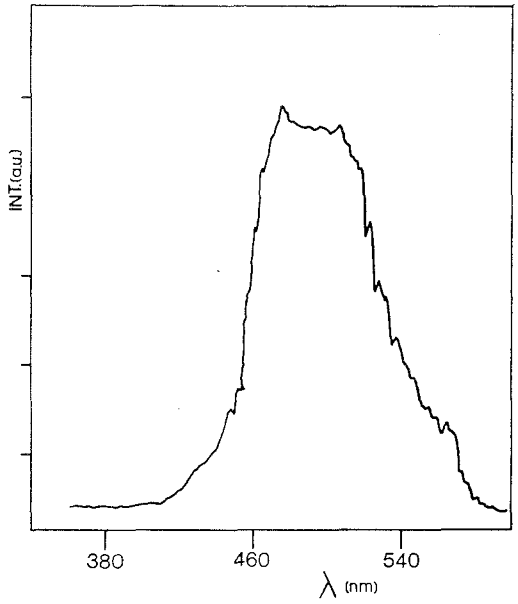

Fig. 4. Emission spectrum of H_2*ppyox* at 77 K in a glass of *EPA* (λ_{ex} = 314 nm)

levels is higher than 3000–4000 cm^{-1} [8, 44, 45]. In the present case such a difference can be evaluated as about 5500 ($^5D_1$) and 7000 cm^{-1} ($^5D_0$), and therefore neither the $^5D_1$ nor the $^5D_0$ europium(III) levels can behave as good energy acceptors. This interpretation is coherent with our data. The presence of the band corresponding to the lowest-energy excited singlet state of the ligand in the excitation spectra of the europium(III) complex suggests that the ligand-to-metal energy transfer occurs through the lowest-energy ligand triplet state; since the last one is too high in energy with respect to the europium(III) $^5D_1$ and $^5D_0$ states, the ligand-to-metal energy transfer is not effective and the emission quantum yield is low; on the contrary, the Eu^{3+} life-time does not drop as much as the emission quantum yield, because the $^5D_0$ excited state decays with poor involvement of the ligand excited states. The ligand-to-metal energy transfer could occur more effectively with the involvement of the upper Eu^{3+} excited states ^5D_j ($j > 1$), but no evidence for such a mechanism appears from the results of our experiments; at any rate, in that case, a "triplet quenching" could cause the not effective population of the europium(III) $^5D_0$ emitting level.

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