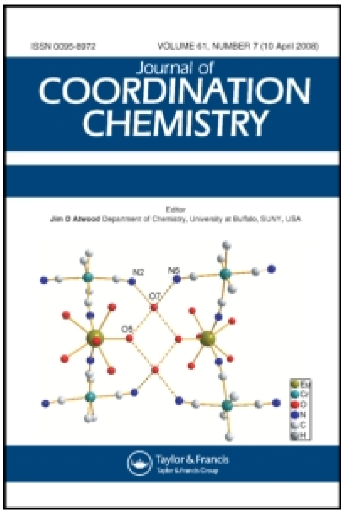

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PHOTOLUMINESCENCE OF THE EUROPIUM(III) AND TERBIUM(III) HOMODINUCLEAR POLYMERIC TETRAAZAMACROCYCLIC COMPOUNDS

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PHOTOLUMINESCENCE OF THE EUROPIUM(III) AND TERBIUM(III) HOMODINUCLEAR POLYMERIC TETRAAZAMACROCYCLIC COMPOUNDS

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The photoluminescence properties of the new $[Eu_2(16\text{-}ANE\text{-}N_4)(NO_3)_3(CHO_2)_3]_7$ (**1**) and $[Tb_2(16\text{-}ANE\text{-}N_4)(NO_3)_3(CHO_2)_3CH_2O_2]_7$ (**2**) compounds at 300 and 20 K show the characteristic fluorescence spectra of the Eu(III) and Tb(III) ions and an intrinsic emission when the samples are excited at 395 and 370 nm, respectively using a xenon lamp. The observed intrinsic emission of these complexes indicates a similar environment around the metals and evidence of the nature of these polymers. The luminescence lifetimes were found to be 1.74 and 2.94 μs for the $^5D_0 \rightarrow {}^7F_2$ (Eu(III)) and $^5D_4 \rightarrow {}^7F_5$ (Tb(III)) transitions, respectively at 300 K. To our knowledge, these are the shortest lifetimes measured for Eu(III) and Tb(III) complexes so far. Both the fluorescence spectra and the luminescence lifetimes of these complexes suggest an isostructural nature of these homodinuclear polymeric compounds.

Keywords: Emission; excitation; intrinsic emission; luminescence lifetime; tetraazacyclohexadecane ligand; homodinuclear lanthanide(III) polymeric compounds

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INTRODUCTION

Interest in the luminescence of lanthanide complexes has increased because this property is used in elucidation of molecular structures of coordination compounds in the solid state and in solution study of catalytic systems and other inorganic compounds. It has also been used in the study of biomolecular structures.[1]

The extremely high sensitivity of the Eu(III) ion has permitted wide application as a structural probe.[1] Taking advantage of the sensitivity, a complete analysis of the $^5D_J \rightarrow {}^7F_J$ transitions allowed us to determine the local symmetry of the metal site.

In addition, the luminescence lifetimes of the Eu(III) and Tb(III) complexes which are quite sensitive to the detailed nature of the ligand environment facilitated their characterization.[1b]

The luminescence lifetimes (τ) of the Eu(III) $^5D_0$ level, for instance, are in the range 0.1–1.0 ms in aqueous solutions; they are longer in anhydrous solutions (up to 2–2.5 ms) and much longer in deutereated solvents (τ_{Eu} = 4–4.4 ms). In the solid state, they may be as long as 5–6 ms. The $^5D_1$ level has a much shorter lifetime, usually < 0.05 ms. It is often strongly temperature-dependent, which is not the case for the lifetime of the $^5D_0$ level.

The luminescence lifetimes of the Tb(III) $^5D_4$ level, $\tau_{Tb}(^5D_4)$, are longer than $\tau_{Eu}(^5D_0)$; 0.4–5.0 ms in aqueous solution. It has been pointed out that in aqueous solution containing Tb(III) nitrates, the lifetimes depend on pH. Thus, it seems that Tb(III) serves as a sensitizer for the photochemical reduction of nitrate to nitrite.

