Porous Metal–Organic Polyhedra: Morphology, Porosity, and Guest Binding

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ABSTRACT: Designing porous materials which can selectively adsorb CO₂ or CH₄ is an important environmental and industrial goal which requires an understanding of the host–guest interactions involved at the atomic scale. Metal–organic polyhedra (MOPs) showing permanent porosity upon desolvation are rarely observed. We report a family of MOPs (Cu-1a, Cu-1b, Cu-2), which derive their permanent porosity from cavities between packed cages rather than from within the polyhedra. Thus, for Cu-1a, the void fraction outside the cages totals 56% with only 2% within. The relative stabilities of these MOP structures are rationalized by considering their weak nondirectional packing interactions using Hirshfeld surface analyses. The exceptional stability of Cu-1a enables a detailed structural investigation into the adsorption of CO₂ and CH₄ using in situ X-ray and neutron diffraction, coupled with DFT calculations. The primary binding sites for adsorbed CO₂ and CH₄ in Cu-1a are found to be the open metal sites and pockets defined by the faces of phenyl rings. More importantly, the structural analysis of a hydrated sample of Cu-1a reveals a strong hydrogen bond between the adsorbed CO₂ molecule and the Cu(II)-bound water molecule, shedding light on previous empirical and theoretical observations that partial hydration of MOPs containing open metal sites increases their uptake of CO₂. The results of the crystallographic study on MOP−gas binding have been rationalized using DFT calculations, yielding individual binding energies for the various pore environments of Cu-1a.

INTRODUCTION

Porous materials such as metal–organic frameworks (MOFs), covalent organic frameworks (COFs), porous organic polymers, and porous molecular solids have been investigated for a wide range of applications, including gas adsorption and separation, conductivity, photochemistry, and catalysis. Each class of materials possesses both strengths and weaknesses in terms of their properties and function such as adsorption capacity, selectivity, tunability, stability, and processability. A detailed understanding of the interactions between guest molecules and the host material is of critical importance to the design of improved functional materials, and in situ diffraction methods have made significant advances in delivering detailed structural insights into host–guest binding interactions in MOFs and porous molecular solids. In contrast, far fewer examples have been reported of permanently porous materials derived from metal–organic polyhedra (MOPs), and many show weak intermolecular forces leading to structural collapse upon desolvation. MOPs are derived from polytopic ligands that bridge metal cations or clusters to give discrete molecular species, often with highly symmetrical architectures. Porosity in MOPs can originate either from the space inside the polyhedral cages or from the spaces between cages when they pack in the solid state to form 3D lattices. Control over the former can be achieved by targeting specific polyhedral topologies and shapes through the combination of appropriate rigid organic linkers and metal centers. Control over the latter is much harder because the assembly of MOPs is directed by poorly directional weak interactions and is thus often unpredictable. More significantly, the tendency to maximize the number of weak contacts during crystallization tends to favor more dense nonporous phases. The formation of a MOP material with permanent porosity therefore requires a rigid MOP assembly which can frustrate efficient packing and resist structural collapse upon desolvation, a combination that is rarely observed. Porous organic molecular materials have been observed in MOFs derived from polytopic ligands such as the pentagonal bipyramidal copper(I) dimer .
Figure 1. (a) Synthesis of metal–organic porous materials Cu-1a, Cu-1b, and Cu-2 by reaction of H₃L¹ and H₃L² with Cu(NO₃)₂. The space groups of their crystal structures are shown underneath the packing views. Molecular cage color code: copper, light blue; water, red; ligands, pink and purple. Hydrogen atoms omitted. Crystal packing view color code: cages of alternating layers, red and blue; hydrogen atoms, white. (b) Conformation of (L¹)³⁻ in Cu-1a. Eight tripodal ligands straddle a triangular face of the octahedral array of copper paddlewheel units (only one ligand is shown). Color code: copper, teal; carbon, black; oxygen, red; hydrogen, white; paddlewheel centroids and connecting edges, blue. (c) Comparisons of measured and simulated PXRD patterns for samples of Cu-1a, Cu-1b and Cu-2. Simulated patterns are generated from the SCXRD structures.

