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Synthesis, crystal structure and luminescence properties of two novel lanthanide coordination polymers containing double chain

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Abstract

Two novel lanthanide(III) two-dimensional (2D) coordination polymers $[Ln_2(PDC)_2(OH)_2(H_2O)_2] \cdot H_2O$ (Ln = Eu (**1**) and Tb (**2**), H_2PDC = pyridine-3,4-dicarboxylic acid) have been prepared under hydrothermal conditions and characterized by elemental analysis, IR, TGA and single-crystal X-ray diffraction. Compounds **1** and **2** crystallize in the triclinic system, space group $P\bar{1}$, they are isostructural and exhibit the same two-dimensional topological network constructed by PDC-connected Ln–O–Ln double chains. Photoluminescence properties of the compounds **1** and **2** have been investigated in the solid state at room temperature.

Keywords: Coordination polymer; Hydrothermal synthesis; Double chain; Lanthanide; Fluorescent properties; Carboxylate

1. Introduction

The rapidly expanding field of crystal engineering of two- and three-dimensional coordination polymers have recently attracted great interest for both the structural and topological novelty as well as for their potential applications to material science as catalytic, conductive, luminescent, magnetic, non-linear optical or porous materials [1–7]. Thus so far, much attention has been drawn to the assembly of metal–organic framework (MOF) and significant development has been witnessed in high-dimensional coordination polymers. The symmetrical multicarboxylate ligands have been generally used in this field. Miao Du et al succeeded in preparing a series of high-dimensional metal–organic coordination with pyridine-2,6-dicarboxylic acid [8]. Whitfield et al. reported 3D complex $Co(pydc)(H_2O)_2$ and 2D layer structure $Ni(pydc)(H_2O)$ (pydc = 3,5-pyridinedicarboxylate) [9]. While pyridine-3,4-dicarboxylic acid (H_2PDC), as a member of asymmetric ligands, has also drawn more and more attention in crystal engineering. On the other hand, investigations of the pyridine-3,4-dicarboxylic acid complexes have mainly focused on the d-block transition–metal [10–16], f-block lanthanide ions have received comparatively less attention than transition–metal ions. However, due to their ability of high coordination number, special magnetic and fluorescence properties, lanthanide complexes is likely to bring unprecedented crystal structures and unique properties [17–20]. Therefore, a further research in this area is still a especially attractive target. Up to now, Frameworks constructed by PDC and lanthanide ion are still limited [21–27]. Herein, we report two new lanthanide metal coordination polymers $[Ln_2(PDC)_2(OH)_2(H_2O)_2] \cdot H_2O$ (Ln = Eu (**1**) and Tb (**2**)), in which Ln–O–Ln double chains are cross-linked by PDC ligands to form interesting two-dimensional framework structures. They present, to the best of our knowledge, the first examples of PDC complexes containing double chain.

2. Experimental

2.1. Materials and methods

Compound $LnCl_3 \cdot 6H_2O$ (Ln = Eu, Tb) were prepared by dissolving their respective oxides in concen-

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trated hydrochloric acid followed by drying. All the other reagents are commercially available and were used as received without further purification. Elemental analyses (C, H, N) were determined with an Elemental Vario EL elemental analyzer. IR spectra were (KBr pellets) recorded in the 4000–400 cm^{-1} range with a FTIR-8900 spectrometer. Thermogravimetric analysis (TGA) was performed under nitrogen with a heating rate of 10 °C min^{-1} using a TGA-7 system. Fluorescent spectra were measured with a Hitachi F-4500 luminescence spectrometer.

2.2. Preparations

2.2.1. $[Eu_2(PDC)_2(OH)_2(H_2O)_2] \cdot H_2O$ (1)

A mixture of $EuCl_3 \cdot 6H_2O$ (0.2 mmol), pyridine-3,4-dicarboxylic acid (0.2 mmol), 4,4′-bipyridine (0.2 mmol) and NaOH (0.4 mmol) in H_2O (8.0 ml) was mixed in a 15 ml Teflon reactor, which was heated to 180 °C for 3d. The resulting solutions were cooled slowly to room temperature. Colorless needle-like crystals of compound **1** suitable for X-ray determination were obtained in 37% yield. The initial pH value of the reactive solution was 4.7 and the final pH value was still 4.7. *Anal.* Calc. for $C_{14}H_{14}Eu_2N_2O_{13}$:C, 23.28; H, 1.95; N, 3.88. Found: C, 23.54; H, 1.60; N, 4.00%. IR spectrum (cm^{-1}): 3526 (m), 2360 (s), 2342 (m), 1573 (s), 1490 (m), 1429 (s), 1395 (s), 1171 (w), 824 (w), 670 (m), 642 (w).