This paper reports the luminescence properties of the recently reported homodinuclear macrocyclic polymeric compounds formed with the 1,5,9,13-tetraazacyclohexadecane ligand, 16-ANE-N_4 and Eu(III) and Tb(III) nitrate salts.[2]

EXPERIMENTAL

The title compounds were prepared and characterized as described elsewhere.[2,3]

Because of the hygroscopic nature of the compounds, the powder samples were sealed into small quartz tubes for luminescence studies.

Emission and excitation spectra at room temperature were recorded with a Perkin Elmer Model MPF-44B fluorescence spectrophotometer and corrected by the lamp intensity and the photomultiplier response. The excitation source was a 150-W xenon lamp. Lifetime data were obtained by pumping the samples with a 20 ns pulsed nitrogen laser and the resultant signal was monitored with a 200 MHz Hewlett-Packard 54200A Digital Oscilloscope. An Air Products liquid helium cycled closed refrigerator was used for obtaining 20 K spectra.

The luminescence spectrum of the hydrated Eu(III) salt was obtained to compare with the present case. The (16)-ANE-N_4 ligand showed no luminescence.

RESULTS AND DISCUSSION

In order to characterize $[Eu_2(16\text{-}ANE\text{-}N_4)(NO_3)_3(CHO_2)_3]_7$ (**1**) and $[Tb_2(16\text{-}ANE\text{-}N_4)(NO_3)_3(CHO_2)_3CH_2O_2]_7$ (**2**) we examined their luminescence and correlated their luminescence properties with their polymeric nature.

Figure 1 shows the emitted light of the lanthanide(III) complexes when irradiated with a pulsed nitrogen laser. The Eu(III) complex **1** shows a reddish light; the Tb(III) complex **2**, shows a sea-green light; and two different

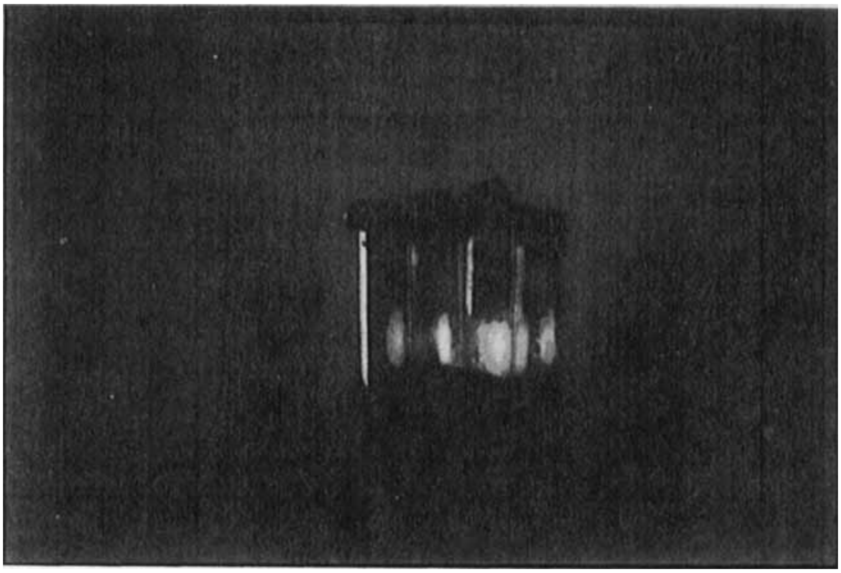

FIGURE 1 (See Colour Plate at back of issue.) Emitted light (from left to right) by erbium(III), europium(III), terbium(III) and erbium(III) homodinuclear polymeric macrocyclic compounds, which were excited with a pulsed nitrogen laser.

crops of the Er(III) compound (not discussed in this paper) show a blue light characteristic of the intrinsic emission band at about 450 nm.

The observation of lanthanide ion and ligand associated fluorescence in these different complexes under ultraviolet excitation is important and reflects the nature of these compounds.

