

Novel 3D Ln^{III}–Cu^I Supramolecular Architecture Based on 2D MOFs with (6,3) Topology

Feng-Qin Wang,^{†,‡} Xiang-Jun Zheng,^{*,†} Yong-Hong Wan,[†] Chang-Yan Sun,[†] Zhe-Ming Wang,[§] Ke-Zhi Wang,[†] and Lin-Pei Jin^{*,†}

Department of Chemistry, Beijing Normal University, Beijing 100875, People's Republic of China, Department of Chemistry, Qufu Normal University, Shandong 273165, People's Republic of China, and State Key Laboratory of Rare Earth Materials Chemistry and Applications, College of Chemistry and Molecular Engineering, Peking University, Beijing 100871, People's Republic of China

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Three novel coordination polymers, [LnCu(PZDC)₃]·[Ln(H₂O)₉]_{0.5}·[(H₂O)₇H⁺]_{0.5} [Ln = La (1), Eu (2), Gd (3)], were synthesized. They are the first 3d–4f heterometallic framework with supramolecular 1D channels, in which lanthanide hydrate cations and lattice water molecules are located.

The design and construction of metal–organic frameworks (MOFs), especially porous coordination polymers, is still attractive because of their structural and topological diversity as well as their potential application as functional materials,¹ while crystal engineering provides a powerful tool for the realization of this target. On the basis of the crystal engineering principle and the coordination geometry of metal ions, reasonable selection of organic ligands can afford assembly of coordination polymers with a variety of topologies. However, much attention has been paid to coordination polymers containing 3d block metals,² while the 3d–4f heterometallic compounds have received less attention.^{3–5} The preparation of 3d–4f metal-based MOF has certain difficulties because of the introduction of 4f metals. On the one hand, a 4f metal ion has a high coordination number (commonly 8 and 9), which frequently leads to interpenetration and consequently results in the decrease of the pore size or even nonporous MOFs.⁶ On the other hand, the competition between 3d and 4f metals in coordinating to the same ligand often gives rise to homometallic coordination polymers rather than heterometallic ones. Therefore, the selection

of the ligand is a key point in the preparation of 3d–4f heterometallic MOFs. A typical strategy is self-assembly from mixed-metal ions and ligands containing hybrid donor atoms such as pyridinecarboxylate ligands.⁴ Pyridine-2,6-dicarboxylic acid (H₂PDCA) has been widely used to construct 3d, 4f, or 3d–4f MOFs.⁵ Generally, when coordinating to 4f metal ions, PDCA adopts a tridentate (ONO) mode: the N atom coordinates with two O atoms from two

* To whom correspondence should be addressed. E-mail: xjzheng@bnu.edu.cn (X.-J.Z.), lpjin@bnu.edu.cn (L.-P.J.). Tel: (+86) 010-58805522. Fax: (+86) 010-58802075.

[†] Beijing Normal University.

[‡] Qufu Normal University.

[§] Peking University.

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adjacent carboxylate groups (each carboxylate group provides one O atom), which requires coplanarity of the whole PDCA ligand, while the other O atoms of the carboxylate groups coordinate to 3d metal ions. If another N atom is introduced to the 4 position of PDCA, the new ligand will possess more coordination sites. Moreover, a N atom has affinity to transition-metal ions. Owing to the structural character, the N atom at the 4 position can only adopt a monodentate mode to coordinate to transition-metal ions. Thus, the new ligand can behave as a proper bridge between 3d and 4f metal ions. As is known, a Cu^{II} ion is apt to be reduced to a Cu^{I} ion in the presence of N-containing ligands under hydrothermal conditions,⁷ and a Cu^{I} ion with a d^{10} configuration tends to form a trigonal-planar or tetrahedral coordination geometry with a low coordination number (3 or 4). So, we synthesized pyrazine-2,6-dicarboxylic acid (H_2PZDC),⁸ which reacts with Ln_2O_3 and CuO to form three coordination polymers, $[\text{LnCu}(\text{PZDC})_3] \cdot [\text{Ln}(\text{H}_2\text{O})_9]_{0.5} \cdot [(\text{H}_2\text{O})_7\text{H}^+]_{0.5}$ [$\text{Ln} = \text{La}$ (**1**), Eu (**2**), Gd (**3**)],⁹ which possess the 3d–4f heterometallic framework with supramolecular 1D channels, in which lanthanide hydrate cations and lattice water molecules are located.

