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Syntheses, structures and luminescence properties of two series of 3D lanthanide coordination polymers based on benzimidazole-5,6-dicarboxylic acid and oxalate

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ABSTRACT

Two serious three-dimensional (3D) lanthanide organic frameworks, $\{[Ln(Hbidc)(ox)_{1/2}(H_2O)]\cdot H_2O\}_n$ [Ln = Pr (**1**), Nb (**2**) and Sm (**3**)] (H_3bidc = Benzimidazole-5,6-dicarboxylic acid, H_2ox = oxalic acid) and $[Ln(Hbidc)(ox)_{1/2}]_n$ [Ln = Eu (**4**) and Gd (**5**)], have been synthesized solvothermally under different temperature conditions. Their structures have been characterized by single-crystal X-ray diffraction, elemental analysis, IR spectra and thermogravimetric analysis. Structure analyses reveal that the five compounds exhibit similar 3D network structures that ox^{2-} and $Hbidc^{2-}$ ligands showing the same coordination mode to link metal centers. The difference between the two kinds of compounds is that the coordination and lattice water molecules are absent in **4**–**5** due to the higher reaction temperature. Additionally, the luminescence properties of compounds **3** and **4** have been investigated in detail.

In recent years, the design and synthesis of new inorganic–organic hybrid materials have provoked significant interests owing to their variety of intriguing structures and fascinating properties [1]. Lanthanide ions, with their high and variable coordination numbers and flexible coordination environments, may possess great behaviors, such as luminescence [2], magnetism [3], catalysis [4], etc., that substantially differs from that of the d-transition metal ions due to the location of the lanthanide f-orbits. Quite a few lanthanide-organic frameworks (LOFs) have been rational designed and constructed. On the other hand, it is more difficult and is still a great challenge to control and generate lanthanide coordination polymers with predicted geometries just because of the higher coordination numbers and more flexible coordination geometries. In addition to the chances of the generation between the ligands and lanthanide, reacting conditions such as solvent system, the molar ratio of the reagents, pH value of the solution, reacting time and temperature [5] can affect the final structures. Apparently, the key to design LOFs with outstanding features mainly depends on the judicious choice of the bridging ligand because it greatly influences on the molecular packing arrangement of the compound. The aromatic N- and O-containing heterocyclic ligands, such as pyridinecarboxylate [6], pyrazinecarboxylate [7] and imidazolecarboxylate [8], etc., are often regarded as an effective strategy for the construction of metal-organic hybrid frameworks (MOFs) with interesting topologies and functional properties. Benzimidazole-5,6-dicarboxylic acid (H_3bidc) has been proven to be a good candidate ligand for constructing new multi-dimensional polymers [9,10]. As a multidentate rigid ligand, H_3bidc has one imidazole ring and one aromatic ring with two carboxylate groups. Therefore H_3bidc can display multiple coordination modes with metal centers and $\pi\cdots\pi$ stacking interaction can be an important non-covalent one in the compounds containing H_3bidc ligands. Up to now, cases of coordination polymers linked by H_3bidc have been presented, containing robust MOFs with transition metal ions (Cu^{2+}, Co^{2+}, Ni^{2+}, Mn^{2+}, Cd^{2+}, etc.) and lanthanide ions (La^{3+}, Pr^{3+}, Sm^{3+}, Gd^{3+}, Eu^{3+}, Tb^{3+}, Dy^{3+}, Er^{3+}, etc.) [9,10], but none of them were constructed simultaneously by H_3bidc and organic carboxylic acid. Oxalate was found to be an efficient assistant ligand because of its versatile coordination modes, as well as the high and variable coordination numbers [11]. In our recent research, using H_3bidc and oxalate, we synthesized successfully five Ln(III) coordination compounds $\{[Ln(Hbidc)(ox)_{1/2}(H_2O)]\cdot H_2O\}_n$ [Ln = Pr (**1**), Nd (**2**) and Sm (**3**)] and $[Ln(Hbidc)(ox)_{1/2}]_n$ [(Ln = Eu (**4**) and Gd (**5**)] through solvothermal synthetic method under different temperatures [12]. Comparing with compounds **1**–**3**, the coordination and lattice water molecules are absent in **4**–**5** because of the higher reaction temperature. This is the first example of lanthanide coordination polymers based on H_3bidc and oxalate.