The emission and excitation spectra of powder samples were obtained at 300 and 20 K. Since at 20 K no significant changes were observed, the luminescence lifetimes were carried out only at 300 K.

$[Eu_2(16\text{-}ANE\text{-}N_4)(NO_3)_3(CHO_2)_3]_7$, 1

Emission Spectrum

The emission spectrum of the Eu(III) compound 1 (Figure 2(c)) was obtained by irradiating the sample at a constant excitation wavelength of 395 nm, that is, exciting to the level $^5L_6$ (395 nm) and emission lines $^5D_0 \rightarrow {}^7F_1$, $^5D_0 \rightarrow {}^7F_2$, $^5D_0 \rightarrow {}^7F_3$ and $^5D_0 \rightarrow {}^7F_4$ were observed. These four transitions are normally observed in Eu(III) compounds, and their intensity and multiplicity elucidate the environment of the europium site.

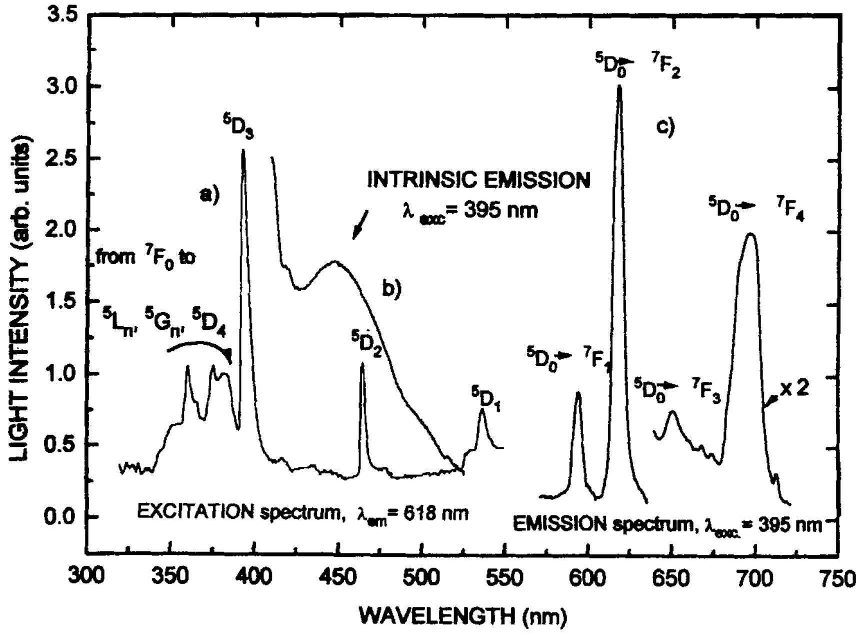

FIGURE 2 Luminescence and excitation spectra of the homodinuclear macrocyclic polymeric Eu(III) compound, 1, at 300 K (a) excitation spectrum, (b) intrinsic emission spectrum, (c) emission spectrum of the powder sample.

The transition $^5D_0 \rightarrow {}^7F_1$ (585–600 nm) is magnetic dipolar and its intensity is almost independent of the environment around the europium. It is an optically intense band only when there is an inversion center. In the $[Eu(NO_3)_2(12C4)]^+$ complex, this band becomes weak due to the lack of an inversion center.[1c] This band is rather weak in our compound as well.

The $^5D_0 \rightarrow {}^7F_2$ (610–625 nm) transition of electric dipolar character is a hypersensitive signal and is absent if the metal ion lies on an inversion center. Since this transition is the strongest and the narrowest in our complex, we conclude that the metal ion is not on an inversion center in this complex.

