



Two new metal–organic frameworks based on cyclic dodecanuclear copper units



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ABSTRACT

Two new metal–organic frameworks based on cyclic-type dodecanuclear copper units, $(\text{Me}_4\text{N})_6[\text{Cu}_{12}(\text{OMe})_6(\text{pz})_6(\text{BTC})_6] \cdot 18\text{H}_2\text{O}$ **1** and $(\text{Me}_4\text{N})_6[\text{Cu}_{12}(\text{OH})_6(\text{pz})_6(\text{BTC})_6] \cdot 21\text{H}_2\text{O}$ **2** (pz = pyrazolate, BTC = 1,3,5-benzenetricarboxylate), have been prepared by the solvothermal reactions of copper salts, Hpz and H_3BTC ligands. The cyclic-type Cu_{12} unit in **1** and **2** is constructed by twelve Cu^{II} ions linked together by $\mu_2\text{-OH}$ or $\mu_2\text{-OMe}$ and unidentate carboxylate groups at the inner- and $\mu\text{-pz}$ and bidentate carboxylate groups at the outer surface of the toroid. In **1** and **2**, each Cu_{12} unit is connected to 12 other units by BTC linkers, leading to 12-connected three-dimensional porous frameworks. The photocatalytic investigations indicate that compounds **1** and **2** exhibit photocatalytic activity for the degradation of RhB.

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Metal–organic frameworks (MOFs) have attracted a great deal of recent interest not only because of their extensive applications in gas storage, catalysis, separation, ion-exchange and drug delivery, but also their intriguing variety of architecture and topologies [1]. One of the main synthetic strategies for MOFs is based on the diversity of polynuclear metallic units known as secondary building units (SBUs) that can be linked with numerous organic linkers [2]. Diverse di-, tri-, tetra- and high-nuclear metal carboxylates have been employed as SBUs to construct MOFs so far [3]. Among diverse metal clusters, cyclic- and wheel-type clusters with nanoscale internal cavities have attracted much attention due to their potential applications in catalysis, magnetism, ion recognition and exchange [4]. However, MOFs based on cyclic- and wheel-type SBUs are very scarce [5]. As a continuation of the synthesis of various MOFs possessing unique structure and property, we are trying to construct new MOFs based on high nuclear cyclic-type clusters, which will open up the possibilities of the combination of porous property of MOFs with the function of cyclic-type clusters stemming from their internal cavities. More recently, we have successfully obtained a new 12-connected MOF $\text{H}_2\text{Na}_4[\text{Cu}_{12}(\text{OH})_6(\text{pz})_6(\text{BTC})_6] \cdot 23\text{H}_2\text{O}$ based on cyclic-type $[\text{Cu}_{12}(\text{OH})_6(\text{pz})_6(\text{COO})_{18}]$ units with large interval cavity (10.115 Å diameter), which shows high ion-exchange capacities with some alkali-metal and transition-metal cations [6]. To our knowledge, it is the first example of MOFs constructed by cyclic SBU with large interval cavity (> 1 nm). In its structure, the internal cavity of cyclic Cu_{12} unit is occupied by Na^+ ion. The existence of Na^+ ion partly blocks the cyclic open of the Cu_{12} unit, which limits the porous

availability of the framework for large size molecules. Hence, it will be of great interest to investigate whether or not the new MOF based on cyclic Cu_{12} unit without counter cations in the interval cavity can be synthesized. The Na^+ in the MOF structure originates from sodium hydroxide solution used for adjusting pH value of reaction solution during the course of synthesis. Thus, in order to get the MOF based on cyclic Cu_{12} unit without cations in the interval cavity, we planned to use organic amine with larger size as pH control reagent to replace NaOH. With the use of tetramethylammonium hydroxide as pH control reagent, we have successfully synthesized two new MOFs based on cyclic Cu_{12} unit without cations in the interval cavity, $(\text{Me}_4\text{N})_6[\text{Cu}_{12}(\text{OMe})_6(\text{pz})_6(\text{BTC})_6] \cdot 18\text{H}_2\text{O}$ **1** in H_2O –MeOH solvent and $(\text{Me}_4\text{N})_6[\text{Cu}_{12}(\text{OH})_6(\text{pz})_6(\text{BTC})_6] \cdot 21\text{H}_2\text{O}$ **2** in H_2O –EtOH solvent.