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**EXPERIMENTAL DETAILS**

Synthesis. H₃L¹ and H₃L² (Figure 1) were prepared according to literature methods.\(^{13a,b}\) Cu-1a, H₃L¹ (3.52 g, 5.29 mmol) and Cu(NO₃)₂·3H₂O (4.90 g, 21.1 mmol) were dissolved separately in portions of DMF before being combined in a round-bottom flask and diluted to a total volume of 530 mL. The solution was purged with N₂ for 30 min before being heated to 85 °C without stirring for 3 days. A fine pale blue precipitate gathered at the bottom of the flask, was collected by filtration while the solution was still hot and was washed with portions of hot DMF. A small number of large (up to 200 μm) fractal-fern-shaped crystals were formed, and these were collected and used for X-ray analysis. The powder was then solvent-exchanged with acetone by soaking the material under acetone, which was replaced daily for 7 days before the solid was dried under a gentle flow of Ar to give Cu-1a as a fine azure blue powder (yield 1.75 g, 38%). Anal. Calcd for Cu₁₂(C₄₅H₂₇O₆)₈(H₂O)₄₀(C₃H₇NO)₃: C, 66.93; H, 4.83; N, 0.62. Found: C, 66.63; H, 4.20; N, 0.63. Cu-1a was treated in a Tousimis Autosamdri-815 Series A supercritical point dryer prior to further analysis: the acetone-exchanged material was suspended in EtOH by pouring into the dryer in a porous crucible. The EtOH analysis: the acetone-exchanged material was suspended in EtOH before it was loaded into the dryer in a porous crucible. The EtOH was purged with liquid CO₂ (BOC, Food fresh grade, 99.8%) for 10 min before being allowed to equilibrate for 50 min. This process was repeated four times. The CO₂ was heated above the supercritical point before the pressure was slowly released over 3 h. Cu₁₂(C₄₅H₂₇O₆)₈(H₂O)₄₀(C₃H₇NO)₃: C, 66.93; H, 4.83; N, 0.62. Found: C, 66.63; H, 4.20; N, 0.63. Cu-1a was treated in a Tousimis Autosamdri-815 Series A supercritical point dryer prior to further analysis: the acetone-exchanged material was suspended in EtOH by pouring into the dryer in a porous crucible. The EtOH was purged with liquid CO₂ (BOC, Food fresh grade, 99.8%) for 10 min before being allowed to equilibrate for 50 min. This process was repeated four times. The CO₂ was heated above the supercritical point before the pressure was slowly released over 3 h. Cu-1b, H₃L² (2.01 g, 3.02 mmol) and Cu(NO₃)₂·3H₂O (2.35 g, 9.71 mmol) were separately dissolved in portions of DMF before being combined in a 1000 mL square Schott bottle and diluted to a total volume of 975 mL. The bottle was capped and chilled to 4 °C for 48 h, after which a fine pale blue precipitate had formed. A small number of large single crystals formed, and these were collected and used for X-ray analysis. The precipitate was collected by filtration and washed sequentially with portions of DMF and acetone before being dried under a gentle flow of Ar. Copper, light blue; carbon, black; oxygen, red; hydrogen, white; paddlewheel centroids and connecting edges, blue. (c) Comparisons of measured and simulated PXRD patterns for samples of Cu-1a, Cu-1b and Cu-2. Simulated patterns are generated from the SCXRD structures.
dried under a gentle flow of argon to give Cu-1b as a pale blue crystalline powder (yield 0.319 g; 10.5%). Anal. Calc'd for Cu$_{12}$(C$_{63}$H$_{39}$O$_6$)$_8$(H$_2$O)$_{55}$: C, 69.51; H, 4.65; N, 0.07. Found: C, 69.68; H, 4.66; N, 0.07. The trace amounts of N in the extract were not accounted for.

Regions of diffuse solvent in the solvated structures were treated with the PLATON SQUEEZE routine.  

Diffraction data for Cu-1b and Cu-2 were collected on a Rigaku Oxford Diffraction SuperNova diffractometer equipped with an AtlasS2 detector and microfocus Cu X-ray source. Diffraction data for Cu-1aH$_2$O and Cu-1aH$_2$O$-CO_2$ were collected on a Rigaku TitanS2 detector and microfocus Cu X-ray source. The raw data were reduced and corrected for Lorentz and polarization effects using CrysalisPro.  

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Supporting Information.

(BSSE).  

Further details of DFT calculations are provided in the Supporting Information.

Analysis of the Fourier map of the gas sorption experiments indicated no residual nuclear density in the large octahedral and small tetrahedral intermolecular voids, including the vacant coordination site of Cu1. The occupancy of a test oxygen atom placed coordinated to Cu1 was refined to zero.  

Residual nuclear density remained inside the cages including at a 242 position consistent with solvent coordination at Cu2, indicating that this region of the structure was not available for gas binding.  

The 3D-31+G* level of theory with the D3 dispersion correction scheme proposed by Grimme.  