2.2.2. $[Tb_2(PDC)_2(OH)_2(H_2O)_2] \cdot H_2O$ (2)

Compound **2** was prepared using a similar method to that employed for the synthesis of compound **1**, with $TbCl_3 \cdot 6H_2O$ (0.2 mmol) in place of $EuCl_3 \cdot 6H_2O$. Colorless needle-like crystals of compound **2** suitable for X-ray determination were obtained in 45% yield. The initial pH value of the reactive solution was 4.7 and the final pH value was still 4.7. *Anal.* Calc. for $C_{14}H_{14}Tb_2N_2O_{13}$: C, 22.84; H, 1.92; N, 3.81. Found: C, 22.93; H, 1.60; N, 3.95%. IR spectra (cm^{-1}): 3525 (m), 2360 (s), 1573 (s), 1490 (m), 1424 (s), 1393 (s), 1171 (w), 824 (w), 701 (m), 675 (m), 651 (w).

2.3. Crystal structure determination

Suitable single crystals of **1** and **2** were carefully selected under an optical microscope and glued to thin glass fibers. Crystallographic data for all compounds were collected with a Bruker SMART-CCD area detector diffractometer with graphite-monochromated Mo Kα radiation ($\lambda = 0.71073$ Å) at $T = 294(2)$ K. Absorption corrections were made using SADABS program [28]. The structures were solved using direct method and refined by full-matrix least-squares methods on F^2 by using SHELX-97 program package [29]. All non-hydrogen atoms and the hydrogen atoms of water molecules are found from the different Fourier maps and refined anisotropically. A summary of the crystallographic data and refinement parameters are given in Table 1. Selected bond lengths for 1 and 2 are given in Table 2.

Table 1
Crystal data and structure refinement details

Compound	**1**	**2**
Empirical formula	$C_{14}H_{14}Eu_2N_2O_{13}$	$C_{14}H_{14}Eu_2N_2O_{13}$
Formula weight	722.19	736.11
Temperature (K)	294(2)	294(2)
Wavelength (Å)	0.71073	0.71073
Crystal system	triclinic	triclinic
Space group	$P\bar{1}$	$P\bar{1}$
a (Å)	8.0134(9)	7.9774(17)
b (Å)	9.4793(10)	9.472(2)
c (Å)	12.6667(14)	12.658(3)
α (°)	76.637(2)	76.408(3)
β (°)	85.157(2)	84.883(3)
γ (°)	83.073(2)	82.958(3)
V (Å^3)	927.70(18)	920.9(3)
Z	2	2
Calculated density (Mg/m^3)	2.585	2.655
$F(000)$	684	692
Absorption coefficient (mm^{-1})	6.776	7.695
θ Range for data collection (°)	2.22–25.02	1.66–25.02
Limiting indices	$-9 \leqslant h \leqslant 9$, $-11 \leqslant k \leqslant 10$, $-11 \leqslant k \leqslant 10$	$-8 \leqslant h \leqslant 9$, $-15 \leqslant l \leqslant 12$, $-15 \leqslant l \leqslant 15$
Reflections collected/unique [R_{int}]	4824/3262 [0.0233]	4728/3211 [0.0234]
Completeness to $\theta = 25.02°$	99.4%	98.8%
Maximum and minimum transmission	1.000000 and 0.430601	1.00000 and 0.664934
Data/restraints/parameters	3262/9/280	3211/9/280
Goodness-of-fit on F^2	1.021	1.028
Final R indices [$I > 2\sigma(I)$]	$R_1 = 0.0335$, $wR_2 = 0.0953$	$R_1 = 0.0251$, $wR_2 = 0.0644$
R indices (all data)	$R_1 = 0.0372$, $wR_2 = 0.0980$	$R_1 = 0.0303$, $wR_2 = 0.0677$
Largest differences in peak and hole (e Å^{-3})	2.809 and −2.061	1.009 and −1.335

