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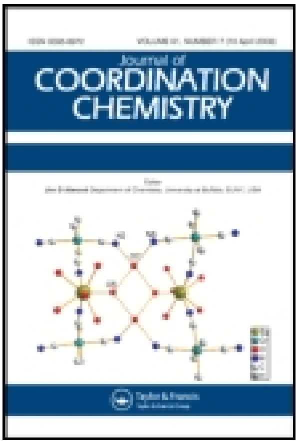

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Hydrothermal syntheses and characterization of four 2-D lanthanide coordination polymers with glutarate and 1,10-phenanthroline

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Hydrothermal syntheses and characterization of four 2-D lanthanide coordination polymers with glutarate and 1,10-phenanthroline

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Four 2-D coordination polymers $Ln_2(phen)_2(C_5H_6O_4)_3$ [Ln = Pr(**1**), Eu(**2**), Er(**3**), Yb(**4**), phen = 1,10-phenanthroline] were obtained *via* hydrothermal reactions and determined by X-ray diffraction analysis. The crystal structure data reveal that these complexes are isostructural. In the asymmetric unit, the two Ln(III) ions are nine-coordinate and have similar coordination environments. The Ln(III) ions are built into 2-D layers by three different coordination modes of glutarate. The resulting 2-D layer forms 3-D supramolecular architecture by two types of $\pi \cdots \pi$ stacking interactions. All the complexes were characterized by IR spectra and thermogravimetric analysis, and the emission spectrum shows that $Eu_2(phen)_2(C_5H_6O_4)_3$ possesses strong luminescence.

Keywords: Lanthanide coordination polymer; Crystal structure; Luminescence; Glutarate

1. Introduction

Metal coordination polymers have attracted considerable attention because of their varieties of structures and potential applications as new materials for molecular recognition, ion exchange, catalysis, and luminescence [1–5]. Lanthanide coordination polymers have attracted interest due to larger coordination spheres, and unique magnetic and luminescence properties [6, 7]. Ligands are a key for the construction of lanthanide ions into coordination polymers. For instance, carboxylates are often used to construct the coordination polymers because of their rich coordination modes [8, 9]. Though benzedicarboxylates are widely used, long-chain dicarboxylates are also excellent ligands due to their flexible bridging capability for the construction of lanthanide coordination polymers [10–12]. Thus, we have been particularly interested in utilization of flexible dicarboxylate ligands together with rigid ligands, such as glutaric

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acid and 1,10-phenanthroline, to construct lanthanide coordination polymers. To our knowledge, only one lanthanide complex with glutaric acid and phen has been reported [13]. We have synthesized a number of lanthanide(III) complexes $Ln_2(phen)_2(C_5H_6O_4)_3$ [Ln = Pr(**1**), Eu(**2**), Er(**3**), Yb(**4**)]. X-ray crystallographic analysis shows that these complexes all have a 3-D supramolecular architecture and emission spectrum reveals the luminescent properties of (**2**). This article presents the hydrothermal synthesis and characterization of these lanthanide(III) complexes.

2. Experimental

2.1. *Materials and methods*

Except $LnCl_3 \cdot nH_2O$, which was prepared in our laboratory, all chemicals, of reagent grade, were commercially available and used without purification. The IR spectra of KBr pellets from 4000–400 cm^{-1} were recorded on a Shimadzu FTIR-8900 spectrometer. Thermogravimetric (TG) measurements were carried out from room temperature to 900°C on pre-weighed samples in a nitrogen stream using a Seiko Exstar6000 TG/DTA6300 apparatus with a heating rate of 10°C min^{-1}. Solid-state powder luminescence spectra were recorded on an HRG9-5-90 fluorescence spectrophotometer.

