

A 12-connected metal–organic framework constructed from an unprecedented cyclic dodecanuclear copper cluster†

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A 12-connected metal–organic framework based on an unprecedented cyclic Cu₁₂ cluster with a large internal cavity has been prepared, and its cation exchange property was determined.

The search for new metal–organic frameworks (MOFs) remains at the forefront of synthetic materials science as their architectures continue to be of interest for many applications in areas such as catalysis, ion exchange, gas separation and storage, luminescence and magnetism.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 The current studies on MOFs have indicated that choosing a suitable SBU is very critical for the achievement of MOFs with required properties, not only because the structural properties of SBUs have significant influence on the topology and stability of MOFs, but also because the functional properties of SBUs can be imparted to the whole framework.³ Although a number of discrete metal carboxylates and metal azolates are potentially useful SBUs in the construction of MOFs,⁴ the reported MOFs are mainly based on surprisingly few bi-, tri-, and tetra-nuclear SBUs, such as Cu₂(OH)₂(CO₂)₄, Cr₃O(OH)₃(CO₂)₆ and Zn₄O(CO₂)₆ units.⁵ Among structural 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.⁶ However, MOFs based on cyclic- and wheel-type SBUs are very scarce.⁷ Currently, we are interested in the construction of MOFs based on a high nuclearity cyclic-type cluster with a large (>10 Å) internal cavity, which will open up the possibilities of the combination of porous property of MOFs with the function of the cyclic-type cluster stemming from its internal cavity. Recently, a pure

inorganic framework based on a high nuclearity cyclic-type P₈W₄₈O₁₈₄ cluster was prepared by the Cronin group, which shows interesting cation exchange property.⁸ This work reinforces our idea to construct MOFs with high nuclearity cyclic-type SBUs. Herein, we report a new MOF, H₂Na₄[Cu₁₂(OH)₆(pz)₆(BTC)₆]·23H₂O (pz = pyrazolate, BTC = 1,3,5-benzenetricarboxylate) **1**,⁹ based on a cyclic-type Cu₁₂ SBU with a 10.115 Å diameter interval cavity.

Solvothermal reaction of Cu(NO₃)₂ with Hpz and H₃BTC in H₂O–MeOH solvent at 150 °C for 72 h afforded blue octahedral-shaped crystals of **1**.† Single crystal X-ray diffraction analysis reveals that **1** crystallizes in the cubic *Pa* $\bar{3}$ space group and displays a 12-connected three-dimensional (3D) porous framework constructed from cyclic-type dodecanuclear copper units and BTC linkers. In **1**, each Cu^{II} ion adopts the square pyramidal geometry, which is coordinated by one nitrogen atom from a pyrazolate ligand, one hydroxyl group, and three carboxyl oxygen atoms from three different BTC ligands. Adjacent Cu^{II} ions are bridged in two distinct ways: One way is that the Cu··Cu vector is held by one bidentate bridging pz ligand and one μ_2 -OH group, the other is that the Cu··Cu vector is linked by two bridging unidentate and one bridging bidentate carboxylate groups derived from three different BTC ligands (Fig. S2, ESI†). The corresponding Cu··Cu distances are 3.310 and 3.218 Å respectively. Twelve Cu^{II} ions are held together by the two ways to form a puckered cyclic-type [Cu₁₂(OH)₆(pz)₆(COO)₁₈] unit with μ_2 -OH and unidentate carboxylate groups at the inner- and μ -pz and bidentate carboxylate groups at the outer surface of the toroid. The cyclic-type Cu₁₂ unit has a diameter of 17.688 Å, with a central cavity of 10.115 Å diameter (Fig. 1).

In **1**, each cyclic-type Cu₁₂ unit is connected to 12 other units by BTC linkers with six linkers in the plane of the Cu₁₂ ring as well as three above and three below the ring (Fig. S3 and S4, ESI†). Each BTC ligand is linked with two cyclic-type Cu₁₂ units with two carboxylate groups connected to one Cu₁₂ unit and one carboxylate group connected to the other Cu₁₂ unit (Fig. S5, ESI†). Thus, from a topological perspective, **1** features a 12-connected face-centered cubic net (fcu) with the Schläfli symbol (3²⁴4³⁶5⁶) when Cu₁₂ units are considered as 12-connected nodes and two-connected BTC ligands as linkers (Fig. 2). Both the presence of a cyclic-type Cu₁₂ SBU and the occurrence of a 12-connected net are notable. To our knowledge,

