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Luminescence of a new Tm^{3+} β-diketonate compound

Osvaldo A. Serra[a,*], Eduardo J. Nassar[a], Paulo S. Calefi[a], Ieda L.V. Rosa[b]

[a]*Laboratory of Rare Earth, Chemistry Department of FFCLRP, University of São Paulo, Av. Bandeirantes, 3900 CEP 14040-901 Ribeirão Preto, SP, Brazil*

[b]*Chemistry Department, CCET, Federal University of São Carlos, Rod. Washington Luiz, Km 235 CEP 13560-970 São Carlos, SP, Brazil*

Abstract

This work reports the results for the synthesis, characterization and photophysical properties of a new $Tm(ppa)_3 \cdot 2H_2O$ complex (ppa=3-phenyl-2,4-pentanedionate). Its characterization was carried out by EDTA titration and TGA analysis, which indicates the presence of the tris-β-diketonate complex with two water molecules completing the metal coordination sphere. The photophysical analyses of the $Tm(ppa)_3 \cdot 2H_2O$ complex were carried out at room (25°C) and liquid nitrogen (77 K) temperatures. Excitation and absorption spectra showed a broad band centered at ~335 nm which is ascribed to the complex, since the ppa absorbance maximum is centered at 296 nm. The emission spectra (λ_{ex}=335 nm) presented the characteristic bands of Tm^{3+} due to the $^1G_4 \rightarrow {}^3H_6$ (478 nm), $^1G_4 \rightarrow {}^3F_4$ (650 nm), $^1G_4 \rightarrow {}^3H_5$ (770 nm) and $^3H_4 \rightarrow {}^3H_6$ (790 nm) transitions. A pyridine adduct was also prepared but no spectral features could be observed in it. The $Gd(ppa)_3 \cdot 2H_2O$ was synthesized in order to determine the triplet state of the ppa. © 1998 Elsevier Science S.A.

Keywords: Thulium; Luminescence; β-Diketones

1. Introduction

Luminescence in rare earth organic compounds is due to intramolecular energy transfer from the excited ligand triplet state to the chelated ion. The efficiency of this energy transfer depends on the efficiency of: (i) the organic ligand absorption, (ii) the ligand-to-metal energy transfer, and (iii) the rare earth luminescence. The energy gap between the excited and ground state levels of the lanthanide and the rigidity of molecular structure contributes to the enhancement of the luminescent intensity of the system [1–4]. The photophysical properties of lanthanide complexes have been used in natural, medical, analytical and bioinorganic sciences [5,6]. The emission of Tm^{3+} in solution is extremely weak. However, the spectroscopic properties of Tm^{3+} solid compounds have been mainly studied in glasses and crystals, where its luminescence is an indication of the potential use of these materials as solid state lasers and optoelectronic devices [7–10]. In a previous work [4], we reported the results of the luminescence properties of the $Tb(ppa)_3 \cdot 2H_2O$ complex and its luminescent inclusion in a K_2SO_4 crystal, where we noticed that the ligand 3-phenyl-2,4-pentanedione (Hppa) efficiently transfers energy to Tb^{3+}. As we know, Tb^{3+} and Tm^{3+} have their lowest emitting levels almost at the same energy, 20 400 and 21 200 cm^{-1}, respectively [4,7]. This fact led us to prepare the complex of Tm^{3+} with ppa. In this communication, we report the results for the synthesis, characterization and photophysical properties of a new $Tm(ppa)_3 \cdot 2H_2O$ complex. Since the ppa is a new ligand and its spectral data are not in the literature, we synthesized the $Gd(ppa)_3 \cdot 2H_2O$ in order to know the triplet energy state of the ligand.

2. Experimental section

The $Tm(ppa)_3 \cdot 2H_2O$ complex was synthesized by the addition of aqueous 1.0×10^{-2} M $TmCl_3$ (from Rhône-Poulenc oxide) to an aqueous-methanolic solution of ppa (Parish) 5.0×10^{-2} M (pH~7.0) and then stirred overnight. The solid complex was filtered and dried at room temperature under reduced pressure. Its characterization was carried out by EDTA titration [11] and TGA analysis (SDT 2690 simultaneous DTA/TGA from TA instruments), which indicate the presence of the tris-β-diketonate complex with two water molecules completing the metal coordination sphere. The Gd^{3+} compound was prepared using this same procedure. A Tm^{3+} pyridine adduct was

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*Corresponding author. Fax: +55 16 6338151; e-mail: osaserra@usp.br

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also made according to the procedure described in a previous paper [4] for the Tb^{3+} analogous compounds. The photophysical measurements of the compounds were obtained using a Spex–Fluorolog II spectrometer at room temperature (25°C) and at 77 K.

3. Results and discussion

Fig. 1 shows the excitation spectra of $Tm(ppa)_3 \cdot 2H_2O$, $\lambda_{em}=478$ nm, recorded at room (Fig. 1a) and liquid nitrogen (Fig. 1b) temperatures. Both excitation spectra showed a broad band centered at 335 nm. This maximum is in agreement with a possible charge transfer due to the complex, since the ppa absorbance maximum is centered at 296 nm. In the excitation spectrum recorded at liquid nitrogen temperature, a narrow band at 344 nm was also observed. This band is ascribed to the $^3H_6 \rightarrow {}^1D_2$ transition. The phenyl group attached to the C3 in the ppa ligand should be an efficient antenna for the transfer of the absorbed energy to the metal ion Tm^{3+} through the enolate conjugated system. In this way, the $Tm(ppa)_3 \cdot 2H_2O$ compound, unlike the Tm^{3+} solutions, presents a very efficient blue emission when excited at 335 nm.

