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Effect of ligand isomerism on the formation of magnesium-based coordination networks

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ABSTRACT

Three magnesium-based coordination polymers, formulated as $Mg(3,4\text{-pyb})_2$ (**1**), $Mg(4,3\text{-pyb})_2$ (**2**), and $Mg_{2.5}(4,4\text{-pyb})_2(HCOO)_2(OH)$ (**3**), have been synthesized under solvothermal conditions, where 3,4-pyb = 3-(pyridin-4-yl)benzoate, 4,3-pyb = 4-(pyridin-3-yl)benzoate, and 4,4-pyb = 4-(pyridin-4-yl)benzoate. Compounds **1** and **2** have (3,6)-connected frameworks with an anatase topology. Compound **3** has a (3,8)-connected framework with an unusual tfz-d topology by regarding $Mg_5(HCOO)_4(OH)_2$ clusters as 8-connected nodes and bridging 4,4-pyb ligands as 3-connected nodes.

Functional coordination polymers have been extensively studied due to their rich framework structures, appealing physical properties and potential applications in gas storage, separation, catalysis and sensing [1–3]. Lightweight main group elements such as magnesium are of particular interest as the nodes in the synthesis of new coordination polymers for their gravimetric advantage [4–8]. The ionic radius of Mg^{2+} (72 pm) is comparable to those of Cu^{2+} (73 pm) and Zn^{2+} (74 pm), indicating that magnesium-based coordination polymers may possess similar structures to those porous coordination polymers such as HKUST-1 or MOF-5 [9–13]. It has been demonstrated that the substitution of zinc atoms in MOF-74 structure by magnesium atoms will result in a roughly 80% increase in its surface area [14]. Furthermore, magnesium-based coordination polymers exhibit strong binding affinities for hydrogen molecules and high CO_2 uptake capacity, suggesting their great potential in energy storage and gas uptake [15].

One of the most successful approaches to preparing new coordination polymers is the use of different organic ligands as the linkers [16,17]. A minor structural change of organic ligand may affect their framework structures [18–20]. For example, nicotinate (nt) and isonicotinate (int) ligands possess the same shape but different coordination geometries with metal centers. The self-assembly between magnesium ions with the two ligands produces different (3,6)-connected frameworks, $Mg(nt)_2$ and $Mg(int)_2\cdot H_2O$, with anatase and rutile topologies, respectively [21]. Inspired by the great success in the reticular synthesis of porous coordination polymers, we expect that the expansion of the organic linkers (i.e., nt and int) under similar synthetic conditions may produce new open-framework structures with large pore apertures.

In this work, three isomeric ligands (i.e., 3,4-pyb, 4,3-pyb, 4,4-pyb) are selected as the linkers since they are the extended analogues of nt and int ligands, where 3,4-pyb = 3-(pyridin-4-yl)benzoate, 4,3-pyb = 4-(pyridin-3-yl)benzoate, and 4,4-pyb = 4-(pyridin-4-yl)benzoate. The reactions of these organic ligands with $Mg(NO_3)_2\cdot 6H_2O$ under solvothermal conditions gave rise to three magnesium-based coordination polymers, formulated as $Mg(3,4\text{-pyb})_2$ (**1**), $Mg(4,3\text{-pyb})_2$ (**2**), and $Mg_{2.5}(4,4\text{-pyb})_2(HCOO)_2(OH)$ (**3**). Structural analyses reveal that compounds **1**–**2** have (3,6)-connected structures with an anatase topology, while compound **3** has a (3,8)-connected structure with a tfz-d topology [22,23].