Single crystal X-ray diffraction analyses [7] reveal that both **1** and **2** show a 12-connected three-dimensional (3D) porous framework constructed from cyclic-type dodecanuclear copper units and BTC linkers. The cyclic-type Cu_{12} units in **1** and **2** possess similar structure with that in previously reported MOF $\text{H}_2\text{Na}_4[\text{Cu}_{12}(\text{OH})_6(\text{pz})_6(\text{BTC})_6] \cdot 23\text{H}_2\text{O}$. The Cu_{12} unit is constructed by twelve Cu^{II} ions in the square pyramidal geometry defined by one nitrogen atom from pyrazolate ligand, three carboxyl oxygen atoms from three different BTC ligands, and one hydroxyl group for **1** or one methoxyl group for **2**. Twelve Cu^{II} ions are linked together by $\mu_2\text{-OH}$ or $\mu_2\text{-OMe}$ and unidentate carboxylate groups at the inner- and $\mu\text{-pz}$ and bidentate carboxylate groups at the outer surface of the toroid (Fig. 1). The cyclic-type Cu_{12} units with the formula $[\text{Cu}_{12}(\text{OH})_6(\text{pz})_6(\text{COO})_{18}]^{6-}$ in **1** and with the formula $[\text{Cu}_{12}(\text{OMe})_6(\text{pz})_6(\text{COO})_{18}]^{6-}$ in **2** have central cavities of 10.115 and 7.593 Å diameters, respectively. Different from the central cavity of cyclic-type Cu_{12} unit was occupied by Na^+ ion in previously reported MOF $\text{H}_2\text{Na}_4[\text{Cu}_{12}(\text{OH})_6(\text{pz})_6(\text{BTC})_6] \cdot 23\text{H}_2\text{O}$, the

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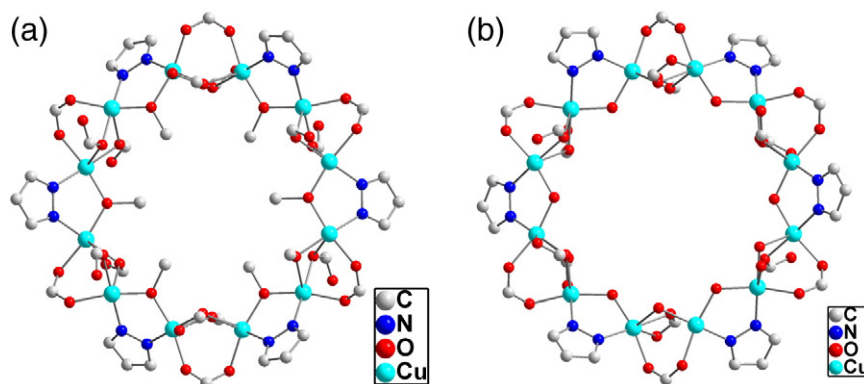


Fig. 1. The cyclic Cu₁₂ SBU of (a) **1** and (b) **2**. For clarity, H atoms are omitted.

central cavities of cyclic-type Cu₁₂ units in both **1** and **2** are filled with neutral water molecules.

In both **1** and **2**, each Cu₁₂ unit is surrounded by 12 BTC ligands with six in the plane of the Cu₁₂ ring as well as three above and three below the ring (Fig. S1). Meanwhile, each BTC ligand coordinates in a bridging fashion to two Cu₁₂ units with two carboxylate group connected to one Cu₁₂ unit and one carboxylate group connected to the other Cu₁₂ unit (Fig. S2). From a topological perspective, each Cu₁₂ unit corresponds to a 12-connected vertex and is linked to 12 crystallographically equivalent Cu₁₂ units into a porous framework. This network can be regarded as a face-centered cubic net (fcu) with Schläfli symbol (3²4³6⁵6) when Cu₁₂ units are considered as nodes and BTC ligands as linkers (Fig. 2). As an fcu net, **1** and **2** feature octahedral and tetrahedral holes with edge length 17.252 Å, which are occupied by Me₄N⁺ cations and solvent water molecules. The accessible void volumes of the octahedral and tetrahedral holes in **1** and **2** are 45.1 and 49.9% of the unit cell volumes estimated by PLATON/SOLV, respectively.