The transition $^5D_0 \rightarrow {}^7F_3$ (640–655 nm) is of electric dipolar nature; it is very weak because it is forbidden and is only observed with J-mixing, because this adds allowed magnetic dipolar character. This band is clearly observed in our polymeric compound and is split into four signals (637–676 nm); this transition has also been observed split in other macrocyclic compounds, *i.e* the $[Eu(NO_3)_2L]_3[Eu(NO_3)_6]$ with L = 18C6, 21C7.[4,5] Therefore, we propose that the characteristic splitting observed in this work is promoted by the nature of the polymer.[2]

The transition $^5D_0 \rightarrow {}^7F_4$ (680–710 nm) is of electric dipolar nature and sensitive to the environment of the europium ion. In compound **1**, the band was intense enough to be observed with a small shoulder at the right end. In other Eu(III) compounds[4,5] it has been observed that the intensity of this band is independent of their nature and the temperature and is more intense than the $^5D_0 \rightarrow {}^7F_3$ transition. In compound **1**, the opposite occurs: the transition $^5D_0 \rightarrow {}^7F_4$ is less intense than the $^5D_0 \rightarrow {}^7F_3$; this can be explained in terms of intramolecular bonds between the two metallic centers in the elemental unit[3] and also intermolecular bonds among the metallic centers in the polymer.

Intrinsic Emission Spectrum

Intrinsic emission is an important aspect in coordination compounds because it reflects the metal–ligand interactions.[1b] In the lanthanide compounds discussed in this paper, we observe a significant intrinsic emission. When the Eu(III) compound is excited at 395 nm, a broad band at 449 nm is observed, assigned to an intrinsic emission (Figure 2(b)). This is a particular feature of this dinuclear Eu(III) polymeric compound; the macrocyclic ligand exhibits no emission spectrum. This means that in this compound, energy transfer between the metal ion and the ligands occurs, supporting our previous proposal[2] that the two lanthanide atoms share the macrocyclic ligand and some bridging nitrates and formates in the elemental unit in the dinuclear polymeric compounds. Simultaneously these are joined together through these ligands, forming a polymer of seven units. Thus, in this dinuclear compound the intramolecular bonds between the two metallic centers in the elemental unit and the intermolecular bonds among the metallic centers in the polymer are responsible for the observed intrinsic emission.

From the analysis of the whole emission spectrum, we conclude that the metal ions in our Eu(III) polymeric compounds are in equivalent sites.

Excitation Spectrum

The excitation spectrum of the $^5D_0 \rightarrow {}^7F_2$ emission line of compound **1**, is given in Figure 2(a). The transitions $^7F_0 \rightarrow {}^5G_n$, $^5D_3$, $^5D_2$, and $^5D_1$ corresponding to the Eu(III) complexes were observed; between 350 and 380 nm there exists a group of transitions from $^7F_0 \rightarrow {}^5G_n$, $^5D_4$, ^5G_n, levels and $^5L_6$, these transitions are not usually analyzed.

Around 400 nm a quite sharp and intense band was observed that corresponds to the transition $^7F_0 \rightarrow {}^5D_3$. In the inorganic polymer: $Eu_2(H_2O)_{12}$-$[Mo_8O_{27}]\cdot 6H_2O$ this band is present at room temperature, although is not properly resolved, but it is better resolved at 4.2 K[6]. In the spectra of ethylenediamine Eu(III) complexes[7] in DMSO at room temperature this transition is also the most intense.

In our compound, this group of transitions and the $^7F_0 \rightarrow {}^5D_3$ are shown very clearly, and seem to be a particular pattern of our polymeric compound. The latter is the most intense excitation band and is consistent with the $^5D_0 \rightarrow {}^7F_3$ emission transition. Indeed, the whole spectrum is very typical in the morphology and intensity of these signals, a fact that can be assigned to the polymeric nature of this compound. The excitation transitions $^7F_0 \rightarrow {}^5D_1$, and $^7F_0 \rightarrow {}^5D_2$ are similar to other Eu(III) coordination complexes. In general, the excitation bands show that the Eu(III) ions in this molecule are equivalent. This is consistent with the conclusions obtained from the emission spectrum.