Colorless crystals of compound **1** were obtained by heating a mixture of $Mg(NO_3)_2\cdot 6H_2O$ (0.022 g), 3,4-Hpyb (0.075 g), and N,N-dimethylformamide (dmf, 0.75 ml) at 180 °C for 7 days (44.4% yield based on magnesium). The experimental X-ray diffraction pattern of as-synthesized compound is in agreement with the simulated one on the basis of single crystal data, confirming the phase purity of as-synthesized compound. The compound crystallizes in the monoclinic space group *C*2/*c* (no. 15). The asymmetric unit comprises one magnesium atom, and one 3,4-pyb ligand. The Mg(1) atom is octahedrally coordinated by four oxygen atoms and two nitrogen atoms from 3,4-pyb ligands, with the Mg–O(N) bond lengths in the region 2.022(2)–2.268(2) Å. Each magnesium connects six 3,4-pyb ligands, and each 3,4-pyb ligand connects three magnesium atoms. Such linkages create a three-dimensional open-framework structure (Fig. 1a). Topological analysis reveals that the framework has an anatase topology by

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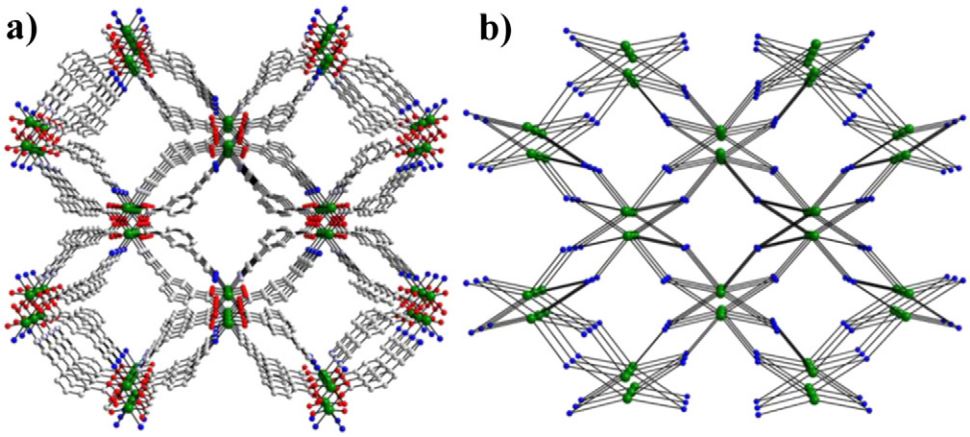

Fig. 1. (a) Perspective view of the structure of **1** along the [001] direction. (b) A view of the anatase-type network of **1** by regarding magnesium atoms as 6-connected nodes and organic ligands as 3-connected nodes.

regarding magnesium atoms as 6-connected nodes and 3,4-pyb ligands as 3-connected nodes (Fig. 1b). Viewed along the [001] direction, the structure of **1** displays large square-shape channels. The pore size of the cross sections of the channel is about 8.4 Å, calculated from the distance between two hydrogen atoms. A void space analysis using the program *PLATON* indicates that the void space occupies 18.4% of the unit cell volume [24].

Colorless crystals of compound **2** were obtained by heating a mixture of $Mg(NO_3)_2 \cdot 6H_2O$ (0.033 g), 4,3-Hpyb (0.099 g), and dmf (0.50 ml) at 190 °C for 4 days (70.1% yield based on magnesium). Powder X-ray diffraction proves the phase purity of as-synthesized compound. The compound crystallizes in the monoclinic space group *C*2/*c* (no. 15). There are one magnesium atom and one 4,3-pyb ligand in the asymmetric unit. The Mg(1) atom is surrounded by four oxygen atoms and two nitrogen atoms from 4,3-pyb ligands, forming a distorted octahedral coordination geometry. The Mg – O(N) bond lengths are between 1.996(1) Å and 2.316(2) Å. The linkages between magnesium atoms and 4,3-pyb ligands give rise to a three-dimensional structure with an anatase topology (Fig. 2a, b). The magnesium atoms act as the 6-connected nodes, and 4,3-pyb ligands act as the 3-connected nodes. Different from compound **1** containing large pore aperture, compound 2 is a dense phase without a solvent accessible space.