2.2. *Synthesis of $Pr_2(phen)_2(C_5H_6O_4)_3$ (1)*

Pale green $PrCl_3 \cdot nH_2O$ was obtained by slow evaporation of a solution of Pr_2O_3 (0.0494 g, 0.150 mmol) dissolved in HCl under reflux. The above $PrCl_3 \cdot nH_2O$, glutaric acid (0.0396 g, 0.300 mmol), and 1,10-phenanthroline (phen, 0.0595 g, 0.300 mmol) in deionized water (10 mL) were adjusted to pH = 7.30 by dropwise addition of NaOH under stirring. Then, the mixture was sealed in a 23 mL Teflon-lined stainless steel autoclave, which was heated at 170°C for 5 days. After slowly cooling the reaction autoclave at 10°C h^{-1} to room temperature, green crystals were collected by filtration, washed with absolute ethanol, and dried in air. Yield: 18% based on Pr(III). IR (KBr pellet, cm^{-1}): 3049vw, 2945w, 2918w, 1599vs, 1533vs, 1427vs, 1404vs, 1346ms, 1311ms, 1142ms, 843s, and 731s.

2.3. *Synthesis of $Eu_2(phen)_2(C_5H_6O_4)_3$ (2)*

Colorless crystals were prepared analogously to **1** except using Eu_2O_3 (0.0528 g, 0.150 mmol) instead of Pr_2O_3. Yield: 20% based on Eu(III). IR (KBr pellet, cm^{-1}): 3076vw, 2924w, 2918w, 1602vs, 1539vs, 1431vs, 1404vs, 1346ms, 1315ms, 1141ms, 845s, and 731s.

2.4. *Synthesis of $Er_2(phen)_2(C_5H_6O_4)_3$ (3)*

Pink crystals were prepared analogous to **1** except using Er_2O_3 (0.0574 g, 0.150 mmol) instead of Pr_2O_3. Yield: 15% based on Er(III). IR (KBr pellet, cm^{-1}): 3078vw, 2923w, 1606vs, 1543vs, 1445vs, 1406vs, 1346ms, 1319ms, 1145ms, 843s, and 729s.

2.5. *Synthesis of $Yb_2(phen)_2(C_5H_6O_4)_3$ (4)*

Colorless crystals were prepared analogous to **1** except using Yb_2O_3 (0.0591 g, 0.150 mmol) instead of Pr_2O_3. Yield: 32% based on Yb(III). IR (KBr pellet, cm^{-1}): 3049vw, 2924w, 1606vs, 1544vs, 1440vs, 1406vs, 1346ms, 1319ms, 1142ms, 843s, and 729s.

2.6. *Crystallographic studies*

Suitable single crystals of **1–4** were selected for single-crystal X-ray diffraction analyses. Data collections were performed at 298(2) K on a RIGAKU RAXIS–RAPID diffractometer with graphite monochromated Mo-Kα radiation ($\lambda = 0.71073$). All calculations were carried out with SHELXTL-97 programs [14, 15]. The structures were refined by full matrix least squares with anisotropic displacement parameters for non-hydrogen atoms. All hydrogens were generated geometrically and treated as riding. Details of crystal data, collection, and refinement of the four complexes are summarized in table 1.

3. Results and discussion

3.1. *Description of crystal structures*

Crystallographic analysis reveals that **1–4** are isomorphous and isostructural with the compound reported by Jin *et al.* [13]. Due to the similarity of **1–4**, this article will only describe the crystal structure of **1** in detail.