Luminescence Lifetime

For Eu(III) complexes, lifetimes ranging from tens of microseconds to milliseconds have been observed for the same $^5D_0$ excitation level. When a metal–metal interaction exists, this time tends to decrease;[1] in our compound this lifetime is very short. Lifetimes of less than 10 ns have been reported for dinuclear complexes, with 2:2 macrocyclic Schiff bases as ligand with closed shell ions (La^{3+}, Lu^{3+}) and the half-filled shell ion,

Gd^{3+}. These lifetimes correspond to a strong ligand fluorescence.[8] However, when the complexes contain lanthanide ions such as Eu(III), Tb(III), Pr(III), Ce(III), they show very weak ligand luminescence, indicative of an effective quenching process. The emission lifetimes are approximately 250 μs for Eu(III) complexes. In general, for other Eu(III) compounds the lifetimes are on the order of milliseconds in whatever environment they are found.[1,9] In addition, there are some reports related to nitrate[10] and NH,[7,8,11] concerning the great decrease in the lifetime of the $^5D_0 \rightarrow {}^7F_0$ transition due to a radiationless de-excitation when these groups are coordinated to Eu(III). Nevertheless, we must consider the possibility of de-excitation through another level, as for example, the $^5D_1$ level[1] or through the ligands. These have shorter lifetimes than the $^5D_0$ level.

In our compound, the lifetime for the $^5D_0$ level is extremely short, 1.74 μs, and as far as we know no lifetime this short has been reported for any other Eu(III) compound.[6,7] The very short found lifetime for complex **1** (see Figure 3) along with its intrinsic emission seems to be associated with the branched nature of the obtained polymer.

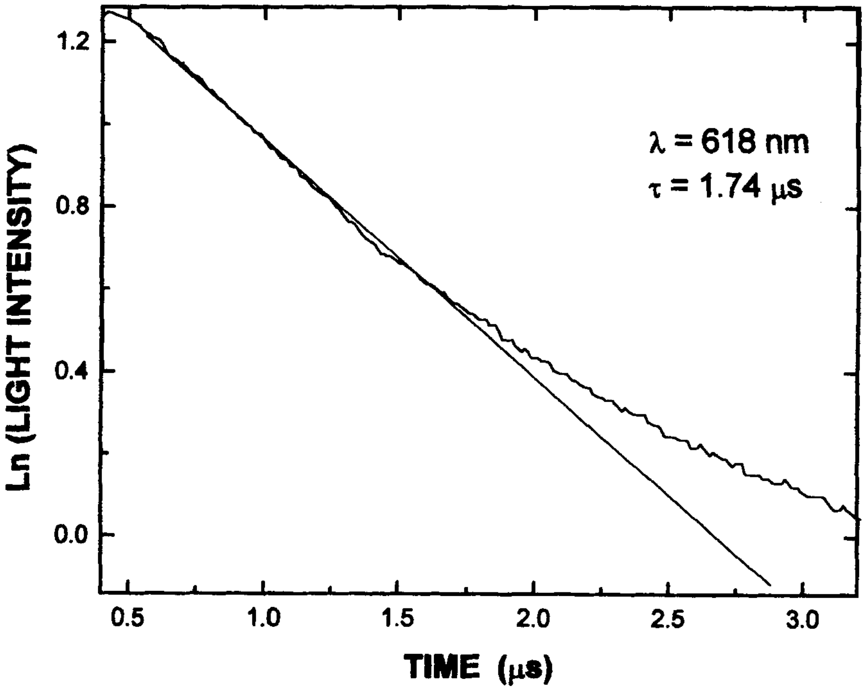

FIGURE 3 Lifetime of the homodinuclear macrocyclic polymeric Eu(III) compound, **1**, at 300 K.

The decay curve (Figure 3) is clearly not a single exponential. This can be explained considering that the excited state decay process in this compound is carried out by different paths promoted by the polymeric nature of the compound.