Table 2
Selected bond lengths (Å) for compounds **1** and **2**

Compound **1**					
Eu(1)–O(3)#1	2.343(4)	Eu(1)–O(7)#2	2.356(4)	Eu(1)–O(11)#1	2.419(4)
Eu(1)–O(10)	2.396(4)	Eu(1)–O(1)	2.401(4)	Eu(1)–O(6)#1	2.446(4)
Eu(1)–O(11)	2.488(4)	Eu(1)–O(9)	2.508(5)	Eu(2)–O(11)	2.342(4)
Eu(2)–O(8)#4	2.385(4)	Eu(2)–O(4)#1	2.404(4)	Eu(2)–O(5)	2.416(4)
Eu(2)–O(10)#3	2.435(4)	Eu(2)–O(2)#3	2.443(4)	Eu(2)–O(10)	2.471(4)
Eu(2)–O(12)	2.584(5)	O(2)–Eu(2)#3	2.443(4)	O(3)–Eu(1)#1	2.343(4)
O(4)–Eu(2)#1	2.404(4)	O(6)–Eu(1)#1	2.446(4)	O(7)–Eu(1)#5	2.356(4)
O(8)–Eu(2)#4	2.385(4)	O(10)–Eu(2)#3	2.435(4)	O(11)–Eu(1)#1	2.419(4)
Compound **2**					
Tb(1)–O(3)#1	2.306(4)	Tb(1)–O(7)#2	2.332(3)	Tb(1)–O(10)	2.366(3)
Tb(1)–O(1)	2.379(4)	Tb(1)–O(11)#1	2.396(3)	Tb(1)–O(6)#1	2.418(3)
Tb(1)–O(11)	2.470(3)	Tb(1)–O(9)	2.491(4)	Tb(2)–O(11)	2.331(3)
Tb(2)–O(8)#3	2.362(4)	Tb(2)–O(4)#1	2.378(4)	Tb(2)–O(5)	2.391(4)
Tb(2)–O(10)#4	2.408(3)	Tb(2)–O(2)#4	2.422(4)	Tb(2)–O(10)	2.455(3)
Tb(2)–O(12)	2.538(4)	O(2)–Tb(2)#4	2.422(4)	O(3)–Tb(1)#1	2.306(4)
O(4)–Tb(2)#1	2.378(4)	O(6)–Tb(1)#1	2.418(3)	O(7)–Tb(1)#5	2.331(3)
O(8)–Tb(2)#3	2.362(4)	O(10)–Tb(2)#4	2.408(3)	O(11)–Tb(1)#1	2.396(3)

Symmetry transformations used to generate equivalent atoms:
1: #1: $-x, -y+1, -z+2$; #2: $x, y-1, z$; #3: $-x+1, -y+1, -z+2$; #4: $-x+1, -y+2, -z+2$; #5: $x, y+1, z$.
2: #1: $-x, -y+1, -z+2$; #2: $x, y-1, z$; #3: $-x+1, -y+2, -z+2$; #4: $-x+1, -y+1, -z+2$; #5: $x, y+1, z$.

3. Results and discussion

3.1. Description of the structures

Single-crystal X-ray analysis reveals that compound **1** is a unique two-dimensional layered framework containing one-dimensional Eu–O–Eu double chain, in which the asymmetric unit consists of two europium atoms, two PDC ligands, two OH^- groups, two aqua ligands, and one isolated water molecular. The local coordination environment around Eu(III) centers (Eu(1), Eu(2)) is depicted in Fig. 1. They all exhibit distorted bicapped trigonal prism geometries. Eu(1) is coordinated by two pairs of carboxylate oxygen atoms from two different PDB ligands [Eu(1)–O(PDB) = 2.343(4)–2.446(4) Å], three binding oxygen atoms from three OH^- groups [Eu–O(OH^-) = 2.396(4)–2.488(4) Å] and one oxygen atom from the terminal water molecular [Eu(1)–O(H_2O) = 2.508(5) Å]; Eu(2) is also defined by two pairs of carboxylate oxygen atoms from two different PDB ligands [Eu(2)–O(PDB) = 2.385(4)–2.443(4) Å], three binding oxygen atoms from three OH^- groups [Eu(2)–O(OH^-) = 2.342(4)–2.471(4) Å] and one oxygen atom from the terminal water molecular [Eu(2)–O(H_2O) = 2.584(5) Å]. The distance of Eu(1)$\cdots$Eu(2) is 3.9163(5) Å, which is comparable to the distance found in the compound $[Na_2[Ln_2(sal)_4(CF_3SO_3)_2(H_2O)_4](CF_3SO_3)_2]_n$ (3.8545(8) Å) [30], which is possibly related to that OH^- groups participate in coordination. Eu(1) and Eu(2) centers are connected together via μ_3-oxygen atoms of OH^- groups in an edge-sharing mode to form a one-dimensional Eu–O–Eu double chain along an axis with adjacent Eu$\cdots$Eu distance of 4.2278(6) and 4.2987(6) Å. These chains are further linked via PDC ligand to a two-dimensional network (Fig. 2). In other words, the 2D layer can be best described as being constructed by PDC-connected Eu–O–Eu double chain. Furthermore, the adjacent layers are further linked via hydrogen bonds