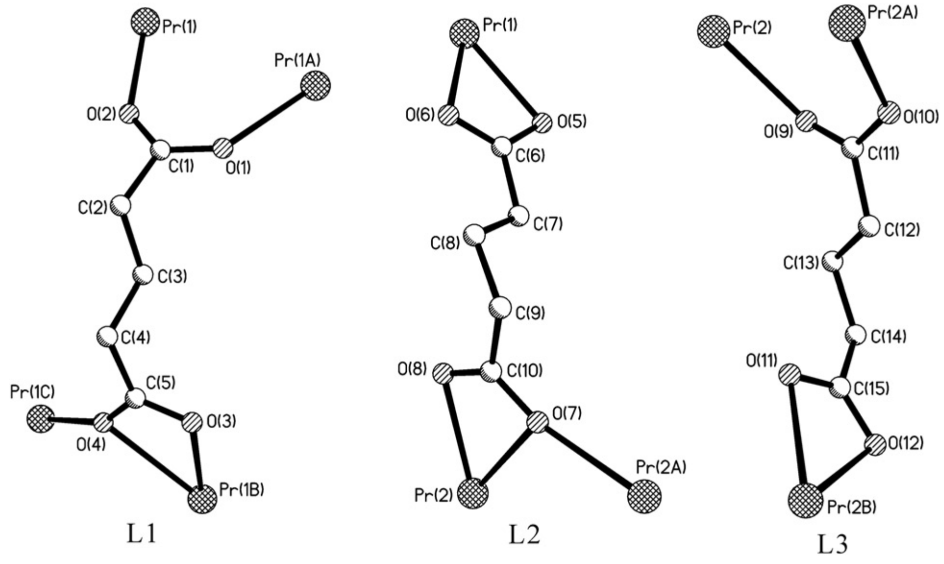
Table 1. Crystal data and structure refinements for **1–4**.

Compounds	**1**	**2**	**3**	**4**
Empirical formula	$C_{39}H_{34}N_4O_{12}Pr_2$	$C_{39}H_{34}N_4O_{12}Eu_2$	$C_{39}H_{34}N_4O_{12}Er_2$	$C_{39}H_{34}N_4O_{12}Yb_2$
Formula weight	1032.52	1054.62	1085.22	1096.78
Crystal system	Triclinic	Triclinic	Triclinic	Triclinic
Space group	$P\bar{1}$	$P\bar{1}$	$P\bar{1}$	$P\bar{1}$
Unit cell dimensions (Å, °)				
a	8.879(2)	8.812(2)	8.755(2)	8.729(2)
b	13.595(3)	13.483(3)	13.375(3)	13.379(3)
c	16.461(3)	16.405(3)	16.391(3)	16.385(3)
α	84.16(3)	84.07(3)	83.88(3)	83.62(3)
β	83.97(3)	84.35(3)	84.39(3)	84.31(3)
γ	75.03(3)	74.99(3)	76.03(3)	75.12(3)
Volume (Å^3), *Z*	1903.2(7), 2	1867.5(7), 2	1846.9(6), 2	1833.0(6), 2
Calculated density ($g\,cm^{-3}$)	1.802	1.876	1.951	1.987
Absorption coefficient μ (mm^{-1})	2.600	3.399	4.585	5.143
F(000)	1020	1036	1056	1064
θ range for data collection (°)	3.04–27.47	3.06–27.48	3.07–27.55	3.08–27.46
Final *R* indices [$I > 2\sigma(I)$]	$R_1 = 0.0448$, $wR_2 = 0.0892$	$R_1 = 0.0248$, $wR_2 = 0.0725$	$R_1 = 0.0619$, $wR_2 = 0.1138$	$R_1 = 0.0307$, $wR_2 = 0.1004$
R indices (all data)	$R_1 = 0.0789$, $wR_2 = 0.0996$	$R_1 = 0.0355$, $wR_2 = 0.0833$	$R_1 = 0.1332$, $wR_2 = 0.1490$	$R_1 = 0.0395$, $wR_2 = 0.1094$
Goodness-of-fit on F^2	1.043	1.206	0.966	1.292

$wR_2 = [\Sigma w(F_o^2 - F_c^2)^2 / \Sigma w(F_c^2)^2]^{1/2}$.

