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Lanthanide complexes with a biphosphonate ester ligand and their fluorescent properties

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ABSTRACT

A bi-phosphonate ligand 4,4′-bis(diethylphosphonomethyl)biphenyl has been designed and synthesized. The ligand reacted with lanthanide nitrates forming three different types of coordination complexes: interwoven net polymer (type I), linear polymer (type II), and ladder polymer (type III). The photophysical properties of Sm^{3+}, Eu^{3+}, Tb^{3+} and Dy^{3+} complexes were investigated. The Sm^{3+}, Eu^{3+} and Dy^{3+} complexes displayed the characteristic spectrum of the lanthanide ions. The Tb^{3+} complex exhibited a prominent strong fluorescence by excitation of 300 nm, which indicated that there may be a luminescence sensitization effect of the complex via excitation of the ligand.

In the past decade, lanthanide coordination polymers have attracted much attention because of their fascinating structure and promising potential applications in luminescence, magnetism, gas adsorption, and catalysis [1]. In contrast to the transition metal ions, the lanthanides have higher coordination number and coordination requirements, so the structure of lanthanide complexes is more variable and unpredictable [2]. Hard donor centers such as polarized oxygen-bearing or oxygen–nitrogen hybrid functional groups are expected to interact strongly with the lanthanide ions. Therefore, acid amide, sulfoxide and phosphonate ligands can be used as well bridging or chelating ligands in lanthanide coordination polymers [3]. We have synthesized and investigated a set of lanthanide radii controlled one-dimensional polymer and binuclear complexes based on bidentate phosphonate ester ligand with interesting fluorescent properties before [4]. Herein, we introduce the synthesis and structural characterization of a few lanthanide complexes with 4,4′-bis(diethyl-phosphonomethyl)biphenyl [5]. The ligand has a rigid biphenyl group and flexible oxyethyl group. Thus, the molecule can be used as a semi-rigid building block. The rigid biphenyl group makes the ligand a stick shaped ligand which can be rotated between the two aromatic rings and leads to the formation of several different coordination frameworks with interesting luminescent properties.

Crystals of complexes which were synthesized from 4,4′-bis(diethylphosphonomethyl)biphenyl and lanthanide have been obtained [6]. The X-ray crystallographic analysis reveals that the crystal structures of these complexes belong to three different forms: interwoven net polymer (type I), linear polymer (type II), and ladder polymer (type III) [7].

The Ce^{3+} complex is assigned to type I and crystallizes in the monoclinic form with space group $P2_1/c$ [8]. There are two crystallographically independent cerium ions and two ligands in the asymmetric unit of the complex. As shown in Fig. 1, the Ce1 atom is ten-coordinated by six oxygen atoms from three bidentate nitrate groups, two oxygen atoms from the phosphonate of two different ligands and two oxygen atoms from H_2O, while the Ce2 atom is nine-coordinated by six oxygen atoms from bidentate nitrate groups, two from the ligands and only one from H_2O. Ce1 and Ce2 ions are linked alternately by ligands between them. The cerium ions and ligands give a 1D zigzag chain. Each ligand connects a Ce1 ion and a Ce2 ion by its two phosphonate groups. The Ce1…Ce2…Ce1 and Ce2…Ce1…Ce2 angles are both 99.16°, and the Ce…Ce separations in the zigzag chain are 18.820 Å and 18.635 Å. The Ce1–O (O═P) distances are 2.412(12) and 2.436(15) Å. The Ce2–O (O═P) distances are 2.38(2) and 2.414(18). These distances are comparable to those reported for other phosphonate oxygen donor Ce^{3+} complexes [9]. The dihedral angles of the biphenyl group in the two ligands are 42.67° and 39.55° respectively. The torsion angles of the two phosphonate groups are 158.47° and 142.72°.

There are two groups of the 1D zigzag chains existing in the complex in two different orientations. The two groups of chains interwoven like warp and weft with a crossing angle of approximately 32° and generate a deflective clothlike 2-D sheet, in which every chain passes alternately over and then under an infinite number of other chains [10].