All these results support the original proposal that the elemental unit of the neutral dinuclear polymeric molecule previously discussed[2,3] is not linear. Nitrate and formate bonds, and perhaps some hydrogen bonds, favor fast decay of the emission. The macrocyclic ligand in this molecule has a determining role in shortening the lifetime, thus giving additional evidence of its coordination to the metal.

$[Tb_2(16\text{-}ANE\text{-}N_4)(NO_3)_3(CHO_2)_3CH_2O_2]_7$, 2

Emission Spectrum

The emission spectrum of compound 2 was obtained by irradiating the sample with a constant excitation wavelength of 378 nm. The following

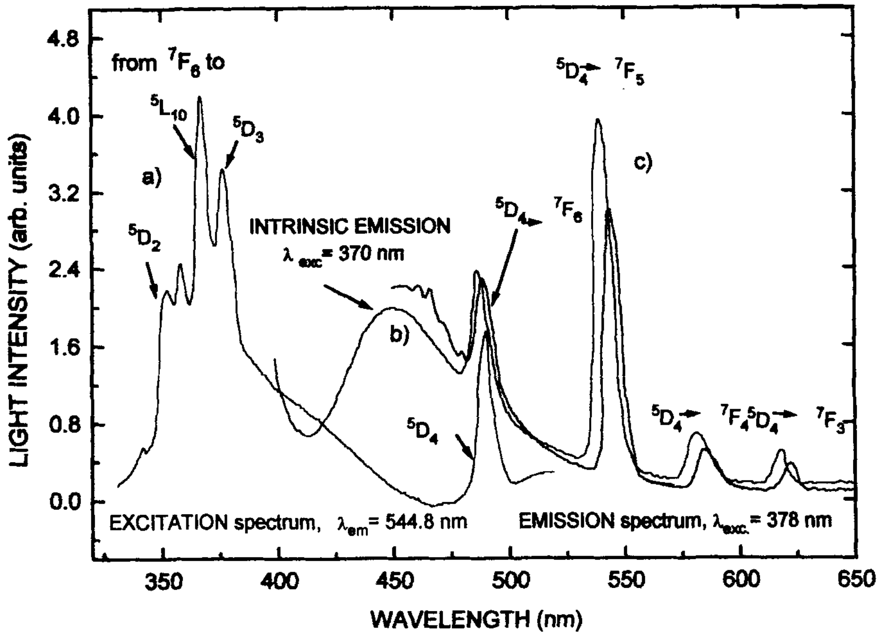

FIGURE 4 Luminescence and excitation spectra of the homodinuclear macrocyclic polymeric Tb(III) compound, 2, at 300 K (a) excitation spectrum, (b) intrinsic emission spectrum, (c) emission spectrum of the powder sample.

emission lines were observed $^5D_4 \rightarrow {}^7F_6$, $^5D_4 \rightarrow {}^7F_5$, $^5D_4 \rightarrow {}^7F_4$ and $^5D_4 \rightarrow {}^7F_3$, as shown in Figure 4(c). This spectrum is very similar to that reported in the literature for terbium compounds. The $^5D_4 \rightarrow {}^7F_6$ transition in this spectrum is more intense than the one usually reported for Tb(III) complexes and is very sensitive to the environment of the metal.[12] The $^5D_4 \rightarrow {}^7F_5$ transition is the most intense of the spectrum. The $^5D_4 \rightarrow {}^7F_4$ transition is also sensitive to the environment and in this compound is less intense than that reported for other Tb(III) macrocyclic compounds.[12b]

The morphology and the positions of the bands suggest that the metals in the polymeric unit have the same chemical environment.

Intrinsic Emission Spectrum

As for compound **1**, an important feature of compound **2** is an intrinsic emission when it is excited at 370 nm. The form of the intrinsic emission band is shown in Figure 4(b), appearing at 455 nm and slightly different to that of the Eu(III) compound, **1**. Therefore, we can assume that they have the same origin, since both complexes emit different light when they are excited at the same wavelength, supporting the fact they are isostructural.