In the process of solvothermal synthesis, several factors can influence the formation of the crystal phases, such as initial reactants, molar ratio, pH value, reaction temperature and time, and so on. In this work, five new lanthanide(III) coordination polymers with two kinds of 3D framework structures have been synthesized under solvothermal conditions by employing benzimidazole-5,6-dicarboxylic

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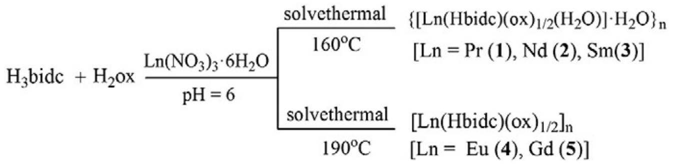

Scheme 1. The reactions of compounds **1–5**.

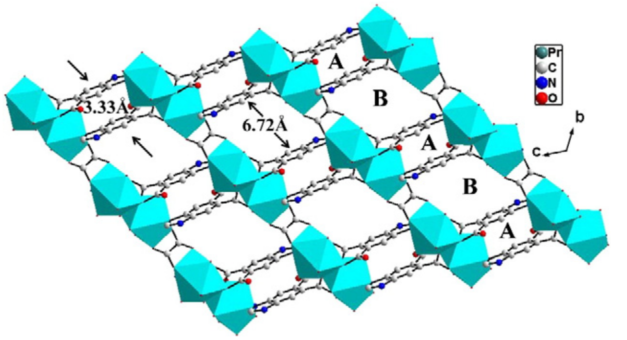

Fig. 2. Perspective views showing the interplanar separation distances of neighboring between the two neighboring aromatic rings of the parallel $Hbidc^{2-}$ ligands in channels A and B in **1** viewed along *a*-axis.

acid (H_3bidc) and oxalate. With the reaction temperature adjusted to 160 °C, we obtained **1**–**3** containing one coordinated water and one lattice water. But when the temperature was increased to 190 °C, **4**–**5** were generated with water absent (Scheme 1). Lower temperature is propitious for water to take part in the reaction. We tried to use $Pr(NO_3)_3·6H_2O$, $Nd(NO_3)_3·6H_2O$ and $Sm(NO_3)_3·6H_2O$ in the syntheses process with the temperature of 190 °C, and $Eu(NO_3)_3·6H_2O$ and $Gd(NO_3)_3·6H_2O$ with 160 °C, but no suitable crystals for single-crystal X-ray diffraction were obtained.

Single crystal X-ray diffraction analyses [13] reveal that compounds **1**–**3** and **4–5** are two series of 3D metal-organic frameworks and crystallized in the triclinic space group $P\bar{1}$. Herein, only the structures of compound **1** and **4** are described in detail as examples. The asymmetrical unit of **1** (Fig. 1a) consists of one Pr(III) cation, one $Hbidc^{2-}$ ligand, one half ox^{2-} ligand, one coordinated and one crystallized water molecules. As shown in Fig. 1b, the central Pr1 is nine-coordinated in distorted tricapped trigonal prism environment. The Pr–O distances range from 2.393(4) Å to 2.647(4) Å and Pr–N distance of 2.600(5) Å, all of which are comparable to those reported for other Ln-O and Ln-N compounds [14]. Two adjacent Pr ions are bridged by O2 and O2#2 (symmetric codes: #2 = −x, 1-y, 1-z) from neighboring $Hbidc^{2-}$ ligands to form a dinuclear secondary building unit (SBU) $[Pr_2O_{12}N_2(H_2O)_2]$. The SBUs are linked into 3D network with two kinds of channels can be observed along *a*-axis in a regular ABAB fashion (Fig. 2). $Hbidc^{2-}$ ligand adopts μ_4-hexadentate bridge coordination mode with C9 carboxyl group exhibiting μ_2-η^1:η^1 chelating coordination mode, C8 carboxyl showing μ_2-η^2:η^1 bridging fashion and N1 adopting monodentate mode (Scheme S1) to link the SBUs into 2D double-layer structures containing channels A [15]. $\pi\cdots\pi$ stacking interactions exist between the two neighboring aromatic rings of the parallel $Hbidc^{2-}$ ligands with the centroid–centroid and the interplanar separation distances of 3.51 Å and 3.33 Å in channels A, respectively. Furthermore, ox^{2-} ligands showing μ_2-quadridentate bridging coordination mode link the neighboring 2D double-layers into a 3D framework, in which ox^{2-} ligands and $Hbidc^{2-}$ ligands are linked by SBUs to form channels B. In channels B, the centroid–centroid and the interplanar separation distances between the two neighboring aromatic rings of the parallel $Hbidc^{2-}$ ligands are 7.69 Å and 6.72 Å, respectively. The coordinated and the lattice water molecules fill in channels B. In compound **4**, the central Eu(III) ion is coordinated to a slightly distorted bicapped trigonal prism environment by five carboxylic oxygen atoms and one imidazole nitrogen from four $Hbidc^{2-}$ ligands and two oxygen atoms from one oxalate, respectively (Fig. 3). The coordination numbers are reduced from nine in compounds **1**–**3** to eight in compounds **4**–**5** as a result of the absent of the coordinated water. Similar to compounds **1**–**3**, there are existing channels A and channels B arranging in ABAB fashion viewed along *b* axis in **4** (Fig. 4). $\pi\cdots\pi$ stacking interactions can be observed between the neighboring aromatic rings of the two parallel $Hbidc^{2-}$ ligands with centroid–centroid and interplanar separation distances of 3.65 Å and 3.48 Å in channels A and distances of 3.97 Å and 3.58 Å in channels B. Owing to the absence of all water molecules in **4**, the separation distances between $Hbidc^{2-}$ ligands are longer in A and shorter in B than those of **1**, respectively. It is found that there are hydrogen bonding interactions between the lattice water and the skeleton (Table S3).