The asymmetric unit of **1** contains two Pr(III) ions, two phen, and three crystallographically distinct glutarate ligands. The coordination environments of Pr(III) 1 and Pr(III) 2 are similar to each other, nine-coordinate with seven oxygens from five glutarates, and two nitrogens from one phen. The coordination sphere of each Pr(III) can be described as a distorted capped trigonal antiprism. The Pr–O bond distances range from 2.418(4) to 2.689(4) Å and the Pr–N distances from 2.651(5) to 2.748(5) Å. For glutarate dianion, the aliphatic carbon backbone may be present in three conformations: anti–anti, anti–gauche, and gauche–gauche [16]. In **1–4**, the three crystallographically distinct glutarate ligands have two different conformations, anti–anti and anti–gauche. In addition, there are also three coordination modes of glutarate in the structure (figure 1). In L1, one carboxylate coordinates to two Pr(III) ions by a bridging mode, and the other adopts a chelating mode to connect two Pr(III) 1 ions, resulting in 1-D infinite polymeric chains along [100] direction. In L3, one carboxylate coordinates to one Pr(III) 2 by a chelating mode, and the other links two Pr(III) 2 ions through a bridging mode. The Pr(III) 2 ions are also linked into a 1-D polymer chain running along [100] direction by aforementioned linking modes of L3. The resulting two different 1-D polymer chains are assembled into a 2-D layer by L2, in which one carboxylate is a chelating bridge to link two Pr(III) 2 ions while the other coordinates to one Pr(III) 1 by a chelating mode (figure 2). A 3-D supramolecular architecture is achieved through two types of $\pi\cdots\pi$ stacking interactions that occur between phen ligands in the adjacent layers with mean interplanar distances of 3.43 and 3.48 Å, respectively.

In the four lanthanide coordination polymers, the a, c, α, γ, and V of cell parameters decrease with the ionic radius contraction from Pr(III) to Yb(III). At the same time, the mean distances 2.503, 2.448, 2.400, 2.391 Å for Pr–O, Eu–O, Er–O, Yb–O and 2.690, 2.633, 2.585, 2.546 Å for Pr–N, Eu–N, Er–N, Yb–N, respectively, also decrease as the ionic radius reduces from Pr(III) to Yb(III).



L1 L2 L3

Figure 1. Three coordination modes of glutarate in **1**.

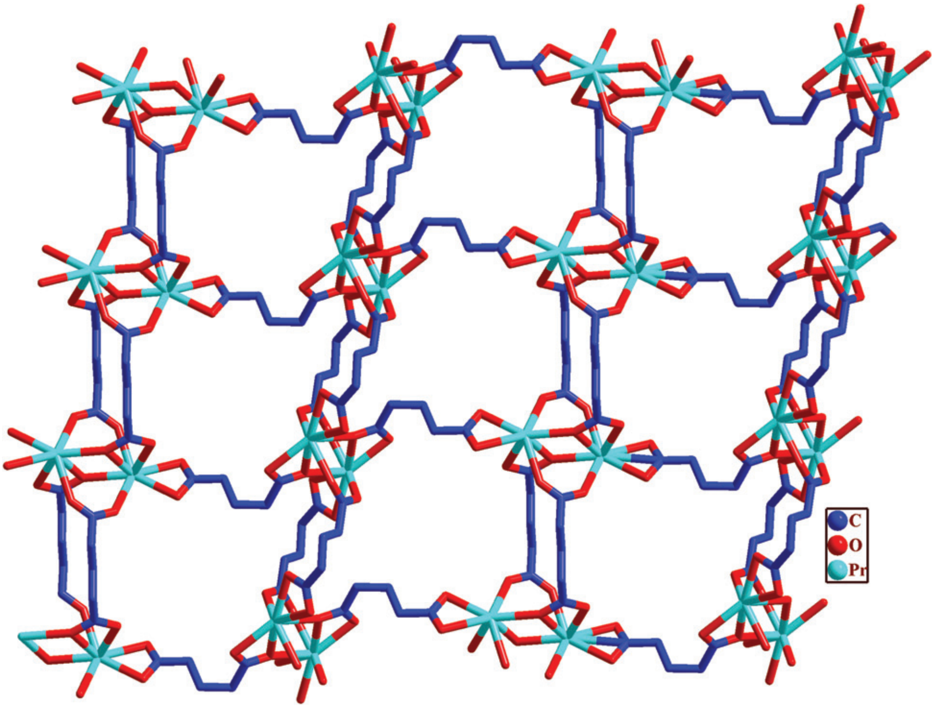


Figure 2. 2-D network in **1** (hydrogens and phen are omitted for clarity).