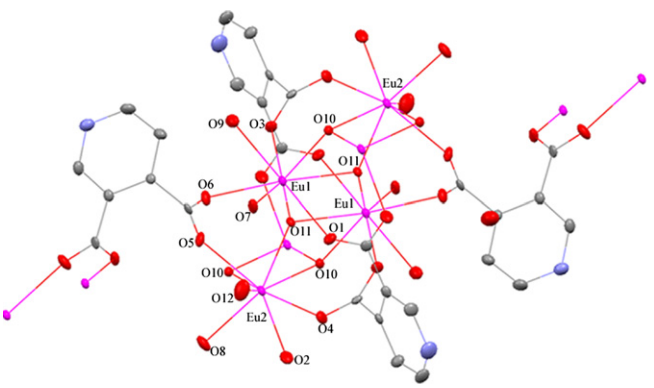

Fig. 1. ORTEP view of the coordination environment around the Europium centers for **1**.

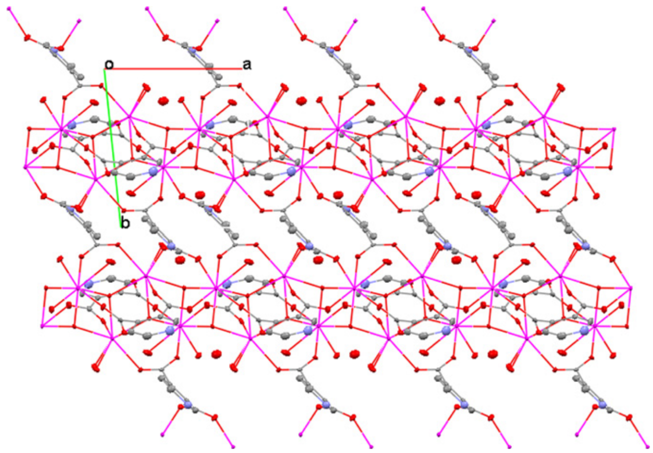

Fig. 2. Two-dimensional layered structures of **1** constructed by PDC-connected Eu–O–Eu double chains.

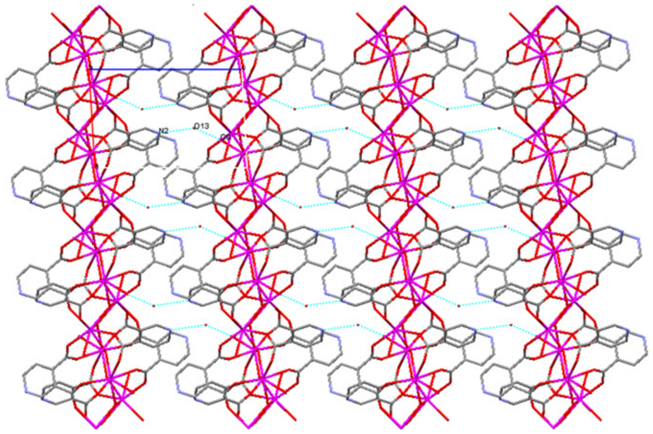

Fig. 3. Hydrogen bonds interactions linking layers into a 3D supermolecular network in **1**.

between pyridyl N atoms, coordinated water molecule and isolated water to form a three-dimensional supramolecular network (Fig. 3). It is interesting that the PDC ligand exhibits its tetradenate coordination modes, all the carboxyl groups adopt a monodenate bridging mode to connect four Eu atoms, pyridine nitrogen atoms are uncoordinated.

It is also noteworthy that OH^- bridging lanthanide clusters as the building unit to form high-dimensional network in respect of lanthanide pyridinedicarboxylate coordination polymers have only one structure $[Tb_2(Dinic)_2(phen)_2(OH)_2(H_2O)]_n \cdot 3nH_2O$ reported [25]. What is different from the above coordination polymer, which possesses a one-dimensional chain structure, is the compound **1** has a two-dimensional layer structure. This could be related to the fact that phen in $[Tb_2(Dinic)_2(phen)_2(OH)_2(H_2O)]_n \cdot 3nH_2O$ serves a chelating ligand serving a 'passivating' role by occupying coordination sites on the metal centers and providing steric constraints, thus preventing spatial extension of skeleton to higher dimensions [31].

X-ray single-crystal diffraction studies reveal that compound **2** adopts a structure very similar to that of **1** (Figs. S1–S3), as shown by the detailed structural data listed in the supplementary materials.