Excitation Spectrum

This spectrum (Figure 4(a)) was obtained for an emission wavelength of 545 nm, to observe the $^7F_6 \rightarrow {}^5L_{10}$, $^5D_2$, $^5D_3$ and $^5D_4$ transitions. The $^7F_6 \rightarrow {}^5L_{10}$ is the most intense band in this spectrum followed by the $^7F_6 \rightarrow {}^5D_3$. The $^7F_6 \rightarrow {}^5D_2$ follows in intensity, between this and the $^7F_6 \rightarrow {}^5L_{10}$ transition, moreover, there appears a band of medium intensity which was not assigned. The observation that the $^7F_6 \rightarrow {}^5D_4$ excitation band coincides with the $^5D_4 \rightarrow {}^7F_6$ emission band confirms the fact that the dinuclear terbium compound **2** possesses a unique ion site. All this is in agreement with the emission results. Therefore, we conclude that the metallic centers share the same chemical environment, consistent with all the chemical evidence discussed previously.[2,3]

Luminescence Lifetime

It has been established that the lifetimes of different isostructural Tb(III) and Eu(III) compounds[1,12–15] are of the same order of magnitude. For instance, in the solid state at room temperature $[Eu(NO_3)_2(2,2)]NO_3$ shows a lifetime of 0.335 ms and the $[Tb(NO_3)_2(2,2)]NO_3$ of 2.02 ms. In this work, we have found that the lifetime of terbium complex (Figure 5) is 2.94 μs, and although it is slightly greater than that of the Eu(III)

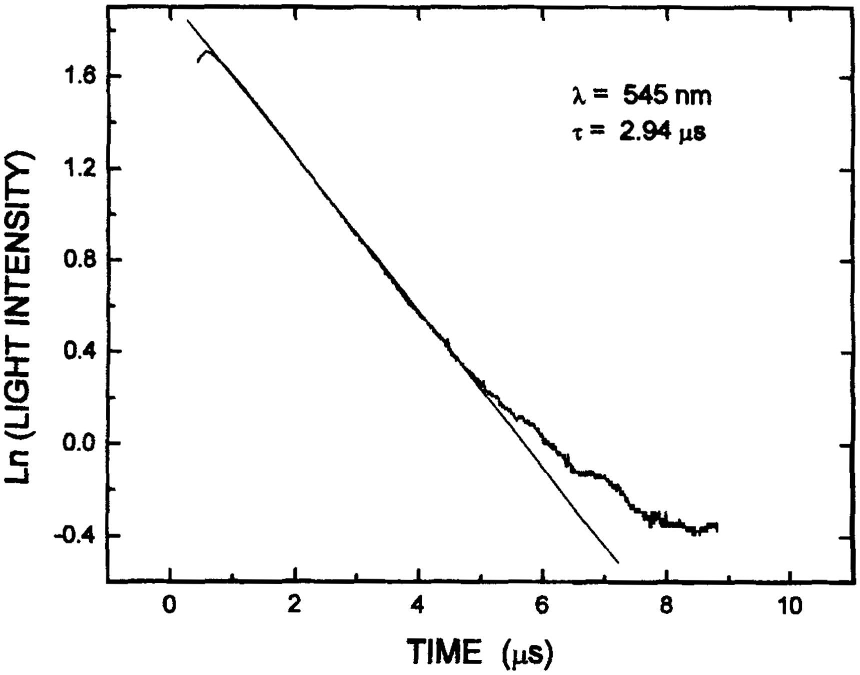

FIGURE 5 Lifetime of the homodinuclear macrocyclic polymeric Tb(III) compound, **2**, at 300 K.

compound **1**, both are the same order of magnitude. As for the Eu(III) compound the decay curve is not a single exponential and this is interpreted in the same way. We conclude that the title compounds are polymeric species of the same nature.

We then conclude that both the intrinsic emission and the luminescence lifetimes of these two complexes are direct evidence of the isostructural nature of these homodinuclear polymeric compounds.

Acknowledgments

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