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Journal of Molecular Structure 751 (2005) 85–94

Journal of MOLECULAR STRUCTURE

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Preparation, crystal structure and optical spectroscopy of the rare earth complexes ($RE^{3+} = Sm$, Eu, Gd and Tb) with 2-thiopheneacetate anion

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Received 18 March 2005; revised 29 April 2005; accepted 2 May 2005
Available online 27 June 2005

Abstract

Rare earth complexes with the formulae $Sm(TPAC)_3 \cdot 3H_2O$, $Eu_2(TPAC)_6 \cdot 5.25H_2O$ and $RE(TPAC)_3 \cdot 3.5H_2O$ (where RE = Gd and Tb), and TPAC = 2-thiopheneacetate) have been synthesized and characterized by complexometric titration, elemental analyses, infrared spectroscopy, and X-ray crystallography. Infrared data suggested the presence of both bridging and chelating TPAC anions. The crystal structure of the $[Eu_2(TPAC)_6 \cdot (H_2O)_3] \cdot 2.25H_2O$ complex in the solid state, determined by X-ray diffraction, revealed that it crystallizes in the orthorhombic crystal system (space group Aba2), with two crystallographically independent Eu^{3+} centers (Eu1 and Eu2). These europium centers are held together by one bidentate bridging and two tridentate bridging carboxylate groups. The existence of two Eu^{3+} centers was also supported by the emission spectrum. The luminescence properties of the RE–TPAC complexes were investigated by measuring the excitation and emission spectra, and the intramolecular ligand-to-rare earth energy transfer mechanisms were discussed. The emission spectra of the Eu^{3+} and Tb^{3+} ions displayed only narrow bands arising from $^5D_0 \rightarrow {}^7F_0$ and $^5D_0 \rightarrow {}^7F_{0\text{–}4}$ transitions, respectively, indicating an efficient luminescence sensitization of these ions by the TPAC 'antenna'. On the other hand, the emission spectrum of the Sm^{3+}-complex displayed a broad band from the phosphorescence of the TPAC ligand which overlapped the $4f^5$-intraconfigurational transitions. The theoretical intensity parameters Ω_λ ($\lambda = 2$ and 4), maximum splitting of the $^7F_1$ state (ΔE) and the ratio between the $^5D_0 \rightarrow {}^7F_0$ and $^5D_0 \rightarrow {}^7F_2$ transition intensities (R_{02}) were calculated based on the X-ray crystalline structure for the Eu^{3+}-complex, and a comparison with experimental data were made. The emission quantum efficiency (η) of the ^5D emitting level of the Eu^{3+} ion was also determined.

Keywords: Rare earths; 2-Thiopheneacetate; Crystalline structure; Intensity parameters; Intramolecular energy transfer

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1. Introduction

Trivalent rare earth ions (RE^{3+}) are well known for their unique spectroscopic and magnetic properties which make them important in several technological, medical, and biological research areas. For example, the luminescence properties of RE^{3+}-compounds are used as optical signal amplifiers, emitting materials in electroluminescent devices, and fluoroimmunoassay probes in biological systems [1–4]. One of the most important properties of RE^{3+}-compounds is the very narrow absorption and emission bands arising from the parity-forbidden intraconfigurational 4f–4f transitions [2]. Consequently, the very weak absorption bands only have oscillator strengths around 10^{-6} and the photoluminescent spectra of the simple RE^{3+} ions in solution are also generally very weak when the excitation is in the ^{2S+1}L levels of the RE^{3+} ion. In order to overcome the effect of this low absorptivity, organic ligands with chromophoric groups are coordinated to the RE^{3+} ions and can act as 'antenna' [5], absorbing and transferring

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doi:10.1016/j.molstruc.2005.05.001

energy efficiently to the rare earth ion and consequently increasing their luminescence quantum yield (q) [6].

The investigation of the luminescence properties of the Eu^{3+} and Tb^{3+} ions are of special relevance because of their strong red (~615 nm) and green (~545 nm) luminescences and also the long lifetimes of the excited $^5D_0$ and $^5D_4$ states, respectively. In particular, the special attention given to the Eu^{3+} ion is mainly due to the non-degenerate emitting level ($^5D_0$) which means that the emission bands arising from the $^5D_0 \rightarrow {}^7F_J$ transitions ($J=0$–4) can provide clearer information about the local symmetry [7]. On the other hand, the $^5D_4$ emitting level of the Tb^{3+} ion is ninefold degenerate which makes the assignment of the site symmetry from the emission spectrum a more difficult task. The Sm^{3+} ion is less studied due to its more complex energy level structure. However, some Sm-complexes exhibit intense orange luminescence arising from the intraconfigurational $^4G_{5/2} \rightarrow {}^6H_J$ transitions ($J=5/2$, 7/2, 9/2 and 11/2). The emitting $^4G_{5/2}$ level of the Sm^{3+} ion (~500 nm) is resonant with the triplet states (T) of many organic ligands and may offer an efficient energy transfer from ligand to rare earth ion ($T \rightarrow Sm^{3+}$) [8].

