



Four lanthanide–carboxylate coordination polymers with mixed 2,3-naphthalenedicarboxylate and phen ligands: Syntheses, structures, luminescent and magnetic properties



Min Hu^a, Hui Zhao^a, E. Carolina Sañudo^b, Min Chen^{a,*}

^aHenan Provincial Key Laboratory of Surface & Interface Science, Zhengzhou, Henan 450002, PR China

^bDepartament de Química Inorgànica i Institut de Nanociència i Nanotecnologia, Universitat de Barcelona, Diagonal 645, 08028 Barcelona, Spain

ARTICLE INFO

Article history:

Received 30 April 2015

Accepted 10 August 2015

Available online 29 August 2015

Keywords:

Lanthanide–carboxylate coordination polymers

2,3-Naphthalenedicarboxylate

Crystal structures

Luminescence

Magnetic properties

ABSTRACT

Four new lanthanide–carboxylate coordination polymers of the formula $[Ln_3L_4(phen)_4(H_2O)_4](ClO_4)_2 \cdot 2H_2O$, ($Ln = Dy$ (**1**), Tb (**2**), Ho (**3**) and Er (**4**), $L = 2,3$ -naphthalenedicarboxylate and $phen = 1,10$ -phenanthroline) were solvothermally synthesized. Their structures as well as magnetic and photoluminescent properties were completely investigated. Complexes **1–4** are isostructural and exhibit 1D ribbon-like chains with envelope-like sixteen-membered rings. The Dy^{III} and Tb^{III} complexes show the corresponding characteristic luminescence in the visible region and the Er^{III} complex shows luminescence in the near-infrared region upon excitation with UV rays. Studies on the magnetic properties are reported. The $Dy(III)$ analog complex **1** exhibits slow magnetic relaxation and could be a new example of a $Dy(III)$ SMM (single molecule magnet).

© 2015 Elsevier Ltd. All rights reserved.

1. Introduction

The design and construction of lanthanide coordination polymers (LCPs) is attracting increasing attention not only due to their desirable structural features [1–2], but also due to their exceptional optical [3] and magnetic properties [4] arising from 4f electrons. So far, many LCPs have been prepared and their use in practical applications has been widely investigated [5]. However, designing a practical method for synthesizing LCPs with predictable and controlled geometries still remains challenging, due to the high and variable coordination numbers and the flexible coordination environments of the lanthanide ions [6]. As is known, rare earth ions have a high affinity for hard donor atoms and ligands containing oxygen or hybrid oxygen–nitrogen atoms, especially multi-carboxylate ligands, which are usually employed in the construction of LCPs with unique structures and useful properties [7]. Among the versatile multi-carboxylate complexes, aromatic benzene- and naphthalene-based derivatives, such as benzenedicarboxyl (1,4- [8], 1,3- [9], or 1,2- [10]), 1,3,5-benzenetricarboxyl [11], 1,2,4,5-benzenetetracarboxyl [12], 1,2,3,4,5,6-benzenehexacarboxyl [13], naphthalenedicarboxyl (1,4- [14] or 2,6- [15]) and 1,4,5,8-naphthalenetetracarboxyl [16], have been extensively used

in the preparation of a variety of lanthanide–carboxylate coordination polymers owing to their reliable and rich coordination modes.

Despite the remarkable achievements in this aspect [8–16], however, to predict and further accurately control the framework array of a given crystalline product still remain a considerable challenge at this stage. This mainly arises from the fact that the subtle assembly progress may be influenced by many intrinsic and external parameters, such as the auxiliary co-ligands [17], solvent [18], counter-anion [19], temperature [20], pH value of the solution [21] and so on, which determine the formation of different thermodynamically favored crystalline products. For instance, the introduction of 1,10-phenanthroline chelating reagents [22] as auxiliary co-ligands into lanthanide–carboxylate reaction systems leads to the formation of interesting coordination architectures. In this context, 2,3-naphthalenedicarboxylate (**L**), with an extended π -conjugated system as an analogous but bulky derivative of 1,2-benzenedicarboxylate (H_2BDC), has virtually not been noticed to fabricate LCPs to date. In our group, we have constructed a series of transition metal complexes ($Zn(II)$, $Cd(II)$, $Ag(I)$, $Cu(II)$ and $Ni(II)$), which exhibit diverse structures from discrete tetranuclear species to 3D networks with luminescent or magnetic properties [17a,b,23].