3.2. Thermogravimetric analysis

To investigate their thermal stabilities, thermogravimetric analyses (TGA) of **1** and **2** were carried out at a heating rate of 10 °C min^{-1}. TG analysis shows that the thermal decomposition behavior of compounds **1** and **2** was similar. The first weight loss in **1** started at *ca.* 70 up to 150 °C giving a weight loss of 2.16%, corresponding to the loss of lattice water molecules (2.49% calculated). On further heating, it lost two coordinated water molecules and two OH^- groups between 150 and 250 °C (10.34% observed, 9.69% calculated). In the range of 250–900 °C, the weight loss of 38.78% should correspond to the decomposition of organic ligands (calc. 39.09%). The remaining weight of 48.72% corresponds to the percentage (48.73%) of Eu and O components, indicating that the final product is Eu_2O_3.

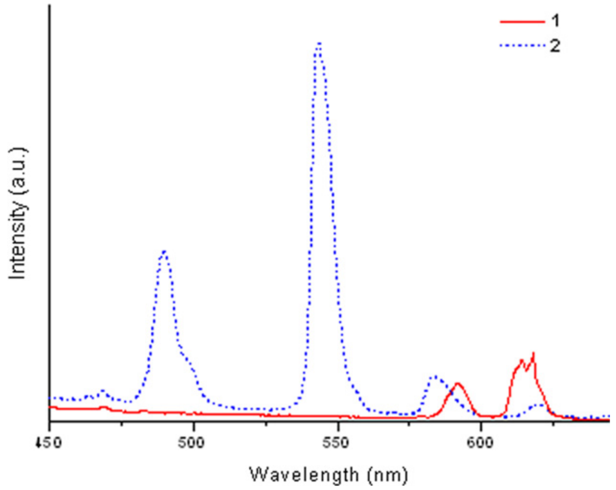

Fig. 4. The emission spectra (emission at 340 nm) of compound **1** and **2** in the solid state.

3.3. Fluorescence properties of *1* and *2*

Fig. 4 shows the emission spectra of **1** and **2** in the solid state at room temperature. Excitation at 340 nm into the lowest energy ligand-centered absorption band results in the luminescence characteristic of Ln^{3+} ion (Ln = Eu, Tb).

The emission peaks of **1** at 579, 591, 614 and 618 nm can be assigned to $^5D_0 \rightarrow {}^7F_J$ ($J = 0, 1, 2$) transitions, while the emission peaks of **2** at 490, 543, 584 and 621 nm can be assigned to $^5D_4 \rightarrow {}^7F_J$ ($J = 6, 5, 4, 3$) transitions, respectively [32–34]. However, these characteristic emission bands indicate that the ligand-to-metal energy transfer is moderately efficient under the experimental conditions [35]. For compound **1**, the symmetric forbidden emission $^5D_0 \rightarrow {}^7F_0$ found at 579 nm reveals that Eu^{3+} occupy sites with low symmetry and without an inversion center. The strongest emission is in the $^5D_0 \rightarrow {}^7F_2$ transition region and the $^5D_0 \rightarrow {}^7F_2$ peak was split into two levels at 614 and 618 nm. It is well known that the $^5D_0 \rightarrow {}^7F_2$ transition induced by the electric dipole moment is hypersensitive to the environment of the Eu ion, while the $^5D_0 \rightarrow {}^7F_1$ transition is a magnetic dipole transition, which is fairly insensitive to the coordination environment of the Eu ion. The intensity ratio $I(^5D_0 \rightarrow {}^7F_2)/I(^5D_0 \rightarrow {}^7F_1)$ is equal to *ca.* 1.8, which indicates that Eu^{3+} ions are not at an inversion center [36]. This is in agreement with the result of the single-crystal X-ray.

4. Conclusion

In summary, we have synthesized two novel lanthanide metal coordination polymers by hydrothermal reactions. The title complexes represent the first examples of PDC complexes containing double chain constructed from OH^- bridging building unit. The fluorescent spectra show that compounds 1 and 2 exhibit the characteristic emission transitions of Eu^{3+} and Tb^{3+} ion, respectively.

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Appendix A. Supplementary material

CCDC 648468 and 648469 contain the supplementary crystallographic data for **1** and **2**. These data can be obtained free of charge from The Cambridge Crystallographic Data Centre http://www.ccdc.cam.ac.uk/data_request/cif. Supplementary data associated with this article can be found, in the online version, at doi:10.1016/j.ica.2007.09.013.

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