



A polymeric europium complex with the ligand thiophene-2-carboxylic acid: Synthesis, structural and spectroscopic characterization



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ABSTRACT

A polymeric complex $[\text{Eu}(\alpha\text{-tpc})_3(\alpha\text{-Htpc})_2]_n$ and its characterization by single crystal X-ray and thermal analysis, infrared and photoluminescence spectroscopies are described. The compound crystallizes in the monoclinic Cc space group. The asymmetric unit is formed from a europium ion bonded to one carboxyl oxygen of five different thiophene carboxylic moieties. Three of these moieties are deprotonated and bridge between neighboring europium ions giving rise to an infinite polymer along the c axis. Besides the europium characteristic emission lines, the emission spectra show unambiguously the crystal size effect on the ${}^5\text{D}_0 \rightarrow {}^7\text{F}_0$ transition. The complex thermal decomposition at 220 °C leads to a stable luminescent complex in which the ${}^5\text{D}_0 \rightarrow {}^7\text{F}_4$ transition reveals a monomeric characteristic. The Judd–Ofelt intensity parameters to the polymeric and the monomeric compound with the same ligand and coordination number were compared.

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1. Introduction

The lanthanide ions have high coordination number and show particular magnetic and luminescent properties. Lanthanide metal–organic framework (MOFs) have attracted much attention [1] due to their potential usefulness in photo [2] and thermal sensing [3,4], biomedical imaging [5], drug delivery [6] and magnet devices [7–9] among other applications [10–13].

The thiophene-based molecules show some interesting applications like in OLED [14,15], electrochromic agents [16–18] solar cells [19,20], linear and nonlinear optical properties [21], photovoltaic devices [22–24], electronics in general [25–28], cancer treating [29–32] and antimicrobial agent [33,34]. The presence of a sulfur atom has major consequences in that it enhances the aromatic character of thiophene. Thiophene stands as a unique five-membered heterocycle as it maintains steadfastly its aromaticity character through all manners of transformations, including fusion with other aromatic rings, resulting in thousands of other aromatic derivatives. The main point is that the thiophene ring is rich in electrons as sulphur increases the electronegativity of the group and so rises the reactivity for any kind of electrophilic reagent [35,36]. This property makes the thiophene-based molecules useful as complexes building blocks [37–41]. Luminescent polymeric complex with trivalent lanthanide ions have been frequently re-

ported [42–45]. In particular, the thiophene ligands have successfully been used to obtain molecular organic frameworks [46–52].

We report here the luminescent properties of the polymeric $[\text{Eu}(\alpha\text{-tpc})_3(\alpha\text{-Htpc})_2]_n$ and its thermally decomposed stable complexes. The polymeric synthesis method is cleaner and considerably softer than that one described in the literature by Yuan [53], for which the synthesis involves ZnO addition.

2. Experimental

2.1. Preparation of the complexes

Thiophene-2-carboxylic acid, $\text{C}_5\text{H}_4\text{O}_2\text{S}$, europium(III) and gadolinium(III) oxides, and zinc acetate dihydrate, were Fluka and Aldrich products respectively, with analytical-grade purities. The europium(III) and gadolinium(III) with thiophene-2-carboxylic acid ($\alpha\text{-tpc}$) complexes were prepared by addition of 1.6×10^{-4} mol of LnCl_3 (previously prepared from Ln_2O_3) to 1.0 mmol of ligand, both in aqueous solution ($T = 60^\circ\text{C}$) with pH solution adjusted to 5.0. The mixture was left in stirring for 24 h. After few days, colorless crystals appeared in the form of needles. Because the Gd(III) ion does not present emitting levels in the visible region, in the Gd(III) homologue complex the triplet ligand level was determined, thus enabling the triplet state determination by the ligand emission.

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2.2. Characterization methods

Thermal analysis was performed on a Thermoanalyzer TGA/DSC simultaneous STA 409 PC Luxx, Netzsch, under the following conditions: synthetic air, 50 mL/min, and heating rate 10 K/min, from 25 to 1300 °C. Infrared spectra were recorded on an FT-IR Spectrum Perkin Elmer 2000 with samples prepared as KBr pellets (10 kbar) using about of 1:10 sample:KBr ratio. The luminescence spectra were recorded at ≈ 298 K and ≈ 77 K in a Spectrofluorimeter Fluorolog Horiba Jobin Yvon FL3–222 model with a 450 W Xenon lamp. The emission lifetime was obtained using a Phosphorimeter Jobin Yvon, model FL-1040 equipped with a xenon arc pulsed lamp (25 Hz). The monomeric complex structure was calculated using semi empirical method which has advantages due the low computer time for calculus and high accuracy in the prediction of bond lengths and bond angles [54–56]. The Sparkle/AM1 methodology [57] was developed and implemented in the MOPAC2009 package [58].

2.3. X-ray structural determination

A colorless prismatic crystal of dimensions $0.26 \times 0.16 \times 0.07$ mm³ was selected and mounted on an Enraf–Nonius Kappa-CCD diffractometer with graphite monochromated Mo K α ($\lambda = 0.71073$ Å) radiation. The final unit cell parameters were based on all reflections. Data collections were made using the COLLECT program [59]; integration and scaling of the reflections were performed with the HKL Denzo–Scalepack system of programs [60]. Absorption corrections were carried out using the GAUSSIAN method [61]. The structure was solved by direct methods with SHELXS-97 and the model was refined by full-matrix least squares on F2 by means of SHELXL-97 [62].