The structures of compounds **1**–**3** were determined by X-ray single-crystal diffraction.¹⁰ The three compounds are isostructural except the small difference in the cavity, 25.0% for **1**, 25.5% for **2**, and 25.6% for **3** per cell unit volume, respectively. So, only the structure of compound **3** will be discussed in detail. The framework is constructed with Gd^{III} or Cu^{I} ions and a pyrazine-2,6-dicarboxylate ligand. The Gd^{III} ion (Gd1) in the framework is nine-coordinate in a tricapped

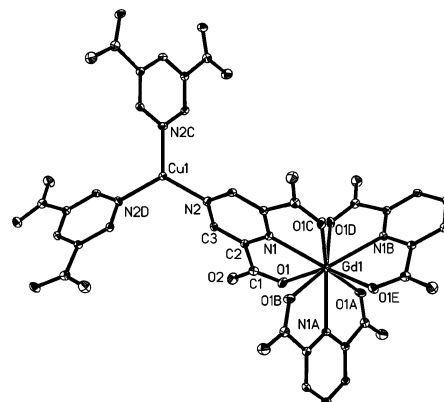


Figure 1. Coordination environment of the Cu^{I} and Gd^{III} ions in the framework in the asymmetric unit of coordination polymer **3**. Thermal ellipsoids are shown at 30% probability. Selected bond lengths [Å]: $\text{Gd1}-\text{O1}$ 2.433(3), $\text{Gd1}-\text{N1}$ 2.532(5), $\text{Cu1}-\text{N2}$ 1.993(5).

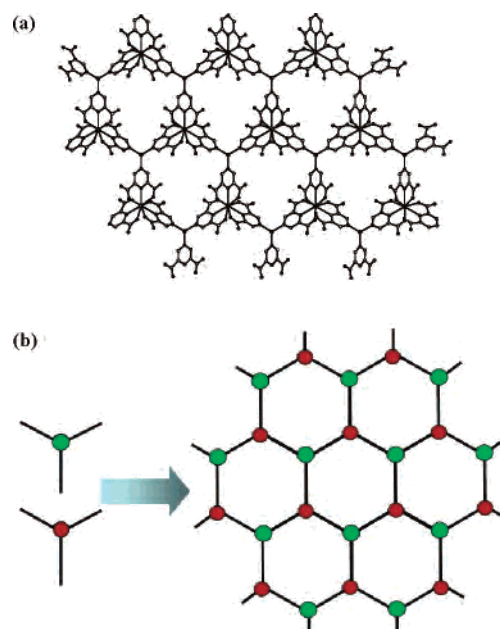


Figure 2. (a) Single 2D (6,3) net showing the alternating nodes and the triangle-like cavities. (b) Architectural strategy of (6,3) topology.

trigonal-prism environment with three N atoms and six O atoms from three pyrazine-2,6-dicarboxylate anions (Figure 1). The N atoms are in the cap positions, and the O atoms are in the vertices of the prism. The two carboxylates and the pyrazine ring of every PZDC ligand are coplanar. PZDC adopts only one coordination mode in the title complexes. One pyrazine N atom together with two adjacent carboxylate O atoms coordinate with a Gd^{III} ion in a tridentate (ONO) mode, while the other pyrazine N atom coordinates with a Cu^{I} ion in a monodentate mode. A Cu^{I} ion has trigonal-planar geometry, being surrounded by three pyrazine N atoms from three PZDC ligands. In the framework, around every metal ion, there are three metal–nitrogen (M–N) bonds, and the angles between them are all 120° . Thus, the PZDC ligand acts as a tetradentate bridge to connect the Gd^{III} and Cu^{I} ions into a 2D coordination layer of a (6,3) net (Figure 2). Figure 2b clearly shows the assembly of (6,3) topology in **3**. Within the (6,3) topological layer, the nodes are provided by monovalent Cu ions and trivalent Gd ions alternately