Until now, through changing pH control reagents and solvents used in the synthetic process, we have obtained three MOFs based on cyclic type Cu₁₂ units, which are compounds **1**, **2** and previously reported compound H₂Na₄[Cu₁₂(OH)₆(pz)₆(BTC)₆] \cdot 23H₂O. The Cu₁₂ units in the three MOFs are [Cu₁₂(OMe)₆(pz)₆(BTC)₆]⁶⁻, [Cu₁₂(OH)₆(pz)₆(BTC)₆]⁶⁻ and {Na₄[Cu₁₂(OMe)₆(pz)₆(BTC)₆]⁵⁻, respectively. Along with the changes of synthetic conditions, the structural changes of the Cu₁₂ units indicate that (1) the [Cu₁₂(OH)₆(pz)₆(BTC)₆]⁶⁻ unit with large interval cavity is not very stable, and the negative charge nature makes it tend to incorporate cations; (2) when no suitable cation can be incorporated, Cu₁₂ unit stabilizes its cyclic-type structure through combining methoxyl group to reduce its interval cavity;

(3) when no suitable cation and organic group can be incorporated or combined, [Cu₁₂(OH)₆(pz)₆(BTC)₆]⁶⁻ unit may be obtained.

The IR spectra of compounds **1** and **2** display the absorption bands of the asymmetric and symmetric vibrations of carboxyl group at 1621, 1567, 1442 and 1371 cm⁻¹, respectively (Fig. S3 and Fig. S4). The $\Delta\nu$ ($\nu_{as}(\text{COO})-\nu_s(\text{COO})$) is 179 and 196 cm⁻¹, which are consistent with the coordination mode of carboxyl groups in compounds **1** and **2**. The broad strong bands with maxima at 3444 cm⁻¹ for **1** and 3438 cm⁻¹ for **2** are assigned to the O–H stretching vibration of the solvent H₂O molecules.

The TG curve of **1** exhibits two weight loss stages occurring at 25–165 and 240–410 °C respectively (Fig. S5). The weight loss, 69.3% in total (calcd: 71.6%), is attributed to the loss of water, methanol molecules, tetramethylamine cations, BTC and pz ligands. The TG curve of **2** shows two weight losses occurring at 25–155 and 230–440 °C respectively (Fig. S6), corresponding to the release of water molecules, tetramethylamine cations, BTC and pz ligands. The whole weight loss of 69.5% agrees with the calculated value of 71.4%.

The experimental and simulated XRPD patterns of compounds **1** and **2** are shown in Fig. S7 and Fig. S8, respectively. Their peak positions are in good agreement with each other, indicating the phase purity of the products. The differences in intensity may be due to the preferred orientation of the powder samples.

It has been shown recently that MOFs are attractive candidates for studying photophysical behavior, especially the UV-assisted decomposition of organic dyes [8]. We selected Rhodamine B (RhB) as a model pollutant in aqueous media to evaluate the photocatalytic effectiveness of compounds **1** and **2**. In a typical process, 80 mg of compounds **1** and **2** was respectively dissolved in 100 mL RhB solutions (2×10^{-5} mol/L), then magnetically stirred in the dark for about

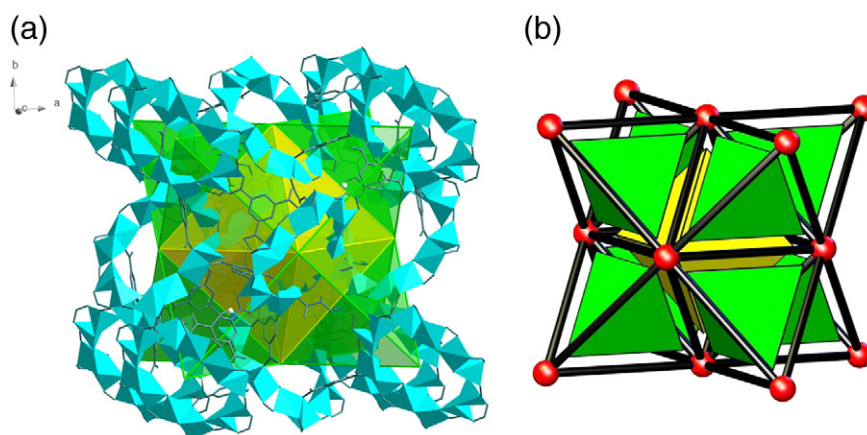


Fig. 2. (a) View of the 3D structure of **1**. The tetrahedral and octahedral holes in the framework are simulated by green tetrahedra and yellow octahedra, respectively; (b) View of the topology of **1**.

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