For Cu atoms the modified m6-31G* basis set has been used. The three-body dispersion contributions have been added in calculations of binding energies using the standalone DFT-D3 (V3.2) code. All presented values of the binding energies have been counterpoise-corrected for the basis set superposition error (BSSE). Further details of DFT calculations are provided in the Supporting Information.
Figure 2. Views of the crystal packing of molecular cages and resultant void spaces in (a) Cu-1a, (b) Cu-1b, and (c) Cu-2. Color code: cages, red, green, blue, yellow, orange, maroon; internal cage cavities colored to match cages; intermolecular voids and channels, yellow. (d) Hirshfeld surfaces of the three cages viewed toward triangular faces (top), along the Cu–Cu axis of paddlewheels (bottom, Cu-1a and Cu-1b) and along the crystallographic a axis (bottom, Cu-2) with viewing directions given as Miller indices. The surfaces are colored to show the property $d_{norm}$: the normalized contact distance between the Hirshfeld surface of the molecule and the nearest nucleus outside the surface. Contacts around the sum of the van der Waals radii of the nuclei are shown in white while shorter and longer contacts are shown in red and blue, respectively. (e) Histograms showing the distributions of contact types between the cage molecules and surrounding space.

RESULTS AND DISCUSSION

Synthesis and Analysis of Crystal Structures. A solvothermal reaction of H$_3$L$^1$ and Cu(NO$_3$)$_2$·3H$_2$O in DMF at 80 °C results in the formation of the porous MOP complex Cu-1a with the formula [Cu$_{12}$(L$^1$)$_3$(H$_2$O)$_5${\textcircled{\textgreek{n}}}(H$_2$O)$_2$]·272 Å$^3$ (Figure 1a). The structure of Cu-1a was determined by single-crystal X-ray diffraction (SCXRD), while the composition and thermal stability of the bulk material were confirmed by powder X-ray diffraction (PXRD), elemental analysis, and thermal gravimetric analysis (TGA) (Figure 1c and Figures S1 and S9). Cu-1a crystallizes in cubic space group Pn$_3$m with unit cell length $a = 33.21$ Å. In the structure of Cu-1a, eight tripodally disposed ligands (L$^1$)$^{3−}$ cap the triangular faces of an octahedral array of six paddlewheels. Each ligand (L$^1$)$^{3−}$ binds three carboxylate groups to three different paddlewheel units to give a rhombic-dodecahedral topology, which mutually satisfies the eight tripodal ligands and six {Cu$_3$} paddlewheels (Figure 1b). The polyhedron encloses an irregular cavity with a potential volume of 272 Å$^3$, occupied by a mixture of disordered solvent molecules bound at inwardly pointing axial sites of the surrounding paddlewheels. Each tripodal ligand (L$^1$)$^{3−}$ adopts a propeller-like twisted conformation, with all eight ligands being twisted in the same sense, resulting in the cage possessing chiral octahedral $O_h$ symmetry, leading to the crystallization of Cu-1a in the chiral space group as a racemic twin: clusters of both handedness are present in the crystal but are not packed together in the same domain.$^{30}$ In Cu-1a the cages pack in a pseudo face-centered-cubic (fcc) arrangement, resulting in two types of intermolecular voids in the lattice: large octahedral cavities with a volume of 3336 Å$^3$ and small tetrahedral cavities with a volume of 114 Å$^3$ (Figure 2a). The two types of intermolecular voids in combination with the internal cage cavities result in the desolvated structure having a total potential void fraction of 39%, as calculated by PLATON.$^{30}$

Interestingly, the same solvothermal reaction as above but at a lower temperature of 5 °C results in the formation of the lower density polymorph Cu-1b, composed of rhombic dodecahedral cages isostructural with those in Cu-1a (Figure 1a). The SCXRD structure shows that Cu-1b has the formula [Cu$_{12}$(L$^1$)$_3$(H$_2$O)$_5${\textcircled{\textgreek{n}}}(H$_2$O)$_2$]·12H$_2$O·18(DMF) and crystallizes in cubic space group Pn$_3$m with the unit cell length $a = 28.75$ Å. Cu-1b has a significantly lower density packing arrangement in comparison to Cu-1a, resulting in a potential void fraction of 50%. The pseudo body-centered-cubic (bcc) packing of cages in Cu-1b results in continuous channels in the structure rather than discrete intermolecular voids in Cu-1a; these channels account for 45% of the porous voids with the remaining 5% found inside the cages (Figure 2b). The cages in Cu-1b have a larger potential internal volume (592 Å$^3$) in comparison to those in Cu-1a (272 Å$^3$) as a result of a flatter conformation of the tripodal ligand (L$^1$)$^{3−}$, which pushes the carboxylate binding moieties further apart.$^{31}$ The individual cages in Cu-1b possess the same chiral octahedral $O_h$
symmetry observed in Cu-1a, but cages of both handedness are found in the centrosymmetric space group. Samples of Cu-1b isolated after short reaction durations of up to 48 h were found by PXRD to be phase pure (Figure 1c), while those isolated after longer durations in solution showed increasingly broad diffraction peaks before transforming into a poorly crystalline phase of Cu-1a. Therefore, it is concluded that the more porous phase Cu-1b is a kinetic product with respect to the more thermodynamically stable but denser phase Cu-1a.

