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Self-assembled microporous lanthanide coordination polymers built by 2-hydroxynicotinic acid and oxalate ligands

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ABSTRACT

Two new microporous lanthanide coordination polymers, namely, $[Eu(Hnica)_2(ox)_2(H_2O)_2] \cdot 5H_2O$ (**1**) and $[Gd(Hnica)_2(ox)_2(H_2O)_2] \cdot 5H_2O$ (**2**), have been successfully synthesized by reaction of 2-hydroxynicotinic acid (H_2nica) in the presence of the coligand oxalate (ox) with lanthanide ions under hydrothermal conditions. Single crystal X-ray diffraction analyses reveal that compounds **1** and **2** are isostructural and exhibit two-dimensional (2D) layer architectures built by the linkage of 1D Ln–ox chains with μ_2- Hnica bridging ligands, which are further connected by strong π–π stacking interactions to form 3D microporous supramolecular frameworks. Furthermore, the thermal stability and solid-state luminescent behavior of compound **1** were also investigated.

In the last decade, much attention paid to the design and construction of novel lanthanide coordination polymers can be attributed to their intriguing architectures and topologies, and potential applications including luminescence, gas storage, magnetism, ion exchange, catalysis and so on [1–5]. However, effectively controlling the structure of the lanthanide coordination polymers is currently a formidable task due to the unique nature of lanthanide ions, such as their large radius, high coordination number, and flexible coordination environments [6]. According to a Cambridge Structural Database (CSD) search, most of the research work has focused on the functional transition metal–organic coordination polymers, while the assembly of analogous chemistry with rare earth metals, particularly the microporous lanthanide coordination polymers, still remains less well developed [7,8].

2-Hydroxynicotinic acid (H_2nica), a potential multidentate ligand containing both carboxyl and hydroxy functional groups, is a good candidate for preparing new lanthanide coordination polymers because of its outstanding features of flexible coordination modes such as *O*, *O*′-chelation and *N*,*O*-chelation under hydrothermal conditions [9]. In addition, the oxalate ligand has versatile coordination modes, which as an auxiliary ligand, not only can meet the high coordination numbers for lanthanide metal ions, but also can stabilize the lanthanide cluster in the crystallization process [10]. Accordingly, some interesting lanthanide coordination polymers have been successfully obtained by our group by employing H_2nica and ox as a mixed ligand to react with lanthanide metal salts [9d, 9e, 9 g]. For example, two novel 3D microporous coordination polymers, $[Ln_3 \cdot (nica)_2 \cdot (ox)_4 \cdot (H_2O)_2] \cdot 4H_2O$ (Ln = Yb or Tm), which contain two types of 1D channels along the *c* axis direction, were prepared in the presence of HNO_3 [9 g]. Prompted by our previous interesting findings, now, we hope to continuously construct more desired lanthanide coordination polymers based on H_2nica and ox ligands by changing the reaction conditions. In this paper, fortunately, other two new microporous lanthanide coordination polymers, formulated as $[Eu(Hnica)_2(ox)_2(H_2O)_2] \cdot 5H_2O$ (1) and $[Gd(Hnica)_2(ox)_2(H_2O)_2] \cdot 5H_2O$ (2), have been synthesized under the similar reaction systems. The microporous structures, thermal stabilities, and luminescent properties have been studied in detail.

Single crystal X-ray diffraction analyses reveal that compounds **1**–**2** are isomorphous and isostructural, and both of them exhibit interesting open frameworks with water guest molecules filled in the cavities of their 1D channels. Therefore, the structure of **1** was selected and described in detail to represent their frameworks. As shown in Fig. 1, compound **1** crystallizes in the monoclinic space group *P*21, and its symmetric unit comprises two independent Eu(III) ions, two $Hnica^-$ ligands, two oxalate ligands, and two coordinated water molecules, as well as five free water molecules. Both Eu(1) and Eu(2) ions are nine-coordinated with distorted tricapped trigonal prismatic geometries, coordinated by three carboxyl oxygen atoms and one phenolic oxygen atom from two $Hnica^-$ ligands, four carboxyl oxygen atoms from