RE^{3+}-carboxylate complexes represent an important area within rare earth coordination chemistry both because the carboxylate group presents various coordination modes which lead to complex structures and because such compounds often display intense luminescence [9–11]. In particular, ligands containing five-membered heterocycles, such as the anions 2-thiophenecarboxylate (TPC), 2-thiopheneacetate (TPAC) and 2-furanecarboxylate (FUR), are excellent complexing agents, presenting three possible sites of coordination to metal ions [12–15], one from the S (TPC and TPAC) or O (FUR) of the heterocyclic group and two from the carboxylate group. However, owing to the hard acid behavior of the RE^{3+} ions, there is a strong affinity of these metal ions for hard base, negatively charged carboxylate oxygen donors. In most RE^{3+}-coordination compounds reported with TPC and FUR, the carboxylate groups are involved in the metal–ligand bonding by chelating and bridging coordination modes, forming dinuclear, polymeric or network structures.

The photophysical properties of RE^{3+}-complexes containing carboxylate anions have been extensively reported [10,16–19] and have been shown to act as luminescent sensitizers, especially for Eu^{3+} and Tb^{3+} ions, by an efficient intramolecular ligand-to-metal energy transfer. The triplet state (T) of TPAC around 25,000 cm^{-1} may act as an energy donor to the excited levels of Sm^{3+}, Eu^{3+} and Tb^{3+} ions (Fig. 1) [15].

This article reports the synthesis, characterization, crystal structure, and photoluminescence properties of the luminescent trivalent rare earth complexes ($RE^{3+}=$Sm, Eu, Gd and Tb) with TPAC. A detailed study of the photoluminescence properties of the RE-TPAC complexes was made in order to obtain information on the energy transfer process from the TPAC ligand to the RE^{3+} ions. Based on the crystal structure of the $[Eu_2(TPAC)_6 \cdot (H_2O)_3] \cdot 2.25H_2O$ complex, the intensity parameters were calculated and compared with the experimental ones. In addition, the radiative and non-radiative rates and experimental emission quantum efficiencies were also investigated.

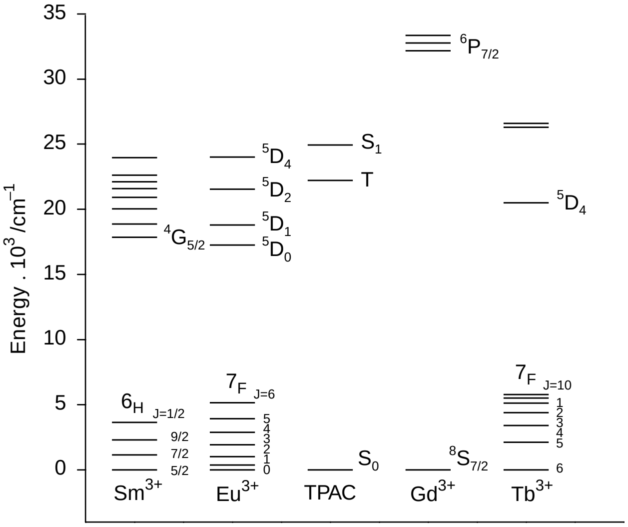

Fig. 1. Partial energy level diagram of the TPAC ligand states obtained from the phosphorescence spectrum of the Gd-complex, and some energy levels of the Sm^{3+}, Eu^{3+}, Gd^{3+} and Tb^{3+} ions.

2. Experimental

2-Thiopheneacetic acid (HTPAC) was purchased from Sigma-Aldrich and used without further purification. The $RECl_3 \cdot 6H_2O$ (RE = Sm, Eu, Gd or Tb) was prepared by reaction between rare earth oxide and hydrochloric acid according to literature procedures [14].

2.1. Synthesis of the RE–TPAC complexes

For the synthesis of the RE^{3+}–TPAC complexes, 2-thiopheneacetic acid (1.0 g, 6.7×10^{-3} mol) was dissolved in water (~30 mL) and the anion was formed by addition of a solution of NaOH (1 mol L^{-1}) was added to pH ~ 7. An aqueous solution of $RECl_3 \cdot 6H_2O$ (0.85 g, 2.34 mmol) was added dropwise to this solution and after 3 days colorless crystal were deposited. The crystal solid was filtered, washed with water and dried under vacuum to give the desired product (yields 80–90%).

2.2. Apparatus

Elemental analyses for carbon and hydrogen in the complexes were carried out on a Perkin–Elmer model 240 microanalyzer, while the RE^{3+} contents were determined by complexometric titration with EDTA. The infrared (IR) spectra were recorded in KBr pellets on a Bomen