

A double-walled triangular metal–organic macrocycle based on a $[\text{Cu}_2(\text{COO})_4]$ square paddle-wheel secondary building unit†

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A metal–organic macrocycle (MOM), $[(\text{Cu}_2)_3\text{L}_6(\text{DMF})_2(\text{H}_2\text{O})_4]$, was prepared using a long and “pseudo-rigid” dicarboxylic acid, 1,4-bis(3-carboxylphenylethynyl)benzene (H_2L), with some rotational flexibility, where the MOM has a double-walled triangular geometry with three Cu paddle-wheel secondary building units (SBUs) doubly connected by the ligands in a *cis*-conformation.

Metal–organic systems (MOSs) have received the attention of researchers because of the fundamental importance of the self-assembly phenomenon of small building components to complex architectures,¹ intriguing topological properties,² and potential as new functional materials.³

A metal–organic macrocycle (MOM) is one of the simplest supramolecular systems made of metal ions and organic ligands.^{1b,4} When all building blocks are topologically ditopic, either infinite 1-D chains or finite macrocycles can be obtained depending on the geometry and nature of the building components.⁵ Even though a triangular MOM is the smallest and simplest MOM, it is still very difficult to predict whether the final self-assembled structure would be a MOM or not based on the building components.⁶ For the self-assembly of triangular MOMs as in other higher-nuclearity MOMs, at least one ditopic component needs to have an appropriate bent or angular geometry.

There are numerous metal–organic frameworks (MOFs) and many metal–organic polyhedra (MOPs) based on secondary building units (SBUs) instead of simple metal components.^{7,8} However, MOMs decorated with SBUs are relatively rare,⁹ probably because of the lack of SBUs with appropriate nodality and geometry.

In this study, we report the preparation and characterization of a double-walled triangular MOM having metal centers augmented with square tetratopic paddle-wheel SBUs (Scheme 1). We used a long dicarboxylate ligand, 1,4-bis(3-carboxylphenylethynyl)benzene (H_2L), which is rigid but has some rotational flexibility because of the two C–C triple bonds. Even though the ligand has a long linear rigid linking moiety between the benzoic acid groups, it is not a linear dicarboxylate ligand but a “pseudo-rigid” potential bent ligand because of the *meta*-positioning of the carboxylic acid groups and the rotational degree



Scheme 1 Schematic diagram showing the synthesis of a double-walled triangular MOM based on copper paddle-wheel SBUs using a long and “pseudo-rigid” dicarboxylic acid and a Cu(II) ion.

of freedom. It is well known that the Cu(II) ion has a strong tendency to form a square tetratopic Cu paddle-wheel SBU with carboxylic acids.¹⁰ The combination of a potential bent ditopic carboxylic ligand with a Cu(II) ion could lead to a MOM having corner components decorated with doubly connected square Cu(II) paddle-wheel SBUs.

A solvothermal reaction of H_2L with $\text{Cu}(\text{NO}_3)_2 \cdot 2.5\text{H}_2\text{O}$ in *N,N'*-dimethylformamide (DMF) : MeOH mixed solvent at 85 °C for 1 d gave a blue needle-shaped crystalline product. ‡ An X-ray diffraction study of a single crystal§ revealed that the product, $[(\text{Cu}_2)_3\text{L}_6(\text{DMF})_2(\text{H}_2\text{O})_4]$ (**1**), was a pseudo- C_3 symmetric double-walled triangular MOM with three square-tetratopic Cu paddle-wheel SBUs doubly connected by dicarboxylate ligands to form a finite cyclic structure (Fig. 1) rather than an extended structure, a MOF. The six ligands in the MOM are all in the same conformation, the two carboxylates are in a *cis*-conformation (the average dihedral angle between the carboxylates is $\sim 10(11)^\circ$, ranging from 0 to 30° , see Fig. 2 and Fig. S1†). Among the six solvent sites of the paddle-wheel units, two sites are occupied by solvent DMF molecules and the remaining four sites are assigned to water molecules. The double-walled MOM has a longest outer dimension of ~ 2.9 nm between the two farthest carbon atoms of the phenyl groups on approximately opposite sides, a wall height of ~ 1.2 nm, and an inner cavity of ~ 1.2 nm in diameter (Fig. 1). The MOMs in the crystal are stacked in a nanotubular arrangement to form two different types of 1-D nanoporous channels; one is a trigonal channel along the inner side of the MOMs (type A) and the other is a rectangular channel between the MOMs (type B) (Fig. 3). The average distance between the inner metal ions of the paddle-wheel units within the MOM is ~ 15.5 Å, while the two distances between the metal centers across the rectangular channel are 11.4 Å and 16.4 Å (Fig. S2†). The solvent pore volume calculated using the SQUEEZE routine of the PLATON program