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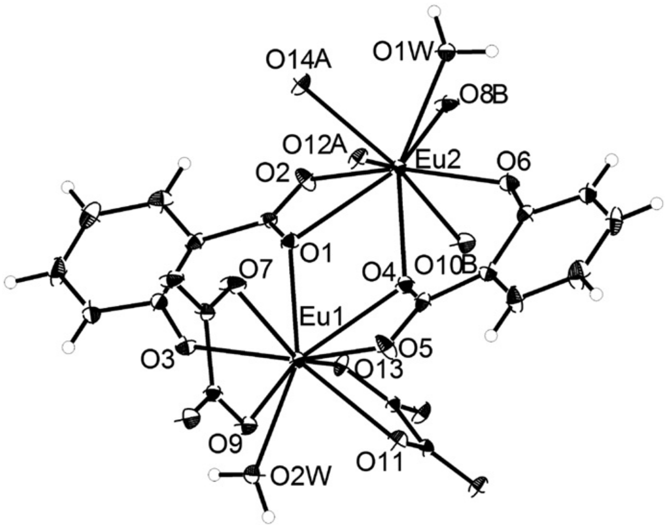
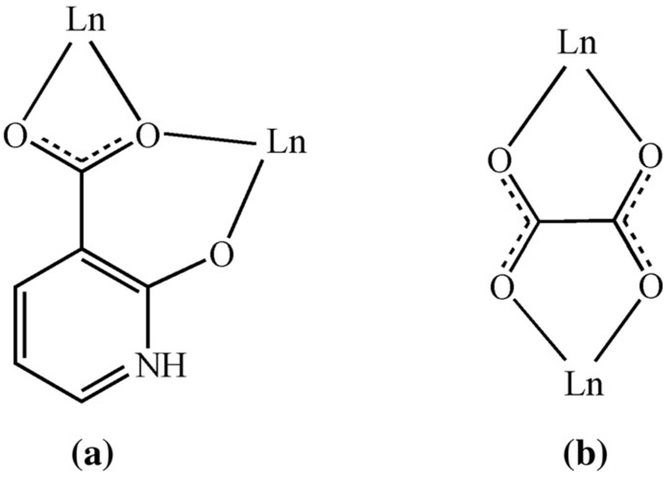


Fig. 1. Coordination environments of the Eu^{3+} ions in 1. An ORTEP drawing with 30% probability displacement ellipsoids is presented.

two oxalate ligands, as well as one oxygen atom from one terminal water molecule. The Eu–O bond lengths vary from 2.380(5) to 2.666(5) Å, and the O–Eu–O bond angles are in the range of 50.10(13)–156.41(14)°, all of which are comparable to those reported for other nine-coordinate Eu(III)–organic frameworks with oxygen donor ligands [11].

There are two kinds of $Hnica^-$ ligands with slightly different configurations in compound **1**: the dihedral angles between the carboxyl group and the correspondingly linked pyridine ring of these two types of $Hnica^-$ ligands are equal to 10.8° and 20.7°, respectively. However, it is noteworthy to mention that each kind of $Hnica^-$ ligands, in which the carboxyl group and the phenolic group are all derotonated, and the pyridine nitrogen atom is protonated, exhibits the same coordination mode: all of them adopt a μ_2-*k*O, O′:*k* O′,O″ mode to bridge two Eu(III) ions in the bis-O,O′-chelating fashion (Scheme 1**a**). Similarly, each ox anion in **1** also acts as a bis(chelating) ligand and coordinates to two Eu(III) centers in bis-O,O′-chelating coordination (Scheme 1**b**).



Scheme 1. Coordination modes of the H_2nica and ox ligands in compounds 1–2.

In compound **1**, two crystallographically independent metal ions Eu1 and Eu2 are alternately bridged by the ox ligands, leading to the formation of 1D lanthanide–oxalate zigzag chain, as illustrated in Fig. 2a. These neighbouring 1D chains are further linked by the two kinds of μ_2-$Hnica^-$ ligands as mentioned above, thus giving rise to a novel 2D network structure in the *ac* plane (Fig. 2b). The 2D layer also can be viewed as the linkage of the secondary building units (SBUs): the hexagonal rings $Eu_6(Hnica)_4(ox)_4$ (Fig. 3). In each SBU, the six Eu(III) ions are not strictly coplanar, with the mean deviation from the least-squares plane being 0.4060 Å, and the Eu(III) ···Eu(III) distances span from 4.1472(4) to 6.2865(4) Å, while the Eu···Eu···Eu angles are within the range from 86.363 (5) to 154.279(5)°. Therefore, these hexagonal SBUs are edge-sharing to each other, producing a 2D honeycomb-like network, which can be considered as a hexagonal honeycomb (6,3) topology if we view the Eu(III) ions as 3-connected nodes, as described in Fig. 3.