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- (9) Synthesis of **1**–**3**: A mixture of H_2PZDC (0.1 mmol, 0.0204 g), Ln_2O_3 (0.025 mmol; $\text{Ln} = \text{La}$, 0.0082 g; Eu , 0.0088 g; Gd , 0.0091 g), CuO (0.05 mmol, 0.004 g), water (5 mL), and isopropyl alcohol (2 mL for **1** and 3 mL for **2** and **3**) was sealed in a 25-mL stainless steel reactor with a Teflon liner and heated at 180°C for 96 h. Light-brown crystals of **1** (0.013 g, 42.6%), **2** (0.018 g, 57.8%), and **3** (0.014 g, 44.6%) were obtained. The mole ratio of Ln/Cu is 1.55, 1.47, and 1.48 for **1**–**3**, respectively. Elem. anal. Calcd for $\text{C}_{18}\text{H}_{22.50}\text{CuLa}_{1.50}\text{N}_6\text{O}_{20}$: C, 23.63; H, 2.48; N, 9.19. Found: C, 23.84; H, 2.39; N, 9.16. IR (KBr): 3433 s, 1627 s, 1580 m, 1386 s, 1356 m, 1215 m, 1043 m, 936 m, 740 m, 587 m. Elem. anal. Calcd for $\text{C}_{18}\text{H}_{22.50}\text{CuEu}_{1.50}\text{N}_6\text{O}_{20}$: C, 23.14; H, 2.43; N, 8.99. Found: C, 23.35; H, 2.33; N, 9.07. IR (KBr): 3441 s, 1627 s, 1585 m, 1390 s, 1361 m, 1219 m, 1047 m, 939 m, 743 m, 593 m. Elem. anal. Calcd for $\text{C}_{18}\text{H}_{22.50}\text{CuGd}_{1.50}\text{N}_6\text{O}_{20}$: C, 22.94; H, 2.41; N, 8.92. Found: C, 23.03; H, 2.41; N, 8.94. IR (KBr): 3416 s, 1627 s, 1390 s, 1363 m, 1220 m, 1047 m, 937 m, 743 m.
- (10) Crystal data for **1**: $\text{C}_{18}\text{H}_{22.50}\text{CuLa}_{1.50}\text{N}_6\text{O}_{20}$, $M = 914.83$, trigonal, $P\bar{3}1c$, $a = b = 12.814(4)$ Å, $c = 9.338(4)$ Å, $\gamma = 120^\circ$, $V = 1327.9(8)$ Å³, $Z = 2$, $\rho_{\text{calcd}} = 2.289$ g cm^{-3} , $T = 294(2)$ K, 7257 measured reflections, $R_1 = 0.0462$ for 751 reflections [$I > 2\sigma(I)$], $wR_2 = 0.1087$ for 909 independent reflections (all data) and 95 parameters. Crystal data for **2**: $\text{C}_{18}\text{H}_{22.50}\text{CuEu}_{1.50}\text{N}_6\text{O}_{20}$, $M = 934.40$, trigonal, $P\bar{3}1c$, $a = b = 12.659(8)$ Å, $c = 9.492(6)$ Å, $\gamma = 120^\circ$, $V = 1317.3(14)$ Å³, $Z = 2$, $\rho_{\text{calcd}} = 2.356$ g cm^{-3} , $T = 294(2)$ K, 7144 measured reflections, $R_1 = 0.0284$ for 751 reflections [$I > 2\sigma(I)$], $wR_2 = 0.0841$ for 904 independent reflections (all data) and 91 parameters. Crystal data for **3**: $\text{C}_{18}\text{H}_{22.50}\text{CuGd}_{1.50}\text{N}_6\text{O}_{20}$, $M = 942.34$, trigonal, $P\bar{3}1c$, $a = b = 12.6203(11)$ Å, $c = 9.4547(17)$ Å, $\gamma = 120^\circ$, $V = 1304.1(3)$ Å³, $Z = 2$, $\rho_{\text{calcd}} = 2.400$ g cm^{-3} , $T = 294(2)$ K, 7141 measured reflections, $R_1 = 0.0303$ for 661 reflections [$I > 2\sigma(I)$], $wR_2 = 0.0755$ for 894 independent reflections (all data) and 90 parameters.

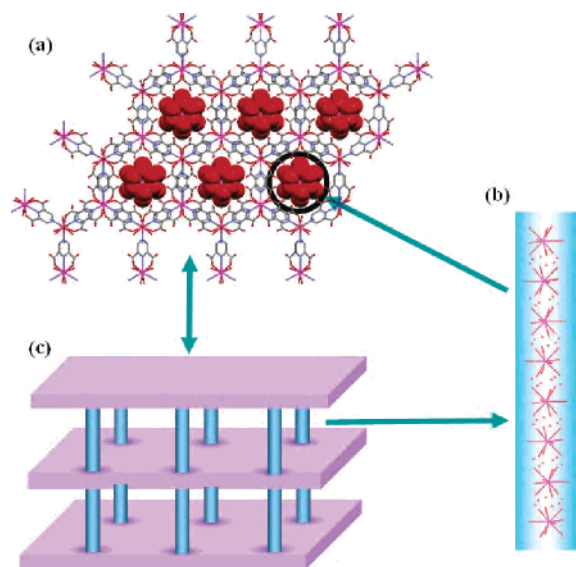


Figure 3. (a) 3D supramolecular network viewed along the *c* axis in polymer **3**. The H atoms are omitted for clarity, and [Gd(H₂O)₉]³⁺ and O atoms of free water molecules are shown as space-filling models. (b) Gd^{III} hydrate cations and lattice water molecules are alternatively arranged and connected by hydrogen bonds, forming a guest column. (c) Schematic diagram of 3D supramolecular architecture based on a 2D MOF and guest column.

forming a hexagonal motif with triangle-like cavities (Figure 2a), while connectors are PZDC.