As an extension of the work mentioned above, as well as to better understand the nature of the luminescence in the structures of lanthanide multi-carboxylates, we present herein the syntheses, structures, photoluminescence and magnetic properties of four

* Corresponding author.

E-mail address: humin@zzuli.edu.cn (M. Chen).

lanthanide–carboxylate coordination polymers based on H₂L and phen ligands. It was hoped that the combination of two types of ligands would enhance the energy-transfer efficiency from the ligand to the lanthanide ions. Meanwhile, utilization of heavy lanthanide ions such as Dy(III) and Ho(III) has also become more popular in the design and synthesis of SMMs due to their larger angular momentum and strong magnetic anisotropy in ground multiple states [24].

2. Experimental

2.1. Materials and general methods

All reagents and solvents for the syntheses were commercially available and used as received. Elemental analyses (C, H and N) were performed on a Vario EL III Elementar analyzer. The IR spectra were recorded in the range 4000–400 cm⁻¹ on a Tensor 27 OPUS (Bruker) FT-IR spectrometer with KBr pellets. The emission spectra in the visible region were tested on an F-7000 (HITACHI) spectrophotometer and those in the near-infrared region were measured on an FLS-980 fluorescence spectrophotometer.

2.2. Synthesis of complexes 1–4

All four complexes were prepared under similar methods. A general synthetic procedure is described as follows, using Dy^{III} complex **1** as an example. A solution of 2,3-naphthalenedicarboxylic acid (H₂L) (10.8 mg, 0.05 mmol), 1,10-phenanthroline (phen) monohydrate (9.0 mg, 0.05 mmol) and NaOH (4 mg, 0.1 mmol) in CH₃OH (10 mL) was carefully layered on top of a H₂O solution (15 mL) of Dy(ClO₄)₃·6H₂O (56.9 mg, 0.1 mmol) in a test tube. Colorless block single crystals suitable for X-ray analysis appeared at the tube wall after ca. three weeks at room temperature.

[Dy₃L₄(phen)₄(H₂O)₄](ClO₄)₂·2H₂O (**1**): Yield: 0.017 g (60.5% based on H₂L). Elemental Anal. Calc. for C₉₆H₆₈ClDy₃N₈O₂₆: C, 50.74; H, 3.02; N, 4.93. Found: C, 50.31; H, 3.27; N, 4.79%. IR (KBr, cm⁻¹): 3443 br, 1615 vs 1558 s, 1464 m, 1405 vs 1348 m, 1094 s, 891 w, 864 w, 842 w, 824 m, 771 m, 725 m, 622 w, 583 m, 556 w, 481 w.

[Tb₃L₄(phen)₄(H₂O)₄](ClO₄)₂·2H₂O (**2**): Yield: 0.019 g (68.2% based on H₂L). Elemental Anal. Calc. for C₉₆H₆₈ClTb₃N₈O₂₆: C, 50.98; H, 3.03; N, 4.95. Found: C, 50.81; H, 3.20; N, 4.80%. IR (KBr, cm⁻¹): 3444 br, 1615 vs 1551 s, 1463 m, 1404 vs 1347 m, 1093 s, 890 w, 864 w, 842 w, 824 m, 771 m, 726 m, 623 w, 583 m, 557 w, 482 w.

[Ho₃L₄(phen)₄(H₂O)₄](ClO₄)₂·2H₂O (**3**): Yield: 0.022 g (76.5% based on H₂L). Elemental Anal. Calc. for C₉₆H₆₈ClHo₃N₈O₂₆: C, 50.58; H, 3.01; N, 4.91. Found: C, 50.31; H, 3.28; N, 4.69%. IR (KBr, cm⁻¹): 3443 br, 1614 s, 1551 s, 1464 m, 1405 s, 1348 m, 1095 s, 893 w, 864 w, 845 w, 823 m, 771 m, 726 m, 640 w, 585 w, 558 w, 481 w.

[Er₃L₄(phen)₄(H₂O)₄](ClO₄)₂·2H₂O (**4**): Yield: 0.023 g (80.6% based on H₂L). Elemental Anal. Calc. for C₉₆H₆₈ClEr₃N₈O₂₆: C, 50.42; H, 3.00; N, 4.90. Found: C, 50.21; H, 3.18; N, 4.84%. IR (KBr, cm⁻¹): 3445 br, 1615 s, 1551 s, 1464 m, 1404 s, 1347 m, 1095 s, 892 w, 844 m, 823 w, 770 w, 725 m, 640 w, 584 w, 481 w.