3.2. *TG analysis*

The isostructural frameworks result in similar thermal decomposition in all four complexes. Taking **1** as an example, the TG curve shows that **1** is thermally stable to 370°C. The differential thermal analysis (DTA) curve of **1** shows one endothermic peak at 413°C, which indicates that the complex undergoes either chemical reactions or physical processes at this temperature. When heating to 1000°C, the residue is about 34.92%, which consists of about 31.94% Pr_2O_3 (Calcd) and traces of organic ligands.

3.3. *Fluorescence properties*

The emission spectrum (figure 3) of solid-state **2** was recorded from 500 to 720 nm under an excitation wavelength of 395 nm at room temperature. Figure 3 shows the three emission peaks at 581, 595, and 616 nm, corresponding to $^5D_0 \rightarrow {}^7F_0$, $^5D_0 \rightarrow {}^7F_1$, and $^5D_0 \rightarrow {}^7F_2$ transitions of Eu(III), respectively. These emission peaks are consistent with characteristic peaks of europium ions, indicating that the effect of the photoluminescence of organic ligands could be negligible in **2**.

4. Conclusions

Four new 2-D isostructural complexes $Ln_2(phen)_2(C_5H_6O_4)_3$ [Ln = Pr(**1**), Eu(**2**), Er(**3**), Yb(**4**)] have been hydrothermally synthesized. The experimental data show that there

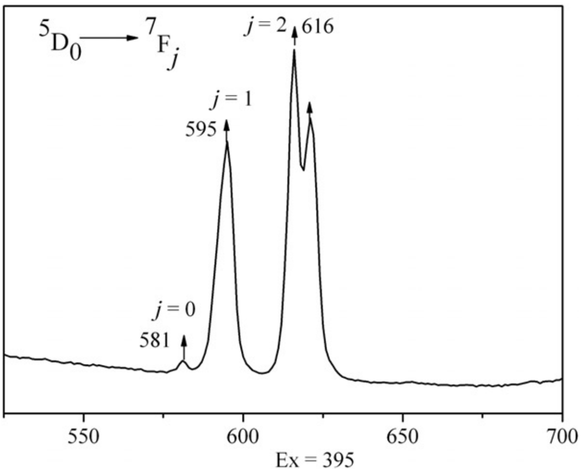


Figure 3. Solid-state emission spectrum of **2**.

are three different coordination modes of glutarate ligands, which bridge nine-coordinate Ln(III) ions into different 2-D layers in these complexes. A 3-D supramolecular architecture is formed *via* two types of $\pi \cdots \pi$ stacking interactions. The four structures imply subtle effects of lanthanide ion radii on the mean bond distances and a, c, α, γ, and V of cell parameters, which decrease as the ionic radius contracts from Pr(III) to Yb(III). The emission spectrum shows that **2** exhibits strong luminescence at room temperature with emission peaks consistent with characteristic peaks of europium.

Supplementary material

CCDC numbers 771035 (**1**), 771034 (**2**), 771033 (**3**), and 771036 (**4**) contain the supplementary crystallographic data for $Ln_2(phen)_2(C_5H_6O_4)_3$ [Ln = Pr(**1**), Eu(**2**), Er(**3**), Yb(**4**)]. These data can be obtained free of charge *via* http://www.ccdc.cam.ac.uk/conts/retrieving.html, or from the Cambridge Crystallographic Data Center, 12 Union Road, Cambridge CB2 IEZ, UK [Fax: +44-1223-336033; Email: deposit@ccdc.cam.ac.uk].

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