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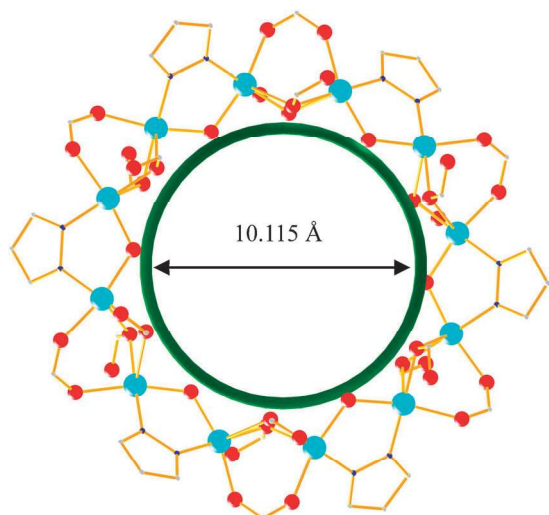


Fig. 1 The cyclic Cu_{12} SBU of **1**. For clarity, H atoms are omitted. Color code: Cu, light blue; O, red; C, gray; N, dark blue.

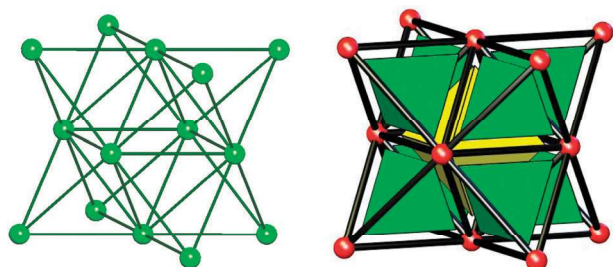


Fig. 2 Schematic representations of the fcu topology of **1**.

MOFs based on cyclic-type SBUs are very scarce. **1** represents the first example of MOFs constructed by cyclic-type SBU with a central cavity bigger than 1 nm diameter. Although high connectivity MOFs are significant due to their enhanced stability, 12-connected MOFs are uncommon,¹⁰ the formation of which is severely hampered by the limited coordination sites of the SBU and the steric nature of organic ligands. The high nuclearity and large surface area features of the cyclic-type Cu_{12} SBU in **1** make it suitable for the construction of high connectivity MOFs. As an fcu net, **1** inherently features octahedral and tetrahedral holes (Fig. 3). Different from other fcu nets, access to the octahedral and tetrahedral holes in **1** is possible not only through triangular windows but also through the central cavity of the cyclic-type Cu_{12} SBU.

The thermal stability of **1** has been investigated by thermogravimetric (TG) analysis (Fig. S7, ESI[†]) and variable-temperature powder X-ray diffraction (VTXRD) (Fig. S8, ESI[†]). The TG curve of **1** displays two weight losses. The first weight loss of 14.06% covering a temperature range from 46 to 175 °C corresponds to the release of guest water molecules (calcd: 13.72%). The second weight loss of 49.54% in the range of 220–505 °C could be assigned to the loss of BTC and pz molecules (calcd: 50.36%). The VTXRD patterns indicate that the framework of **1** is stable up to 250 °C.

To study the porous property, the Ar gas sorption isotherm of **1** was measured. Prior to measurement, the samples of **1** were heated at 50 °C for 15 h under vacuum to remove the solvent water molecules. The isotherm of **1** reveals a type-I