Caution: Although no problem was encountered in this study, perchlorate complexes are potentially explosive and should be handled with the proper precautions!

2.3. X-ray crystallographic studies of complexes 1–4

X-ray single-crystal diffraction data for complexes **1–4** were collected on an Agilent diffractometer at ambient temperature

with Mo K α radiation ($\lambda = 0.71073$ Å). There was no evidence of crystal decay during the data collection. The program SAINT [28] was used for integration of the diffraction profiles and a semi-empirical absorption correction was applied using the SADABS program [29]. All the structures were solved by direct methods using the SHELXS program of the SHELXTL package and refined by full-matrix least-squares methods with SHELXL [30]. The final refinements were performed by full-matrix least-squares methods with anisotropic thermal parameters for all non-H atoms on F^2 . The C-bound hydrogen atoms were generated with the assigned isotropic thermal parameters, and those of water molecules were first located in the difference electron density map and then placed in their calculated positions with fixed thermal factors. The disordered ClO₄⁻ anion was restrained in order to obtain reasonable thermal parameters. Crystallographic data and structural refinement details for complexes **1–4** are summarized in Table 1, and selected bond lengths and angles are shown in Tables S1–S4.

2.4. Magnetic measurements

Magnetic measurements were carried out at the Unitat de Mesures Magnètiques (Universitat de Barcelona) on polycrystalline samples (circa 30 mg) with a Quantum Design SQUID MPMS-XL magnetometer equipped with a 5 T magnet. Diamagnetic corrections were calculated using Pascal's constants and an experimental correction for the sample holder was applied.

3. Results and discussion

3.1. Descriptions of the crystal structures for complexes 1–4

Single crystal X-ray diffraction analyses revealed that complexes **1–4** are isostructural and crystallize in the tetragonal system, $P4/ncc$ space group (see Tables 1 and S1–S4 in Supplementary material). Thus, complex **1**, as a representative example, is selected to describe the crystal structure in details. As depicted in Fig. 1a, the asymmetric unit contains one and a half occupied Dy^{III} cations, one deprotonated L ligand, one phen ligand and one coordinated water molecule, as well as one free perchlorate anion and half a free water molecule, exhibiting a butterfly-like configuration. There are two categories of Dy^{III} ions in the unit and both kinds of Dy^{III} ions are octa-coordinated, exhibiting a slightly distorted square antiprismatic geometry, but with different coordination environments. The Dy1 ion is coordinated by four carboxylate oxygen atoms from four different L ligands and four oxygen atoms from terminal water molecules to give a Dy₁O₈ sphere. In contrast, the Dy2 ion is surrounded by four carboxylate oxygen atoms from two different L ligands and four pyridine nitrogen atoms from two phen ligands to give a Dy₂O₄N₄ sphere. The distances of the Dy–O [Dy–O_{carboxylate} = 2.285(7)–2.323(6), Dy–O_{hydroxyl} = 2.430(5) Å] and Dy–N [Dy–N = 2.531(7)–2.542(9) Å] bonds are comparable to the reported Dy^{III} complexes [24c].

It is noteworthy that the carboxylic group of the L ligand adopts two different coordination modes (see Fig. S1). The carboxylic group [O1 and O2] of the L ligand is bound in the μ_1 - η^1 : η^0 monodentate mode to coordinate the Dy2 ion. However, the other carboxylic groups [O3 and O4] of the L ligand adopt the μ_2 - η^1 : η^1 -syn, anti-bis-(bridging) bidentate mode to bridge adjacent Dy1 and Dy2 ions and simultaneously to form a dinuclear unit with a Dy \cdots Dy separation of 5.9249(1) Å. Every two dinuclear segments are further grafted to form an envelope-like sixteen-membered ring, which is defined by the atoms Dy1, O4, C2, O3, Dy2, O3A, C2A, O4A, Dy1B, O4B, C2B, O3B, Dy2C, O3C, C2C, O4C and leads to intrachain Dy \cdots Dy distances of 7.8757(3) Å (see Fig. 1b) (Symmetry code: A = $-x + 1, -y + 1, -z + 3/2$; B = $x - 1/2, y + 1/2, -z + 3/2$;

Download English Version:

<https://daneshyari.com/en/article/1336844>

Download Persian Version:

<https://daneshyari.com/article/1336844>

[Daneshyari.com](https://daneshyari.com)