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Preparation, luminescent properties of *N*-phenyl-2-{2′-[(phenyl-ethyl-carbamoyl)-methoxy]-biphenyl-2-yloxy}-*N*-ethyl-acetamide (**L**) lanthanide complexes and the supramolecular structures of $[La(pic)_3L]$ and $2[La(NO_3)_3L(H_2O)] \cdot H_2O \cdot 0.5C_2H_5OH$

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Abstract

A new amide-based ligand, *N*-phenyl-2-{2′-[(phenyl-ethyl-carbamoyl)-methoxy]-biphenyl-2-yloxy}-*N*-ethyl-acetamide (**L**) was synthesized. Solid complexes of lanthanide picrates with this new ligand were prepared and characterized by elemental analysis, conductivity measurements, IR, electronic and ^1H NMR spectroscopies. Under excitation, the europium picrate complex exhibited strong characteristic emissions. The europium nitrate complex exhibited quite weak characteristic emissions. The counter anion factor influencing the fluorescence properties was discussed. The lowest triplet state energy level of the ligand in the picrate complex matches better to the resonance level of Eu(III) than Tb(III) ion. The crystal structures of the complex $La(Pic)_3L$ and $2[La(NO_3)_3L(H_2O)] \cdot H_2O \cdot 0.5C_2H_5OH$ have been determined by single-crystal X-ray diffraction. The $La(Pic)_3L$ crystal structure shows that the La(III) ion is coordinated with four oxygen atoms from the ligand **L** and six from three bidentate picrates. Furthermore, the $La(Pic)_3L$ complex units are linked by the significant intermolecular π–π interactions between coordinate picrates to form a one-dimensional (1-D) supramolecular zigzag chain. The $2[La(NO_3)_3L(H_2O)] \cdot H_2O \cdot 0.5C_2H_5OH$ crystal structure shows that **L** gives two different arrangements around La(III) ions and induces axial chirality directed by metal ions in the assembly process of the organic ligands with metal ions, each La(III) ion is coordinated with four oxygen atoms from the ligand **L**, six oxygen atoms from three bidentate nitrate groups and one coordinate water molecule. Furthermore, the $[La(NO_3)_3L(H_2O)]$ complex units are linked by the intermolecular hydrogen bonds and π–π interaction to form a three-dimensional (3-D) netlike supramolecule.

Keywords: Lanthanide complexes; Luminescent properties; Supramolecular structure; π–π Interaction; Hydrogen bonds

1. Introduction

Over the past decades, considerable attention has been devoted to the design and synthesis of luminescent lanthanide complexes due to their interesting photophysical properties, which have potential applications in sensors, liquid crystalline materials, optical fiber lasers and amplifiers, luminescent label design for specific biomolecule interactions, magnetic molecular materials and electroluminescent materials [1–6].

Amide-based open-chain crown ethers offer many advantages in extraction and analysis of the rare earth ions because of their ring-like coordination structure and terminal group effects [7,8]. However, luminescent properties on open-chain crown ethers with lanthanide complexes have

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been rarely reported [9]. Our group is interested in the supramolecular coordination chemistry of lanthanide ions with amide-based open-chain crown ethers that have strong coordination capability to the lanthanide ions and terminal group effects [10]. So we have designed a series of multi-functional amide-based open-chain crown ethers having the ability to coordinate lanthanide ions and thus enhance luminescence of lanthanide complexes by providing chromophores suitable for energy transfer, i.e., aryl substitutes.

