

Porous Metal–Organic Polyhedra: 25 Å Cuboctahedron Constructed from 12 Cu₂(CO₂)₄ Paddle-Wheel Building Blocks

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Construction of large molecules that are amenable to design and functionalization is of primary current interest as it represents an important step in the achievement of molecular complexity.^{1–8} We believe that large porous molecules serve as intriguing initial objects in this direction since the openings to their voids may be useful in regulating the selective release and binding of smaller molecules.⁹

At present there are at least two challenges that must be addressed for larger and more complex systems to be realized. First, single crystals of large molecules are difficult to obtain, thus precluding their full structural characterization; second, design of rigid entities that maintain their structure in the absence of guests in order to allow for reversible access to the voids as well as chemical functionalization of their voids and outside surface remains largely unexplored.

Given these challenges and considering our recent work on metal–organic frameworks (MOFs), where we have demonstrated the use of secondary building units (SBUs) as means to the construction of rigid networks with permanent porosity, we sought to use the paddle-wheel cluster adopted by copper(II) acetate, Cu₂(CO₂)₄, as a rigid SBU for addressing these challenges. Significantly, the assembly of such SBUs with polytopic carboxylate linkers generated rigid porous frameworks with open metal sites where it is possible to functionalize the pores with different ligands.¹⁰

The possible structures in which square SBUs (such as the paddle-wheel) are linked by identical links are derived from four-connected nets in which there is a planar (or near planar) vertex arrangement where all links are equivalent (quasiregular).¹¹ Replacing the vertices by (in the present report) a square of vertices is a process which we have called *augmentation*.^{10c} In the case of polyhedral structures the augmentation process is usually called truncation, and there are three possibilities¹¹ for square units: The truncated octahedron with 6 squares, the truncated cuboctahedron with 12 squares, and the truncated icosidodecahedron with 30 squares. We have previously used 1,4-benzenedicarboxylate (BDC) with 180° (straight) links to produce an infinite periodic structure.^{10c} The analogous 1,3-benzenedicarboxylate (*m*-BDC) with 120° between functional groups is ideal for building a finite truncated cuboctahedron structure with 12 linked paddle-wheels. Here we have used this design principle toward the synthesis of large discrete molecular units.

We report the synthesis of a porous metal–organic polyhedron Cu₂₄(*m*-BDC)₂₄(DMF)₁₄(H₂O)₁₀·(H₂O)₅₀(DMF)₆(C₂H₅OH)₆, hereafter termed *a*-MOP-1 (*a* = anorthic = triclinic) which is constructed from 12 paddle-wheel units bridged by *m*-BDC to give a large metal–carboxylate polyhedron.

Equimolar amounts of *m*-BDC acid (0.014 g, 0.084 mmol) and Cu(NO₃)₂·2.5H₂O (0.019 g, 0.082 mmol) in a solvent mixture of DMF/C₂H₅OH (1.5/0.5 mL) were placed in a quartz tube (10 mm diameter and 140 mm length). The tube was sealed under vacuum and heated at a constant rate 1 °C/min to 80 °C for 24 h, then cooled at a constant rate 0.1 °C/min to room-temperature in stepwise fashion (65 °C for 10 h and 50 °C for 4h). The blue crystals of *a*-MOP-1 were washed with DMF/ethanol mixture (3 × 4 mL) and DMF (3 × 4 mL) to give 0.015 g (65% yield). The crystals were formulated by elemental microanalysis and single-crystal X-ray diffraction studies.^{12,13}

Crystals of *a*-MOP-1 are composed of large discrete molecules constructed from the paddle-wheel clusters bridged by *m*-BDC units (Figure 1a). The simplest way to view the structure is by considering its relationship to the cuboctahedron, where each square and link have been replaced by the paddle-wheel (square SBU) and the *m*-BDC (two-connector) units, respectively, to give an *expanded-augmented* cuboctahedron (truncated cuboctahedron, 4.6.8 Archimedean polyhedron) (Figure 1b)—a motif also adopted by α -Keggin structure.¹¹

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(12) Microanalysis for Cu₂₄(*m*-BDC)₂₄(DMF)₁₄(H₂O)₁₀·(H₂O)₅₀(DMF)₆(C₂H₅OH)₆ (*a*-MOP-1): Calcd. C, 38.28; H, 4.77; N, 3.38. Found C, 38.24; H, 3.91; N, 2.80. There is an inherent difficulty in formulating the number of guest molecules in such open structures due to their volatility and the possibility of exchange as explained in the text.