An attempt was made to increase the size of the MOP cages, and thus the porosity of the resultant material, by reacting the extended ligand \( H_3L_2 \) with \( Cu(OH)_2 \cdot 3H_2O \) in DMF, resulting in formation of large platelike crystals (Figure 1a). The complex Cu-2 was shown by SCXRD to have the formula \( [Cu_{12}(L^2)\text{(H}_2O)_{12}]\cdot(H_3O)_3\cdot60\text{(DMF)} \) consisting of isostroical rhombic dodecahedral cages in comparison to those described in Cu-1a and Cu-1b. Despite elongation of the ligand arms in \( H_3L_2 \) with a phenyl spacer ligand, the cages in Cu-2 possess an octahedral arrangement of six paddlewheels similar to those found in Cu-1a and Cu-1b; the longer ligand fulfills the geometric requirements of the topology through adjustments in torsion angles between phenyl rings. In the structure of Cu-2 the homochiral cages crystallize in trigonal space group \( R3_1 \) and pack in a pseudo fcc arrangement with very large potential void regions totaling 58% inside and 42% between them. The void fraction outside the cages totals 56% with 2% inside the cages; thus, the major portion of permanent porosity resides between polyhedra rather than within. Inside the cage are six full-occupancy \( Cu(II) \)-bound \( H_2O \) ligands and eight half-occupancy free \( H_2O \) residues, each nestled in the 3-fold symmetric cleft of a ligand. The contents of the external void were diffuse and could not be determined (Figure 2c).

The PXRD pattern of Cu-2 after solvent exchange shows some differences from the pattern derived for the solvated form, indicating some rearrangement of packing in the structure upon loss of solvent from void spaces (Figure 1c).

**Permanent Porosity and Structural Stability.** The permanent porosity of the three MOP materials was confirmed by \( N_2 \) adsorption isotherms at 77 K. The \( N_2 \) isotherm for Cu-1a after solvent and supercritical \( CO_2 \) exchange followed by activation at 150 °C shows reversible type I behavior with type IVb characteristics and a pore volume of 0.381 cm\(^3\)/g, showing good agreement with that obtained from the crystal structure (0.378 cm\(^3\)/g) (Figure 3a, Figures S2 and S3, and Table 1). The \( N_2 \) isotherm for Cu-1b after it was rinsed with acetone and activated at 120 °C shows reversible type I behavior with type IVb characteristics and a degree of hysteresis beyond ca. \( p/p^0 \) 0.4. The porosity of 0.495 cm\(^3\)/g is slightly lower than the crystallographically indicated value (0.588 cm\(^3\)/g). The BET surface areas for Cu-1a and Cu-1b of 751 and 885 m\(^2\)/g, respectively, are high for MOPs, particularly Cu-based ones, though a surface area nearly twice as large has been reported recently. The \( N_2 \) isotherm for Cu-2 after solvent exchange with acetone and activation at 120 °C shows type I behavior with type IVb characteristics; hysteresis on the return isotherm remains open to \( p/p^0 \) 0.1. The pore volume is 0.289 cm\(^3\)/g, and a lower BET surface area of 508 m\(^2\)/g is observed. The measured porosity of Cu-2 is unsurprisingly lower than the crystallographically indicated value (0.578 cm\(^3\)/g) because of the observed structural collapse. The structural integrity of Cu-1a and Cu-1b and the collapse of Cu-2 is also reflected in pore size distributions calculated from the \( N_2 \) adsorption using nonlocal density functional theory (NLDFT) methods (Figure 3b). The pore distributions for all three materials exhibit a combination of micro- and mesopores in agreement with their crystal structures, accounting for the mixture of type I and type IVb characteristics observed in their \( N_2 \) isotherms.

