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Preparation, characterization, and circularly polarized luminescence of lanthanum and europium 1,1'-binaphthyl-2,2'-diyl phosphate complexes

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Abstract

Solvated *tris*-complexes of (*R*)- and (*S*)-1,1'-binaphthyl-2,2'-diyl phosphate with lanthanum(III) and europium(III) centers were prepared and characterized by spectroscopic methods and elemental analysis. Circularly polarized luminescence (CPL) spectra for the optically active isomers of the europium complexes are also reported.

Keywords

Circularly polarized luminescence; Europium; Lanthanum; 1,1'-Binaphthyl-2,2'-diyl phosphate

1. Introduction

The preparation and characterization of lanthanide chelates with strong luminescence properties continues to be of great interest due to their potential to be sensitive and selective probes in a wide variety of biological and material-science applications [1]. In the design of useful lanthanide-based luminescent systems it is usually the case that one is interested in the inclusion of strongly absorbing organic chromophores in the chelate to overcome the low molar absorbance coefficient associated with the intraconfigurational $f \rightarrow f$ transitions of lanthanide (III) ions. An additional feature is the exploitation of chiral structures in the chelate for the purpose of enhancing chiral selectivity, and the ultimate goal of preparing chiral sensors based on lanthanide luminescence. In the overall light-conversion process, the quantities that contribute to the total lanthanide luminescence intensity are the efficiency of the ligand absorption, the ligand-to-metal energy transfer rate, and the luminescence efficiency. 1,1'-binaphthyl-2,2'-diol and its derivatives is one example of a chiral ligand that can be used in the preparation of lanthanide complexes. These compounds are of potential interest because of their use as catalysts in asymmetric reactions probes, and for the sensing of chirality in biological substrates [2]. Herein we report the preparation, and the spectroscopic investigation of lanthanide complexes of the general formula $\text{Ln}(\text{pbn})_3(\text{H}_2\text{O})_6$ ($\text{Ln} = \text{La}, \text{Eu}$, $\text{pbn} = (\text{R})$ - or (*S*)-1,1'-binaphthyl-2,2'-diyl phosphate). The primary focus of this work is on the connection

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of the ligand chirality to the absolute structure and stability of the complexes, and the preliminary evaluation of these types of systems as chiral luminescence probes.

2. Results and discussion

The lanthanide complexes with the general formula $\text{Ln}(\text{pbn})_3(\text{H}_2\text{O})_6$ (**1a**, **1b**, **2a**, and **2b**) were obtained by the reaction of pbn with alkali metal hydroxide in water with further addition of corresponding lanthanide(III) chloride in methanol (Scheme 1) and were isolated by filtration of the reaction mixture as stable microcrystalline compounds in 38–86% yield.

The resulting compounds were characterized by ^1H NMR and IR spectroscopy as well as elemental analysis. In addition, luminescent properties of the Eu(III) complexes dissolved in THF were investigated using circularly polarized luminescence (CPL) spectroscopy [3]. The ^1H NMR spectra of diamagnetic compounds **2a** and **2b** clearly support the coordination of chiral ligands to the lanthanide ions with expected appreciable changes in the chemical shifts of the chiral ligand, along with significant broadening of the peaks of interest due to the conformational rigidity near lanthanide metal. Elemental analysis of the complexes **1** and **2** reveals that the final products were isolated in a form of hydrates with the inclusion of six molecules of water. This was also confirmed by IR spectroscopy (strong peak at 3376 cm^{-1}). In addition, IR spectra of all complexes show only slightly perturbed bands characteristic for the pbn ligands suggesting predominantly ionic character for lanthanide-ligand interactions. For instance, the P O ($1255, 1230\text{ cm}^{-1}$) and P O ($1075, 1051\text{ cm}^{-1}$) ligand bands upon complexation were shifted to $1238, 1214$ and $1103, 1067\text{ cm}^{-1}$, respectively in the case of lanthanum complexes. Circularly polarized luminescence (CPL) was used to investigate the chiral-optical properties of the Eu(III)-containing complexes.[3] The CPL spectra of **1a** and **1b** confirm the presence of a chiral emitting species and clearly indicate the influence of the chiral ligand on the chiral configuration of the metal complex. Indeed, the CPL spectra of the enantiomers **1a** and **1b** for the transition $^5\text{D}_0 \rightarrow ^7\text{F}_1$ are almost mirror images of each other as expected (Fig. 1). This transition is particularly well suited for CPL measurements since it satisfies the magnetic dipole selection rule, $\Delta J = 0, \pm 1$ (except $0 \leftrightarrow 0$), where it is predicted that the CPL signal should be large. In the spectra shown, the magnitude of the luminescence dissymmetry factor, g_{lum} , which may be defined as:

$$g_{\text{lum}} = \frac{\Delta I}{(1/2)I} = \frac{I_{\text{L}} - I_{\text{R}}}{(1/2)(I_{\text{L}} + I_{\text{R}})}$$

where I_{L} and I_{R} refer to the intensity of left and right circularly polarized light respectively, is approximately the same ($+0.038$ and -0.037) at the peak wavelength. Finally, it should be mentioned that each CPL spectrum displays two bands corresponding to crystal-field splitting of the electronic level, which are amenable to structural interpretation. A complete CPL study aimed at getting quantitative and/or qualitative chiral structural information of *tris*-(lanthanide) complexes of 1,1'-binaphthyl-2,2'-diyl phosphate will be described in a forthcoming publication.

3. Conclusions

Several new neutral *tris*-complexes of lanthanum and europium with (*R*)- or (*S*)-1,1'-binaphthyl-2,2'-diyl phosphate were prepared and characterized by a variety of spectroscopic techniques. Circularly polarized luminescence data support the chiral environment around the lanthanide center, although conclusions concerning the influence of the chiral ligand on the absolute configuration around the lanthanide ion awaits the growing of crystals suitable for X-ray structure determination.

4. Experimental section

4.1. General procedure for the preparation of 1 and 2 [4]

0.47 mL (1.39 mmol) of 3N aqueous sodium hydroxide was added to a stirred solution of (*R*)- or (*S*)-Hpbn (500 mg, 1.43 mmol) in methanol (12 mL) at room temperature. Solution of lanthanide chloride hexahydrate (167 mg, 0.455 mmol) in methanol, and the mixture was stirred and refluxed for 24 h. After cooling, the precipitate was filtered, washed with methanol and dried at 120 °C for 15 h in vacuo to yield the desired complexes as a white powder (223 mg, 38%). Characterization data for **2a** as a typical example: ^1H NMR (dms- d_6 , tms, δ): 8.12 (br, s, 2H), 8.02 (br, d, 2H), 7.66 (br, s, 2H), 7.44 (br, s, 4H), 7.30 (br, s, 1H), 7.23 (br, s, 1H); IR (KBr, cm^{-1}): 3376s (H_2O), 3064m (Ar-H), 1621m, 1589s, 1507s, 1464m, 1326m, 1238vs, 1213s, 1099vs, 1074s, 964vs, 816s, 752s, 719m, 656m, 596m, 582m, 567s, 535m; elemental analysis observed (calculated for $\text{La}_1\text{C}_{60}\text{H}_{48}\text{O}_{18}\text{P}_4$): C, 56.50 (55.91); H, 3.51 (3.75).

4.2. Physical methods

NMR spectra were recorded on 500 MHz Varian Inova spectrometer, while IR spectra were obtained using Hewlett-Packard 7600 spectrometer. Elemental analysis was conducted at Atlantic Microlab Inc. (Atlanta, Georgia). Circularly polarized luminescence and total luminescence spectra were recorded on an instrument described previously, operating in a differential photon-counting mode [3].

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Fig. 1.

The total luminescence (lower curve) and CPL spectra (upper curves) of the $^5D_0 \rightarrow ^7F_1$ transition for 10^{-2} M solutions of **1a** (black) and **1b** (red) complexes in THF at 298 K, upon excitation at 392 nm. (For interpretation of the references to colour in this figure legend, the reader is referred to the web version of the article.)

Scheme 1.
Preparation of lanthanide complexes **1** and **2**.