3. Results and discussion

3.1. Crystal structure

As shown by the X-ray analysis the formula $[\text{Eu}(\alpha\text{-tpc})_3(\alpha\text{-Htpc})_2]_n$, results. The structure is disordered in that all thiophenolic rings occupy alternatively two positions related to one another by an 180° rotation about the C–C sigma bond. In this situation the sulfur and one carbon atom of the ring occupy the same position. Therefore sulfur and carbon atoms were assign to that site with occupancies constrained to add up to one. For the five different thiophenes the occupancy factors for the shared sites converged to minimum and maximum values of 0.5004 and 0.8280. This strategy produced a much lower R1 factor but, of course, it introduced bias in the geometry and displacement parameters of the rings. For this reason, hydrogen atoms were not included in the model. The asymmetric unit is formed from a europium ion bonded to one carboxyl oxygen of five different thiophenecarboxylic moieties. Three of these moieties are deprotonated and bridge between neighboring europium ions giving rise to an infinite polymer along the *c* axis. The other two moieties have their second oxygen atom protonated [as indicated by their longer interatomic distances, O(32)–C(31) = 1.338(7) and O(52)–C(51) = 1.323(8)] and are therefore uncharged, as required to balance the overall electric charge. The compound crystallizes in the monoclinic system, space group Cc (No. 9). Data collection and experimental details are summarized in Table 1. An ORTEP [63] projection of the asymmetric unit is shown in Fig. 1.

According to the Fig. 1, the following formula, $[\text{Eu}(\alpha\text{-tpc})_3(\alpha\text{-Htpc})_2]_n$, was proposed. The view along the *b* and *c* axis is showed in Fig. 2a and b, respectively. In the Table 2 are the selected bond lengths [Å] and angles [°] for the polymeric $[\text{Eu}(\alpha\text{-tpc})_3(\alpha\text{-Htpc})_2]_n$

Table 1
Crystal data and structure refinement.

Empirical formula	C ₂₅ H ₁₇ EuO ₁₀ S ₅
Formula weight	789.65
Temperature (K)	293(2)
Wavelength (Å)	0.71073
Crystal system	monoclinic
Space group	Cc
Unit cell dimensions	
<i>a</i> (Å)	20.5494(5)
<i>b</i> (Å)	14.1831(4)
<i>c</i> (Å)	9.7897(3)
α (°)	90
β (°)	92.021(2)
γ (°)	90
Volume (Å ³)	2851.47(14)
<i>Z</i>	4
Density (calculated) (mg/m ³)	1.839
Absorption coefficient (mm ⁻¹)	2.621
<i>F</i> (000)	1560
Crystal size (mm)	0.260 × 0.162 × 0.070
Theta range for data collection (°)	2.69–26.00
Index ranges	–24 < <i>h</i> < 25, –17 < <i>k</i> < 16, –12 < <i>l</i> < 11
Reflections collected	9604
Independent reflections (<i>R</i> _{int})	5333 (0.0652)
Completeness to theta = 26.00°	99.7%
Refinement method	Full-matrix least-squares on <i>F</i> ²
Data/restraints/parameters	5333/2/380
Goodness-of-fit on <i>F</i> ²	1.034
Final <i>R</i> indices [<i>I</i> > 2σ(<i>I</i>)]	<i>R</i> ₁ = 0.0332, <i>wR</i> ₂ = 0.0869
<i>R</i> indices (all data)	<i>R</i> ₁ = 0.0345, <i>wR</i> ₂ = 0.0881
Absolute structure parameter	–0.029(11)
Largest difference in peak and hole (e Å ⁻³)	0.551 and –2.094

complex. Structure data have been deposited with the Cambridge Crystallographic Data Centre (CCDC 922603).

3.2. Thermal analysis

The thermal analysis of the $[\text{Eu}(\alpha\text{-tpc})_3(\alpha\text{-Htpc})_2]_n$ shows the mass loss at about 100 °C, which was attributed to 1.5 H₂O molecules (3.16% Anal./3.06% Calc.) that were probably adsorbed in the complex surface. There is also a loss of one ligand molecule starting close to 200 °C (14.6% Anal./14.5% Calc.) and subsequently two more ligands molecules are observed to be lost at 390 °C (30.1% Anal./29.1% Calc.). The residual mass is attributed to a Eu₂(SO₄)₃ [64] molecule (33.6% Anal./33.5% Calc.), Fig. 3.

It is important to note that there is a stable product in the region around 180–380 °C that was attributed to a product resulting from one ligand molecule lost. This stable intermediate product, denominated $[\text{Eu}(\alpha\text{-tpc})_3(\alpha\text{-Htpc})]$, will be described in the following sections.

3.3. FT-IR analysis and theoretical calculations

The ligands containing the carboxylic groups can be coordinated to the metal by monodentate or bidentate modes. When the coordination is bidentate, it can occur by chelate or bridge mode and analyzing the infrared spectra, specifically the $\nu_{\text{asym}}(\text{COO}^-)$ and $\nu_{\text{sym}}(\text{COO}^-)$ bands, it is possible to make a coordination mode prediction. When the difference between the $\nu_{\text{asym}}(\text{COO}^-)$ and $\nu_{\text{sym}}(\text{COO}^-)$ bands is larger than in the ligand salt, the coordination mode is monodentate. If this value is significantly less than the anionic value the ligand mode is chelate and if this value is close to that of the isolated ligand, the coordination is bridging [64].

The vibrational frequencies related to $\nu_{\text{asym}}(\text{COO}^-)$ and $\nu_{\text{sym}}(\text{COO}^-)$ and the difference between them ($\Delta_{\text{asym-sym}}$) for

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