Fig. 2 presents the emission spectra of $Tm(ppa)_3 \cdot 2H_2O$ complex at room (a) and liquid nitrogen (b) temperatures, both excited at 335 nm. These spectra show the characteristic emission bands due to the $^1G_4 \rightarrow {}^3H_6$, $^1G_4 \rightarrow {}^3F_4$ and $^1G_4 \rightarrow {}^3H_5$ transitions of Tm^{3+} at 478, 650 and 770 nm, respectively. It was noticed that when the spectrum was recorded at liquid nitrogen temperature (Fig. 2b) the $^1G_4 \rightarrow {}^3H_6$ transition of Tm^{3+} at 478 nm was split into at least five components. The pyridine adduct of the $Tm(ppa)_3$ complex, as the analogue $Tb(ppa)_3 \cdot phen$, showed a pronounced decrease in emission intensity. This emission was so weak that it was not possible to measure it.

The emission spectra of $Gd(ppa)_3 \cdot 2H_2O$ ($\lambda_{exc}=340$ nm, 77 K) showed a large band with a maximum at 520 nm (19 200). If we consider this band to be the 0→0 T to S_0 transition, the triplet energy level is at 19 200 cm^{-1}. That is, a lower energy than the emitting levels for Tb^{3+} and Tm^{3+} at 20 400 and 21 200 cm^{-1}, respectively. Even considering it as a 0→1 transition, the triplet state should be only ~1500 cm^{-1} higher and would still not have enough energy to populate the Tm^{3+} emitting level. The only assumption that we can make is to consider a direct transfer from the system charged level situated above the $^1G_4$ level of Tm^{3+}, as indicated in Fig. 3. In Fig. 2, we can also observe a weak and broad band centered at ~525 nm due to a possible triplet emission.

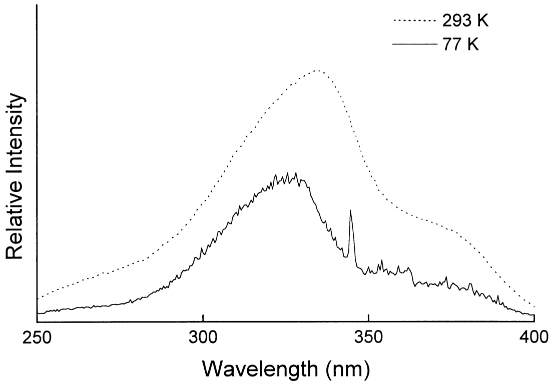

Fig. 1. Excitation spectra of $Tm(ppa)_3 \cdot 2H_2O$, $\lambda_{em}=478$ nm, at 293 and 77 K.

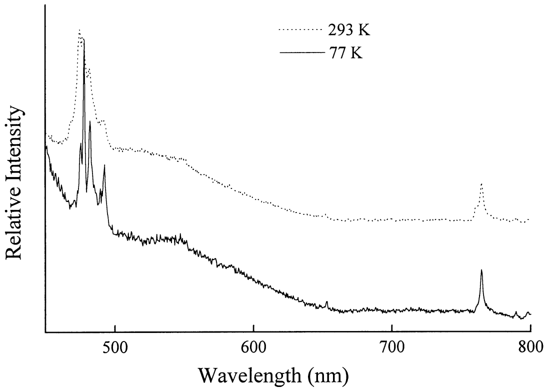

Fig. 2. Emission spectra of $Tm(ppa)_3 \cdot 2H_2O$, $\lambda_{exc}=335$ nm, at 293 and 77 K.

As we have demonstrated, a solid luminescent Tm^{3+} organic complex was synthesized and characterized photophysically for the first time. Several Tm^{3+} complexes that show some emission in organic solvents have been described by Sharma and van Doorn [7], the one with dipycolinate (dpa) being the most intense in acetone

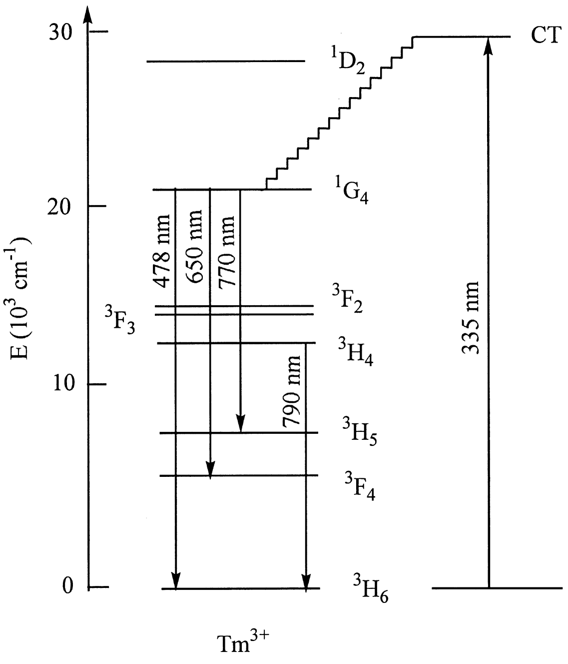

Fig. 3. Energy level scheme for Tm^{3+} [12] and the CT energy level.

solution. In order to compare it with our compound, we prepared $(NH_4)_3Tm(dpa)_3 \cdot 6H_2O$ [13]; however, the luminescence was so weak that we were unable to register the emission spectrum.

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