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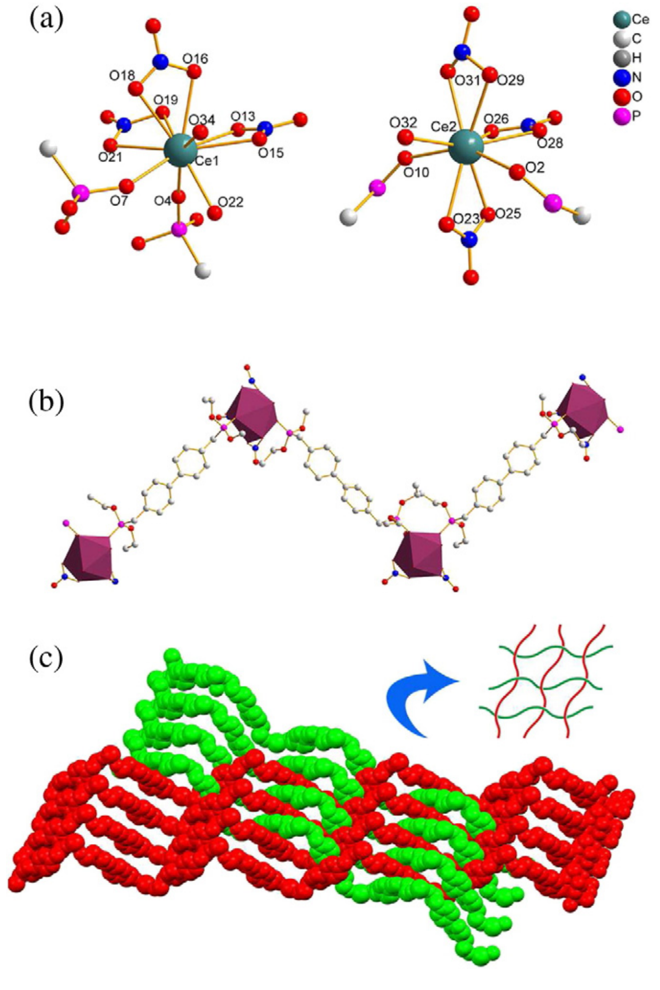

Fig. 1. Structure type I. (a) The coordination environment of Ce1 and Ce2 ions. (b) The single chain of the zigzag polymer. (c) The interwoven network of complex 1 and the sketch of clothlike 2-D sheet in the crystal.

The Nd^{3+}, Dy^{3+}, and Ho^{3+} complexes form type II structures [11]. They crystallize in the triclinic space group $P-1$ and possess a 1-D linear framework constructed from an extended array of nine-coordinated Ln^{3+} (Ln = Nd, Dy, and Ho) centers and bidentate ligands (Fig. 2). Each lanthanide ion is coordinated by six oxygen atoms from three bidentate nitrate groups, two oxygen atoms from the phosphonate of the different ligands and one oxygen atom from H_2O. The ligands act as bridging linkers through their phosphonate oxygen atoms. The Nd…Nd separation is 19.006 Å. The dihedral angle of the biphenyl group in the ligand is 19.92°. The torsion angle of the two phosphonate groups is 9.93°.

Type III complex is synthesized from Eu(III) and the biphosphonate ester ligand and crystallizes in the triclinic space group $P-1$ and forms a ladder polymer [12]. Compared to type II polymer, type III polymer contains europium ions which is nine-coordinated by no oxygen atom from H_2O but another one more oxygen from a ligand molecule that bridges two parallel linear chains in the ladder by coordination with two europium ions in the two chains respectively (Fig. 3). The Eu…Eu separation in one linear chain is 18.731 Å, which is close to the average Ce…Ce separation (18.728 Å) in type I and a little shorter than the Nd…Nd separation (19.006 Å) in type II. However, the separation of two europium ions in parallel chains linked by a ligand is 15.424 Å, much shorter than the separation in one linear chain. The Eu…Eu…Eu angle is 40.95°, and the distance between two linear chains in one ladder is 10.109 Å. The dihedral angles of the biphenyl group and the torsion angle of the two phosphonate groups in the ligand that form the linear chain is 40.01° and 127.64° respectively, these angles are 0° and 180° in the ligand that bridges the two parallel chains. The biphenyl group in the bridging ligand has π–π stacking interactions with the benzene rings on both sides of the parallel chains.