In this work, we introduced biphenyl groups as the basic molecular frame and obtained a new open-chain crown ether ligand, *N*-phenyl-2-{2′-[(phenyl-ethyl-carbamoyl)-methoxy]-biphenyl-2-yloxy}-*N*-ethyl-acetamide (**L**), and reported the synthesis, luminescent properties of lanthanide complexes with the new ligand and the supramolecular structures of $La(pic)_3L$ and $2[La(NO_3)_3L(H_2O)]\cdot H_2O\cdot 0.5C_2H_5OH$. The results indicate that under excitation, the Eu(III) picrate complex had strong characteristic luminescence whereas the terbium picrate complex showed no luminescence. The lowest triplet state energy level of the ligand in the picrate complex which was calculated from the phosphorescence spectrum of the Gd(III) picrate complex at 77 K, and indicates that the triplet state energy level of the ligand matches better to the resonance level of Eu(III) than Tb(III) ion. The Eu(III) nitrate complex exhibited quite weak characteristic emissions. The $La(Pic)_3L$ crystal structure shows that the La(III) ion could be effectively encapsulated and protected by the coordinated ligand. Furthermore, the $La(Pic)_3L$ complex units are linked by the significant intermolecular π–π interactions between coordinate picrates to form a one-dimensional (1-D) supramolecular zigzag chain. The $2[La(NO_3)_3L(H_2O)]\cdot H_2O\cdot 0.5C_2H_5OH$ crystal structure shows that **L** gives two different arrangements around La(III) ions, and induces axial chirality directed by metal ions in the self-assembly process. Each La(III) ion is coordinated with four oxygen atoms from the ligand **L**, six oxygen atoms from three bidentate nitrate groups and one coordinate water molecule. Furthermore, the $[La(NO_3)_3L(H_2O)]$ complex units are linked by the intermolecular hydrogen bonds and π–π interaction to form a three-dimensional (3-D) netlike supramolecule.

2. Experimental

2.1. Materials

Lanthanide picrate [11] and *N*-ethyl-*N*-phenylchloroacetamide [12] were prepared according to the literature methods. All commercially available chemicals were of A.R. grade and were used without further purification.

2.2. Methods

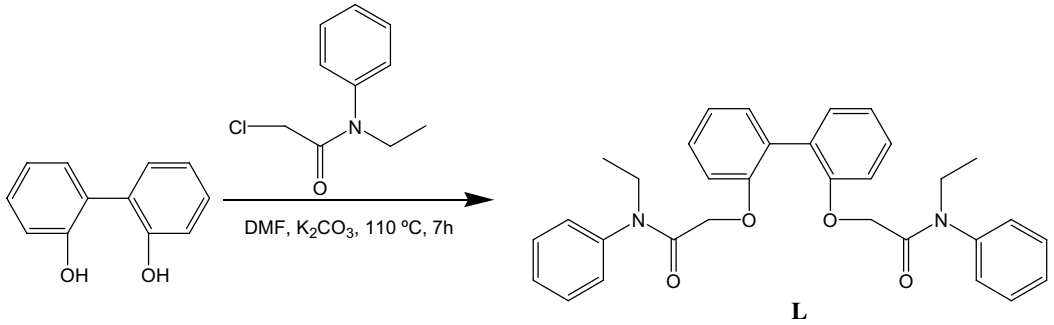
The metal ions were determined by EDTA titration using xylenal orange as indicator. C, H and N were determined using an Elementar Vario EL. Conductivity measurements were carried out with a DDS-307 type conductivity bridge using 10^{-3} mol dm^{-3} solutions at 25 °C. IR spectra were recorded on Nicolet FT-170SX instrument using KBr discs in the 400–4000 cm^{-1} region, ^{1}H NMR spectra were measured on a Varian Mercury plus 300 M spectrometer in $CDCl_3$ solution with TMS as internal standard. Fluorescence and phosphorescence measurements were made on a Hitachi F-4500 spectrophotometer. Mass spectra were obtained on a VG-ZAB-HS mass spectrometer.

2.3. Synthesis of the ligand

The synthetic route for the ligand is shown in Scheme 1. Anhydrous K_2CO_3 (5.6 g, 41 mmol) was added into the 15 mL DMF solution of 2,2′-dihydroxybiphenyl (1.86 g, 10 mmol) at 100 °C. After 1 h, a solution of *N*-ethyl-*N*-phenylchloroacetamide (5.92 g, 30 mmol) in 10 mL DMF was added dropwise to the mixture and maintained at 110 °C for 7 h. When cool, distilled water (60 ml) was added and the turbid solution was extracted with chloroform (3×40 mL). The combined organic phases were washed with water and dried with anhydrous Na_2SO_4. The solvent was removed and the residue was chromatographed to afford the ligand **L**; yield: 85%.

2.4. Synthesis of the lanthanide picrate complexes

To a solution of 0.2 mmol lanthanide picrate in 5 ml of ethanol was added dropwise the solution of 0.2 mmol **L** in



Scheme 1. The synthetic route for the ligand **L**.