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† Electronic supplementary information (ESI) available: Crystallographic details, ball-and-stick diagram of the ligands, a packing diagram of **1**, a photograph of the crystals, and IR spectra. CCDC reference number 738019. For ESI and crystallographic data in CIF or other electronic format see DOI: 10.1039/c0dt00185f

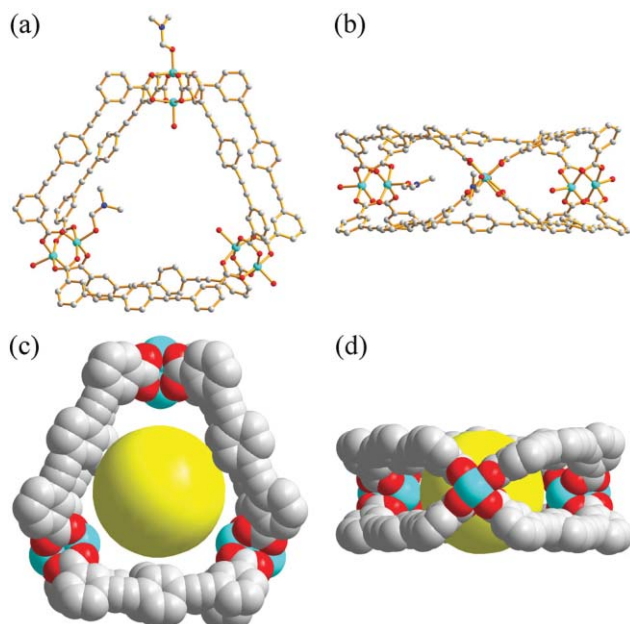


Fig. 1 Ball-and-stick diagrams of **1** in a top view (a) and a side view (b). The corresponding CPK diagrams in a top view (c) and a side view (d) with no ligated solvent molecules in the cavity, where the yellow dummy ball of 1.2 nm in diameter represents the approximate size of the solvent cavity. All hydrogen atoms are omitted for clarity (copper, cyan; carbon, gray; nitrogen, blue; oxygen, red).

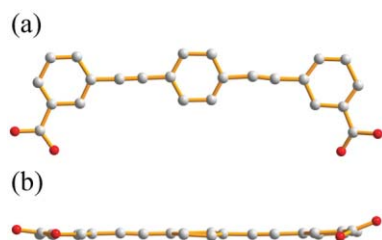


Fig. 2 A ligand conformation in **1** showing the two carboxylate groups in a *cis*-conformation, (a) one view of the ligand approximately perpendicular to the ligand plane and (b) another view of the same ligand approximately parallel to the ligand plane.

is 5988 Å³ per unit cell (597 solvent electrons [~15 DMF molecules] per unit cell), which corresponds to 52.7% of total unit cell volume.

Although the bulk crystalline sample looks homogeneous through a microscope (Fig. S3†), the powder X-ray diffraction (PXRD) pattern of the bulk crystalline sample is different from the simulated pattern of the single-crystal structure of **1** (Fig. 4). The loss of small amounts of guest solvent molecules may lead to the structural transformation of **1**. A change in the PXRD pattern of the sample vacuum-dried at 120 °C, **1a**, was observed and this change is irreversible. Neither the simulated PXRD pattern (Fig. 4(a)) nor the as-synthesized PXRD pattern (Fig. 4(b)) could be recovered by exposure of the activated sample to the solvent DMF, but a further change in the PXRD pattern was observed as shown in Fig. 4(d).

Unfortunately, the activated sample, **1a**, did not show any significant gas sorption for various gas molecules such as N₂, H₂, CO₂, and CH₄. The crystal transformation caused by the activation may lead to the movement of the MOM building blocks to a non-

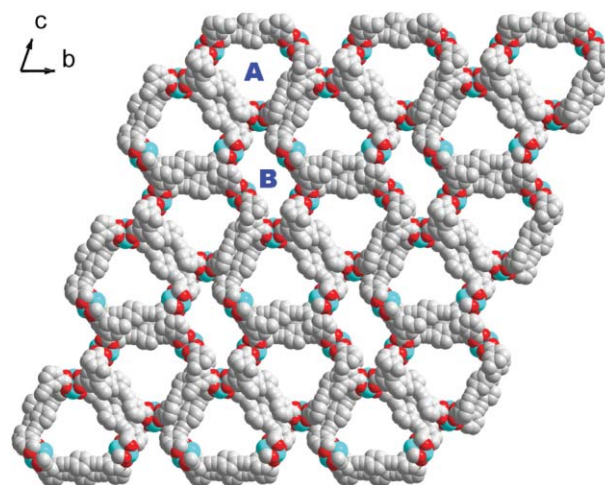


Fig. 3 A space-filling view of **1** showing two types of 1-D channels along the crystallographic *a*-axes, channel A along the inner side of the MOMs and channel B between the MOMs. All hydrogen atoms and solvent molecules are omitted for clarity (copper, blue; carbon, gray; oxygen, red).