In addition, the 2D layers are stacked in an -ABAB- sequence by strong π–π stacking interactions between the pyridine rings of the two neighbouring $Hnica^-$ ligands [with a centroid–centroid distance of 3.557 Å], thereby forming a 3D porous supramolecular framework (Fig. 4). The pores are opened along the *a* axis, and are filled with lots of free water molecules. If the free solvent molecules are removed, compound **1** has 279.2 $Å^3$ potential solvent volume (21.8%), estimated by PLATON [12]. The potential solvent area is close to the porosities of the 3D novel microporous lanthanide coordination polymers, which have been published by our group recently [9 g].

To investigate their thermal stabilities, and owing to the similarity of structures **1** and **2**, compound **1** was selected for thermal gravimetric analysis (TGA) to examine the thermal stability from room temperature to 800 °C with a heating rate of 10 °C min^{-1} under an air atmosphere. As shown in Figure S1 (in the ESI), the TG curve of **1** revealed a gradual weight loss of 10.3% from room temperature to 250 °C, corresponding to the release of five guest water molecules per formula unit (calc. 10.2%). Then the coordinated water molecules are lost with the temperature rising. The large weight loss occurs above 330 °C, which can be ascribed to decomposition of the whole coordination framework. The TG analysis of **1** indicated that all the water guest molecules in the 1D channels can be easy to remove from the framework by heating to 250 °C, and the resulting empty framework still retains stable until 330 °C; thus, it probably can be used for gas storage.

The IR spectra of compounds **1** and **2** are similar. The observed broad bands in the region of 3600–3200 cm^{-1} can be attributed as the characteristic peaks of O–H and N–H vibrations. While the sharp bands in the ranges of 1638–1561 and 1470–1384 cm^{-1} may be assigned to asymmetric and symmetric stretching vibrations of carboxylic groups, respectively. The absence of strong IR bands around 1700 cm^{-1} in compounds **1** and **2** shows that the carboxyl groups are deprotonated [13].

Taking into accounting the excellent luminescent property of Eu(III) ion, the photoluminescence of compound **1** in the solid state was investigated at room temperature. When excited at 395 nm, compound **1** displays intense red luminescence and exhibits the characteristic emission bands for f–f transitions of Eu(III) ion in the visible region (Fig. 5). The strong intense emission at 616 nm is assigned to the $^5D_0 \rightarrow {}^7F_2$ transition, and the medium strong intense emission at 593 nm is attributed to the $^5D_0 \rightarrow {}^7F_1$ transition. While the three weak peaks at 580 nm, 653 nm and 703 nm may be ascribed to the $^5D_0 \rightarrow {}^7F_0$, $^5D_0 \rightarrow {}^7F_3$ and $^5D_0 \rightarrow {}^7F_4$ transition, respectively. The intensity of the $^5D_0 \rightarrow {}^7F_2$ transition is much stronger than that of the $^5D_0 \rightarrow {}^7F_1$ transition with an intensity ratio $I(^5D_0 \rightarrow {}^7F_2)/I(^5D_0 \rightarrow {}^7F_1)$ of ca. 2.3, suggesting that Eu(III) ion adopts a noncentrosymmetric coordination environment without a center of inversion [14], which is in agreement with the result of the single-crystal X-ray analysis.

In summary, we have successfully constructed two new lanthanide metal–organic frameworks by reaction of H_2nica and oxalate ligands with lanthanide ions under hydrothermal conditions. Both compounds **1** and **2** are 2D layer networks constructed from the linkage of 1D Ln–ox chains with μ_2-$Hnica^-$ bridging ligands, which are further connected by strong π–π stacking interactions to form 3D microporous supramolecular frameworks. The water guest molecules in the 1D