Thermogravimetric analyses (TGA) of compounds **1**–**5** were investigated on a Netzsch Sta449C thermoanalyzer under a N_2 atmosphere with a ramp rate of 10 °C/min. The isomorphous frameworks lead to the similar thermal decomposition processes, so we took compounds **3** and **4** as representative examples for TGA to study the thermal stability of the two type compounds (Fig. S1). For compound **3**, that the weight loss of 8.90% (cal. 8.47%) from room temperature to 110 °C is attributed to the release of crystallographic water and coordinated water. The skeleton of compound **3** begins to decompose at 520 °C. Compared with the TGA of compound **3**, compound **4** stands stabilized until 464 °C and the framework begins to decompose. The TGA behavior indicates that no water molecule presents in compound **4**, which is in good agreement with the single-crystal structure.

The luminescent properties of compounds **3**, **4** and H_3bidc ligand in the solid state at room temperature are investigated on an Edinberg EI920 fluorescence spectrophotometer (Fig. 5 and Fig. S2). Under excitation at 391 nm, compound **3** exhibits a luminescence with five groups of signals (Fig. 5a). An intense emission of the free H_3bidc ligand was observed with wavelength of 416 nm (λ_{ex} = 345 nm), which could be attributed to π^*–π transitions. Under excitation at 391 nm, compound **3** displays emission bands at

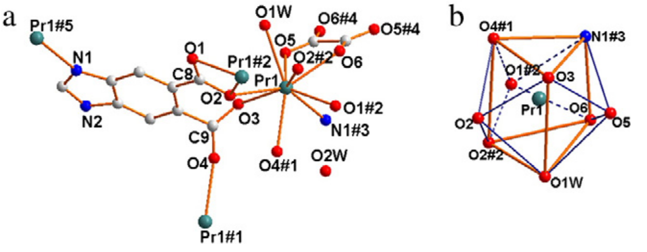

Fig. 1. (a) Coordination environment of Pr1 in **1**. All the H atoms are omitted for clarity. Symmetry codes: #1, 1−x, 1−y, 1−z; #2, −x, 1−y, 1−z; #3, x, y, −1+z; #4, −x, −y, −z; #5, x, y, 1+z. (b) The distorted tricapped trigonal prism environment of Pr1 in **1**.

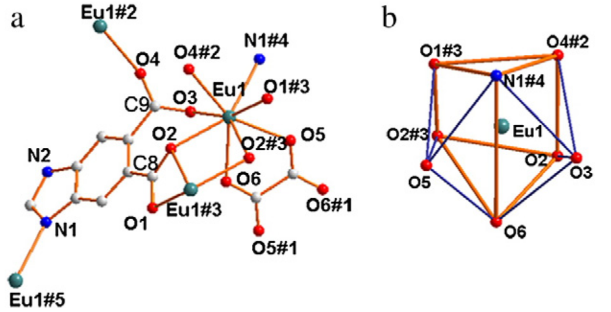

Fig. 3. (a) Coordination mode of Eu in compound **4**. All the H atoms are omitted for clarity (Symmetry codes: #1, −x, −y+2, −z+2; #2, −x+1, −y+1, −z+2; #3, −x+1, −y+2, −z+2; #4, x, y, z+1; #5, x, y, z−1). (b) The distorted bicapped trigonal prism environments of Eu1 in **4**.