The solid-state excitation and emission spectra of the Sm^{3+}, Eu^{3+}, Tb^{3+} and Dy^{3+} complexes at room temperature are shown in Fig. 4. The excitation spectrum of the Eu^{3+} complex has negligible contributions from the ligand and exhibit a series of sharp line characteristic of the Eu^{3+} energy-level structure. The maximum emission intensities of Eu^{3+} at 591 and 616 nm, respectively, were observed for the $J = 1$ and 2 transitions. The $J = 2$ so-called "hypersensitive" transition is extremely intense. The intensity of the $^5D_0 \rightarrow {}^7F_2$ transition (electric dipole) is stronger than that of the $^5D_0 \rightarrow {}^7F_1$ transition (magnetic dipole), which indicates that the coordination environment of the Eu^{3+} ion is asymmetric. It is in agreement with the result of single crystal X-ray analysis. Sm^{3+} and Dy^{3+} complexes were as same as the Eu^{3+} complex but have lower emissions. The fluorescence quantum yield Φ of the Sm^{3+}, Eu^{3+}, and Dy^{3+} complexes in the solid state was found to be 12.38%, 13.20% and 11.67% respectively using an integrating sphere.

The emission spectrum of the Tb^{3+} complex exhibits the characteristic emission bands for Tb^{3+} and the bands are centered at 490 and 546 nm. These emissions result from deactivation of the $^5D_4$ excited state to the corresponding ground state ^7F_J ($J = 6, 5$) of the Tb^{3+} ion. The most intense emission is centered at 546 nm and corresponds to the hypersensitive transition $^5D_4 \rightarrow {}^7F_5$. The excitation spectrum for the Tb^{3+} complex exhibits several line-like bands between 370 and 400 nm, which is attributable to the 4f–4f transitions from the ground state $^7F_6$ level to the $^5L_9$(360), $^5L_{10}$ (372), and $^5D_3$ (380) excited states, while the strongly broad peak at about 300 nm indicates a possibly energy transduction from ligand to the ion. However, despite the strongly emission, the fluorescence quantum yield Φ of the Tb complex in the solid state was found to be 2.81%, due to the extremely forceful absorption at 300 nm.

In conclusion, we presented here a serial of lanthanide complexes with a bi-phosphonate ligand of three types of structures. The Sm^{3+}, Eu^{3+}, Tb^{3+} and Dy^{3+} compounds exhibit interesting luminescent properties. Although the luminescence sensitization of the complex via excitation of the ligand is not efficient on the Sm^{3+}, Eu^{3+}, and Dy^{3+} ions, it is likely to be efficient in the Tb^{3+} complex.

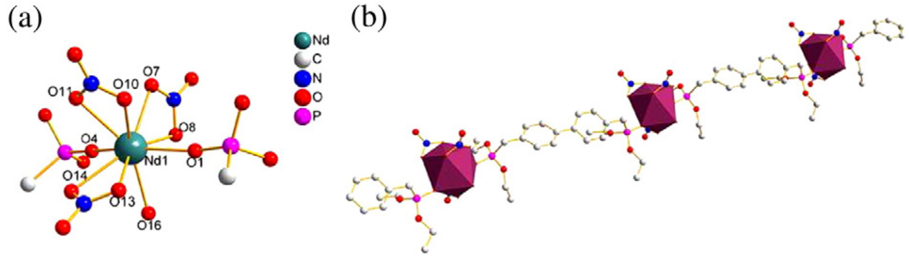

Fig. 2. Structure type II. (a) The coordination environment of Nd^{3+}. (b) The 1-D structure of the linear polymer.