(13) A blue prismatic crystal (0.34 × 0.16 × 0.16 mm) of *a*-MOP-1 was coated with a light hydrocarbon-based inert oil and mounted on a standard Siemens SMART CCD-based X-ray diffractometer equipped with a normal focus Mo-target X-ray tube ($\lambda = 0.71073$ Å) operated at 2000 W power (50 kV, 40 mA). The X-ray intensities were measured at 158(2) K; the detector was placed at a distance of 4.939 cm from the crystal. A total of 2432 frames were collected with a scan width of 0.3° in ω and φ with an exposure time of 30 s/frame. The frames were integrated with the Siemens SAINT software package with a narrow frame algorithm. The integration of the data using triclinic unit cell yielded a total of 76620 reflections to a maximum 2θ value of 42.00° of which 25727 were independent and 11169 were greater than $2\sigma(I)$. The final cell constants were refined with 4358 reflections above $10\sigma(I)$. Analysis of the data showed negligible decay during data collection; the data were corrected for absorption using an empirical method (SADABS) with transmission coefficients ranging from 0.552 to 0.914. The structure was solved by direct methods and the subsequent difference Fourier methods and refined with the Siemens SHELXTL (version 5.10) software package, using the centrosymmetric space group *P*1 with *Z* = 1 for the formula and *a* = 23.5283 (15) Å, *b* = 24.3224 (16) Å, *c* = 25.0401 (16) Å, $\alpha = 61.479$ (1)°, $\beta = 82.864$ (1)°, $\gamma = 75.298$ (1)°. Final full matrix least-squares refinement on *F*² converged to *R*1 = 0.1710 (*I* > $2\sigma(I)$) and *wR*2 = 0.4618 (all data) with GOF = 1.371.

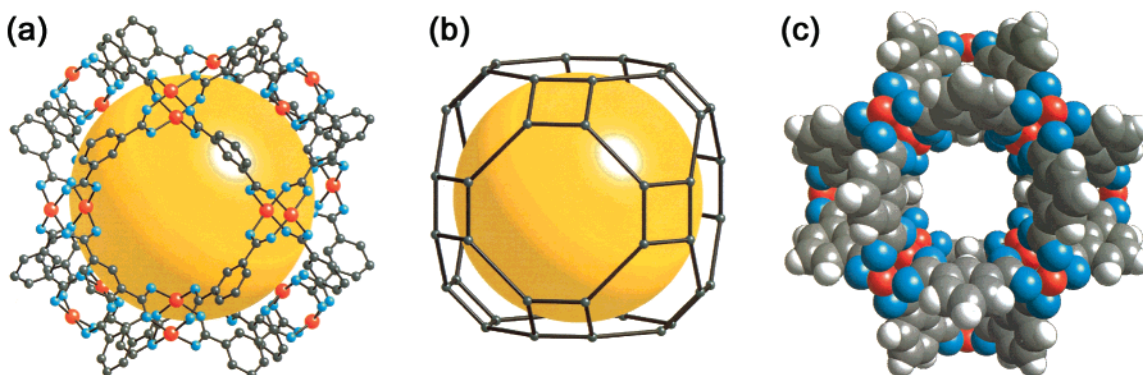


Figure 1. The crystal structure of MOP-1 (drawn using coordinates obtained for *c*-MOP-1) showing (a) 12 paddle-wheel units (Cu, red; O, blue, C; gray) linked by (*m*-BDC) to form a (b) large truncated cuboctahedron of 15 Å diameter void (yellow sphere), the gray spheres represent the polyhedron constructed by linking together only the carboxylate C atoms in (a) to form linked square SBUs, an arrangement that provides for a (c) large porous polyhedron with triangular and square windows. Hydrogen atoms in light gray otherwise same coloring scheme as in (a). All terminal ligands pointing in the cavities and away from the surface have been omitted in (a-c).