The distance between adjacent Gd^{III} and Cu^I ions is 7.286 Å. There are two uncoordinated carboxylate O atoms in every edge of the hexagon, so the cavities are hydrophilic. In the cavities are located cationic guests [Gd(H₂O)₉]³⁺ or [(H₂O)₇H⁺] whose occupancy is 0.5, respectively. The coordination geometry of the Gd center in [Gd(H₂O)₉]³⁺ is also a tricapped trigonal prism. The water molecule in the vertex position of the prism is probably hydrogen bonded to the uncoordinated carboxylate O atoms of the framework from the same layer (2.643 Å for O⋯O) and from the adjacent layer (2.899 Å for O⋯O), while the water molecule in the cap position is simultaneously hydrogen bonded to the uncoordinated carboxylate O atoms from two adjacent layers (2.785 Å for O⋯O). For the cation [(H₂O)₇H]⁺, the O atoms are disordered and protonated water molecules are obtained by charge balancing.¹¹ The water molecules are connected via hydrogen bonding with uncoordinated carboxylate O atoms from the same layer and from the adjacent layer. Moreover, the adjacent layers are eclipsed, packed with Gd^{III} and Cu^I coincident along the *c* axis. The interlayer distance is 4.727 Å. Thus, the adjacent layers are connected via hydrogen bonding between the water molecules and the uncoordinated carboxylate O atoms from the framework to form a 3D supramolecular structure with 1D channels (Figure 3). To the best of our knowledge, the title coordination polymers are the first examples of Ln³⁺ cations encapsulated in 1D channels based on the 3d–4f heterometallic anionic framework, being different from the reported inclusion complex that possesses a 3d metal-based framework containing an encapsulated [Gd(dmf)₈]³⁺ cation¹² and that possesses a 4f metal-based framework

containing multiencapsulated Cu(bpy)²⁺ cations within a charged cage.⁴ They are also unusual host–guest compounds in the rarely reported Ln^{III}–Cu^I metal-based MOFs.

The presence of a Cu^I ion in the title complex was confirmed by its X-ray photoelectron spectrum (Figure S1 in the Supporting Information). The spin–orbit component (²P_{3/2} and ²P_{1/2}) of the Cu 2p peak at approximately 932.0 and 952.0 eV with a spin–orbit separation of 20.0 eV suggests the presence of Cu^I in the compound. This is in agreement with the results of the single-crystal X-ray analysis. The Cu^{II} ion with a d⁹ configuration tends to form a square-pyramidal or elongated-octahedral coordination geometry because of the strong Jahn–Teller effect, but in the title complex, the Cu ion is in a trigonal-planar geometry. The coordination geometry of Cu ions in combination with a X-ray photoelectron spectrum indicates that Cu is monovalent. The thermogravimetric analysis curves of complexes **1–3** (Figure S2 in the Supporting Information) show that complicated decomposition reactions take place simultaneously when lattice water molecules are lost above 58 °C for **1**, 60 °C for **2**, and 67 °C for **3**, indicating that the 3D supramolecular network as well as 2D Ln^{III}–Cu^I MOFs collapses, which shows that hydrogen bonds play an important role in the assembly of a 3D supramolecular network constructed from a 2D Ln^{III}–Cu^I MOF with (6,3) topology. The characteristic emission of a Eu^{III} ion in **2** located at 590, 614, 648, and 687 nm was observed when excited at 338 nm (Figure S3 in the Supporting Information), corresponding to ⁵D₀ → ⁷F_{*J*} (*J* = 1–4) transitions of a Eu^{III} ion, but they are weak. This may be attributed to the coordinated and free water molecules in **2**, which quench luminescence of a Eu^{III} ion.

In conclusion, on the basis of the coordination mode of PZDC and the coordination geometry of Cu^I and Ln^{III} ions, we have synthesized three novel lanthanide–transition metal coordination polymers, which are the first examples of Ln cations encapsulated in a 3d–4f heterometallic framework. Ln^{III} and Cu^I ions have the same architectural characteristics, though the former has nine coordinated atoms composed of a tridentate ONO mode in **1–3**, and thus they can provide a new method or an idea for those who are interested in the construction of coordination polymers with a microcavity, especially microporous materials. It can be predicted that the introduction of a linear second ligand into the present system or a proper combination of 3d and 4f metals with PZDC will result in 3D porous MOFs. Further research on the MOFs based on 4f and other 3d metals is in progress.

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Supporting Information Available: X-ray crystallographic files in CIF format for **1–3** and Figures S1–S3. This material is available free of charge via the Internet at <http://pubs.acs.org>.

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