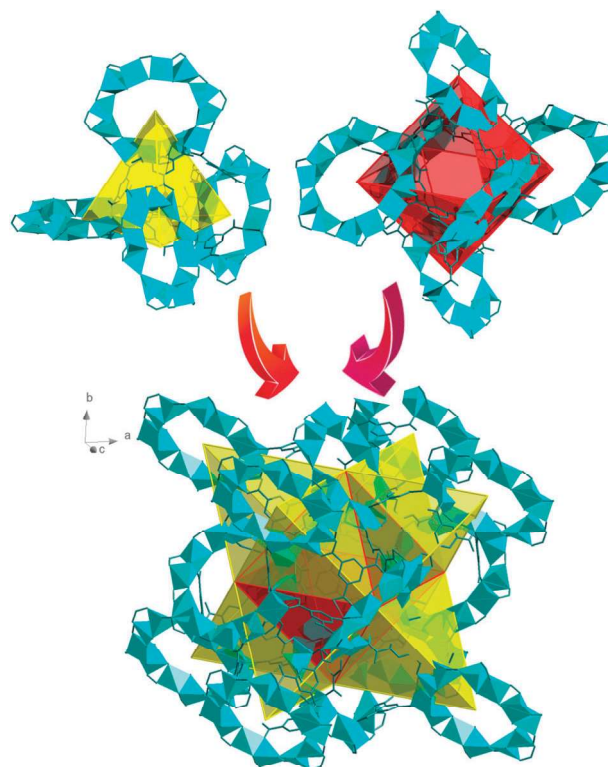


Fig. 3 Structure of **1**. Cyclic Cu_{12} SBU is connected to 12 other Cu_{12} SBUs by BTC linkers. Thus, tetrahedral (a) and octahedral (b) holes are formed. (c) View of the arrangement of the tetrahedral and octahedral holes in the framework. For clarity, the C atoms in pz ligands and all H atoms are omitted. ($\{\text{CuNO}_4\}$, blue square pyramid; the tetrahedral and octahedral holes are simulated by yellow tetrahedra and red octahedra, respectively.)

sorption behavior, which is characteristic of solids with micropores (Fig. S9, ESI[†]). The adsorption data were fitted to the BET equation to give a BET surface area of 813 $\text{m}^2 \text{g}^{-1}$. The pore volume was calculated from the sorption isotherm by using an NLDFT method¹¹ to be 0.30 $\text{cm}^3 \text{g}^{-1}$.

Recently, the ion-exchange studies have attracted extensive interest in the field of porous materials. Through ion-exchange investigation, the ion incorporated activity of porous material and interaction type and strength between framework and guest ions can be detected. Moreover, through ion exchange, the adsorption property and other guest-dependent properties of porous material can be tuned.¹² Thus, ion exchange is also viewed as a post-synthesis modification method of porous material. The ion-exchange properties of zeolite-type porous material have been extensively studied.¹³ However, as most MOFs have neutral frameworks, the ion-exchange study in this type of porous material has only been carried out in a limited number of cases.¹⁴ Because of the framework of **1** with large internal voids and in addition to solvent water molecules the voids contain only the alkali-metal cations Na^+ , the cation exchange property of **1** could be investigated through facile cation exchange experiments. Ion exchanges were performed with alkali-metal cations (Li^+ , K^+ and Cs^+) and transition-metal cations (Mn^{2+} , Ni^{2+} and Cu^{2+}). Saturated solutions of LiCl, KCl, CsCl, MnCl_2 , NiCl_2 and CuCl_2 were separately added to the freshly prepared crystals of **1** (20 mg in each vial)

at room temperature. After 12 h, exchanged samples were filtered and washed with water and methanol several times. Except that the crystals in Cu^{2+} solution change into light blue powder, the crystals in other salt solutions retain their original crystal shape. The metal content of the exchange samples were tested using ICP and EDX techniques. The measurements revealed that the Na^+ ions in **1** were nearly completely exchanged with Li^+ , K^+ , Cs^+ , Mn^{2+} and Ni^{2+} ions respectively (Table S2, ESI[†]). This result shows that **1** possesses high ion-exchange capacities. Not only Li^+ , K^+ , Mn^{2+} and Ni^{2+} with radius similar to that of Na^+ , but also Cs^+ with radii much larger than that of Na^+ can exchange with Na^+ in **1** (Table S3, ESI[†]), which may be ascribed to the occurrence of the large openings (a 1 nm diameter cavity of the Cu_{12} unit) of the pores in **1**. The powder XRD of the exchanged samples with Li^+ , K^+ , Cs^+ , Mn^{2+} and Ni^{2+} ions shows patterns similar to that of the as-synthesized compound **1**, indicating that the basic framework remains unchanged upon ion exchange (Fig. S10, ESI[†]). Whereas, the powder XRD of the exchanged sample with Cu^{2+} ions exhibits that the framework has collapsed.

In conclusion, the new 12-connected MOF **1** based on cyclic Cu_{12} units has been successfully prepared, representing the first example of MOFs constructed by cyclic SBUs with a large interval cavity (>1 nm). Ion-exchange investigation shows that **1** possesses high ion-exchange capacities with some alkali-metal and transition-metal cations. Other novel MOFs based on cyclic SBUs with large interval cavities should be obtainable by following a similar synthetic route. Further research in this area is ongoing in our group.

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Notes and references

† Crystal data for **1**: $\text{C}_{72}\text{H}_{90}\text{Cu}_{12}\text{N}_{12}\text{Na}_4\text{O}_{65}$, $M_r = 3018.00$, cubic, space group $Pa\bar{3}$, $a = 24.3984(7)$ Å, $V = 14523.9(7)$ Å³, $Z = 4$, $F(000) = 5594.0$, $\rho_{\text{calcd}} = 1.380$ g cm⁻³, $S = 1.075$, $R_1(wR_2) = 0.0533$ (0.1399) with $I > 2\sigma(I)$; CCDC 854446.

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