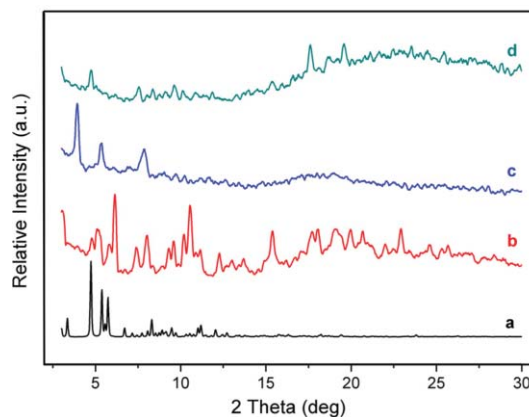


Fig. 4 (a) A simulated PXRD pattern from the single-crystal structure of **1**, (b) as-synthesized bulk sample, (c) activated at 120 °C, **1a**, and (d) solvent added to the activated sample, **1b**.

porous structure or to a porous structure but with no accessible cavity.

The MOM could only be dissolved in a mixed solvent system containing pyridine. However, precipitate is formed shortly after dissolution and the precipitate is not soluble in water and/or any organic solvents. Based on some similarity of the peak positions in the IR spectra of the MOM and the precipitate (Fig. S4†), we speculate that the pyridine might have transformed the finite MOM system to an infinite and insoluble MOF system.

Conclusions

In conclusion, we could prepare a Cu-based MOM, **1**, using a long and “pseudo-rigid” dicarboxylic ligand, 1,4-bis(3-carboxylphenylethynyl)benzene, with some degree of rotational flexibility. When the Cu(II) ions were self-assembled with the ligand in DMF, a discrete copper paddle-wheel-based triangular MOM was obtained, where the paddle-wheels were doubly connected by the ligands in the *cis*-conformation. Although the crystal packing showed two different 1-D channels, the guest removed material did

not show any significant gas sorption behavior, probably because of the collapse of the pores or the inaccessibility of the pores.

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Notes and references

‡ Synthesis of **1**: a 23.5 mg (0.100 mmol) sample of $\text{Cu}(\text{NO}_3)_2 \cdot 2.5\text{H}_2\text{O}$ and a 36.8 mg (0.100 mmol) sample of H_2L were dissolved in 5 mL DMF:MeOH mixture (4.5:1 v/v). The resulting solution was divided into five equal portions, and each of the solutions was charged into a Pyrex tube, which was tightly sealed and heated to 85 °C for 1 d. The blue needle-shaped crystals were collected and washed with fresh DMF (yield: 37.7 mg). The activated sample, **1a**, was prepared by soaking **1** in fresh DMF for several days, before drying under a dynamic vacuum overnight at 120 °C, and then by exposing to air (yield: 21.9 mg, 47.2%). Elemental analysis for **1a**. Calcd for $[(\text{Cu}_2)_3\text{L}_6(\text{DMF})_2(\text{H}_2\text{O})_4]$, $\text{C}_{150}\text{H}_{94}\text{N}_2\text{O}_{30}\text{Cu}_6$: C, 64.68; H, 3.40; N, 1.01. Found: C, 64.39; H, 3.31; N, 0.98.

§ Crystal data for **1**: ($\text{C}_{165}\text{H}_{131}\text{N}_7\text{O}_{36}\text{Cu}_6$): $M = 3169.01$, triclinic, space group $P\bar{1}$, $a = 11.499(2)$, $b = 31.249(6)$ (6), $c = 33.737(7)$ Å, $V = 11352(4)$ Å³, $T = 100(2)$ K, $Z = 2$, $\mu(\lambda = 0.90000 \text{ Å}) = 0.605 \text{ mm}^{-1}$, $\rho = 0.927 \text{ g cm}^{-3}$, $F(000) = 3264$, GOF = 1.194. Of 42 032 total reflections collected, 22 362 were unique ($R_{\text{int}} = 0.0585$). $R_1(wR_2) = 0.1160$ (0.3199) for 13 814 reflections [$I > 2\sigma(I)$], $R_1(wR_2) = 0.1370$ (0.3366) for all 22 362 reflections.

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