This arrangement results in a porous polyhedron having 8 triangular and 6 square crevices that are 8 and 12 Å across, respectively, and a benzene unit depth (Figure 1a,c).¹⁴ These open into an internal spherical cavity having an average diameter of 15 Å and a volume of 1766 Å³. Each paddle-wheel unit of the Cu–O–C polyhedron has two terminal ligands: one pointing into the internal cavity toward the center of the polyhedron while the other is bound to the copper center outside pointing away from the outside surface of the polyhedron. Thus, the paddle-wheel units have a total of 24 terminal DMF and water ligands. These are distributed as follows: 4 units have only DMF (8 DMF), 6 units have 1:1 DMF:water (6 DMF and 6 water), and 2 units have only water ligands (4 water). A combination of 8 DMF and 4 water ligands point toward the center of the polyhedron, while additional 6 DMF and 6 water ligands point away from the surface of the polyhedron to give it an overall size of 34 Å (with terminal ligands) or 25 Å (without terminal ligands) in diameter.¹⁴

Further examination of the X-ray single-crystal structure of *a*-MOP-1 revealed the presence of 50 water, 6 ethanol, and 6 DMF molecules acting as free guests: in the internal cavity (2 DMF, 4 ethanol, and 11 water), triangular and square crevices (2 DMF and 16 water), and the interstitial voids as solvates (2 DMF, 2 ethanol, 23 water).

It is worth noting that the expected cubic symmetry for the polyhedron backbone is lowered to triclinic in *a*-MOP-1 due to the presence of DMF ligands. Remarkably, re-examination of the crystals after they have been left in the mother liquor for three months showed complete substitution of the DMF by water ligands and maintenance of the integrity of the Cu–O–C crystal structure. X-ray single-crystal analysis on these fully hydrated crystals (*c*-MOP-1) showed that they were body-centered cubic and revealed the absence of DMF ligands originally bound to the polyhedron.¹⁵

(14) van der Waals radius of C (1.70 Å) was employed in determination of distance parameters. Bondi, A. *J. Phys. Chem.* **1964**, *68*, 441–451.

Preliminary evidence indicates that the Cu–O–C structure in *a*-MOP-1 is stable as it is possible to completely dissolve the solid in refluxing DMF and to recrystallize it by cooling to room temperature. Thermal gravimetric analysis performed on a crystalline sample (5.23 mg) showed two distinct weight-loss steps of 7.3% at 60 °C and 9.3% at 180 °C, due to the loss of both free and coordinated guests, then reaching a plateau between 200 and 300 °C—indicating similar stability of *a*-MOP-1 to the paddle-wheel based *extended* porous structures.^{10a–c}

At the outset of this study large metal–organic polyhedra have been restricted to those assembled by metal–pyridine-type linkages with their structures obtained from X-ray single-crystal diffraction^{2,3,5,6} and NMR data,^{2–4} and to a recent example of a *polyhedral* cluster prepared from Mo₂⁴⁺-carboxylate⁷—all significantly smaller than MOP-1. This study illustrates the feasibility of obtaining *crystals* of large porous metal–organic polyhedra in which rigid SBUs are an integral part of a well-defined structure. Current work is focused at functionalizing the links and open metal sites and using other links for the synthesis of larger polyhedra, assembled monolayers, and mesophases.

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Supporting Information Available: Crystallographic data, bond lengths, and angles for *a*-MOP-1 and *c*-MOP-1 (PDF). This material is available free of charge via the Internet at <http://pubs.acs.org>.

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(15) Blue crystals of Cu₂₄(*m*-BDC)₂₄(H₂O)₂₄·(H₂O)₄₂ = (*c*-MOP-1) are cubic, *Im* $\bar{3}$ *m* (No. 229) with *a* = 27.722(3) Å, *V* = 21306(4) Å³, *Z* = 2, *d*_{calc} = 1.029 g cm⁻³, *T* = 173 (2) K, Siemens SMART CCD diffractometer, Mo Kα (*λ* = 0.71073 Å), *μ* = 12.38 cm⁻¹. Final full matrix least-squares refinement on *F*² with all 1116 reflections and 90 variables converged to *R*₁ (*I* > 2σ(*I*)) = 0.1004, *wR*₂ (all data) = 0.3427 and GOF = 1.053.