Colorless crystals of compound **3** were obtained by heating a mixture of $Mg(NO_3)_2 \cdot 6H_2O$ (0.192 g), 4,4-Hpyb (0.187 g), and dmf (1.0 ml) at 180 °C for 4 days (15.3% yield based on magnesium). The phase purity of as-synthesized compound was confirmed by powder X-ray diffraction. The compound crystallizes in the triclinic space group *P*-1 (no. 2). The asymmetric unit consists of three crystallographically independent magnesium atoms, two 4,4-pyb ligands, two formate ligands, and one hydroxyl group. Because no formic acid was used as the starting material, the formate ligands should be generated in situ by the hydrolysis of dmf molecules under solvothermal conditions. The Mg(2) atom locates on an inversion center, which is octahedrally coordinated by six oxygen atoms. The Mg(1) atom has a trigonal bipyramidal coordination geometry, bonded by five oxygen atoms. The Mg(3) atom is coordinated by five oxygen atoms and one nitrogen atom, forming a distorted octahedral coordination geometry. The Mg – O(N) bond lengths are between 1.970(2) Å and 2.345(2) Å.

The framework structure of **3** consists of $Mg_5(OH)_2(HCOO)_4$ cluster as the secondary building unit (SBU), as shown in Fig. 3a. These clusters share common formate oxygen atoms to form chain-like structures (Fig. 3b), which are further connected by 4,4-pyb ligands to give rise to a three-dimensional structure (Fig. 3c). There are two types of 4,4-pyb ligands in the structure. Type one ligands connect three $Mg_5(OH)_2(HCO_2)_4$ clusters, and type two ligands act as terminal species to the $Mg_5(OH)_2(HCO_2)_4$ clusters.

By regarding $Mg_5(OH)_2(HCO_2)_4$ clusters as the 8-connected nodes and bridging 4,4-pyb ligands as 3-connected nodes, the framework structure of **3** can be simplified as a tfz-d topology (Fig. 3d). The point symbol for the net is $(4^3)^2(4^6 \cdot 6^{18} \cdot 8^4)$. The (3,8)-connected topology is exceedingly rare in coordination polymer chemistry, which can be understood as the packing of kgd-type layers along the [010] direction in an AAAA sequence [25]. It should be noted that compound **3** was obtained unexpectedly because the solvothermal reaction was designed to prepare an open-framework rutile-type network analogous to a known magnesium isonicotinate, $Mg(int)_2 \cdot H_2O$. The in-situ generated formate ligand provides an additional factor to affect the framework structure of the final product.

Thermogravimetric analysis was carried out to evaluate the thermal stabilities of the three compounds. For compound **1**, the weight loss of 12.9% below 150 °C is attributed to the departure of solvent molecules in its square-shape channels. There is a plateau region in the temperature

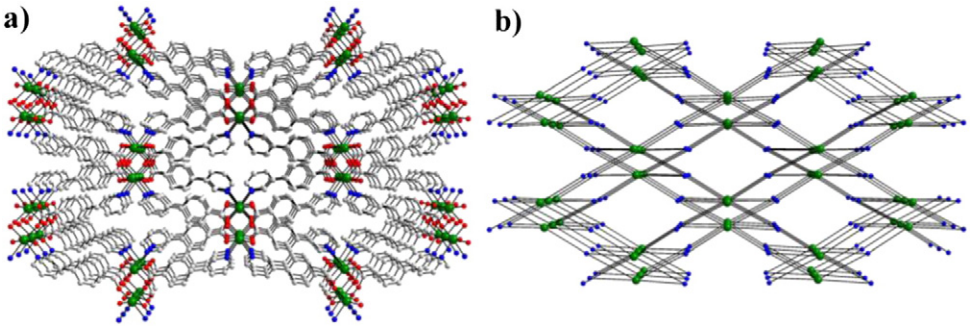

Fig. 2. (a) Perspective view of the structure of **2** along the [001] direction. (b) A view of the anatase-type network of **2** by regarding magnesium atoms as 6-connected nodes and organic ligands as 3-connected nodes.