Hirshfeld surfaces calculated for the MOPs with non-coordinated solvents omitted illustrate subtle differences in packing interactions among the phases, allowing rationalization of the consequent differences in their stabilities with respect to their porosities: Cu-1a > Cu-1b > Cu-2 (Figure 2d). The surfaces are colored to represent the value \( d_{norm} \), which describes the distance between the Hirshfeld surface of the

![Figure 3](https://dx.doi.org/10.1021/acs.inorgchem.0c01935)
Table 1. Surface Areas, Porosities, and Densities of MOP Materials

|                | Cu-1a | Cu-1b | Cu-2  |
|----------------|-------|-------|-------|
| BET surface area (m²/g) | 751 ± 3.2 | 885 ± 2.8 | 508 ± 0.8 |
| measd N₂ capacity (cm³/g) | 246.2 | 319.9 | 187.0 |
| measd N₂ pore volume (cm³/g) | 0.381 | 0.495 | 0.289 |
| crystallographic pore volume (cc/g) | 0.378 | 0.588 | 0.578 |
| crystallographic pore fraction | 0.386 | 0.499 | 0.578 |
| desolvated density (g/cm³) | 1.022 | 0.849 | 0.692 |

The BET surface areas and measured pore volumes are determined from N₂ adsorption isotherms measured at 77 K. Crystallographic properties are calculated by PLATON with a 1.2 Å probe from SCXRD structures with all solvent molecules omitted.

In Situ IR Spectroscopy. To probe the interaction between Cu-1a and CO₂ further, in situ IR spectroscopy was used to monitor changes in the combination band region for CO₂ at temperatures of 195 K and 273 K. Two gas-phase IR combination bands are observed, centered at 3714 and 3618 cm⁻¹, which are assigned to the 2ν₁ + ν₃ and ν₁ + ν₃ bands, respectively (Figure 4a). When a solvent-exchanged and degassed sample of Cu-1a pressed in a KBr pellet was exposed to various pressures of CO₂ at temperatures of 195 and 273 K, two bands were observed to grow at 3690 and 3583 cm⁻¹ with increasing pressure of CO₂. These bands are consistent with adsorption of CO₂ within the pores of Cu-1a. The IR spectrum of KBr + CO₂; (b) spectrum of KBr + CO₂ + Cu-1a; (c) difference spectrum (b) with the spectrum of the MOF background subtracted as a function of pressure.

Figure 4. In situ FTIR spectra of CO₂ at various pressures (0–1 bar) in the combination region at 195 K (a–d) and 273 K (e): (a) spectrum of KBr + CO₂; (b) spectrum of KBr + CO₂ + Cu-1a; (c) spectrum (b) with the spectrum of the MOF background subtracted from it; (d) spectrum (c) minus spectrum (a) at 195 K; (e) spectrum (d) at 273 K.Insets: plots showing the normalized band areas of the two peaks assigned to adsorbed CO₂ in Cu-1a as a function of pressure.
Spectrum of Cu-1a contains a broad band in this region, which does not appear to change significantly with increasing pressure. Therefore, the spectrum recorded at 0 bar of CO2 was used as a background to produce a free spectrum for Cu-1, showing changes as the pressure of CO2 was increased from 0 to 1 bar (Figure 4c). After background subtraction, spectra were obtained free of contributions from the host material and gas-phase CO2 (Figure 4d) and these showed two peaks assigned to the adsorbed CO2 phase. The band areas of the adsorbed phase were obtained (Figure 4d, inset), showing the change in CO2 uptake with pressure. These data were normalized such that the band areas at 1 bar have been set to 1; the same procedure was performed at 273 K, and the spectra obtained after subtraction of the gas phase are shown in Figure 4e. Two bands for adsorbed CO2 are observed at 195 and 147 K. Reitveld refinements of data measured at 10 K with loadings of 6 CO2, 18 CO2, and 6 CD4 molecules per Cu12 cage revealed three binding sites common to both CO2 and CD4 guests in the resultant structures Cu-1a·6.7CO2, Cu-1a·18.6CO2, and Cu-1a·6.1CD4 (Figure 5). Site occupancies for guests CO2A–C and CD4A–C were refined with globally fixed atomic displacement parameters, meaning that a valid discussion is limited to broad trends. Contrasting binding site preferences are evident for CO2 and CD4: the most populated site in Cu-1a·6.7CO2 is CO2A adjacent to external Cu(II) sites, whereas the most populous site in Cu-1a·6.1CD4 is CD4A located in the small tetrahedral void. This observation agrees with the expectation that CO2 can act as a weak Lewis base, allowing it to coordinate to the open Cu(II) site (O(1A)···Cu(1) distance 2.46(5) Å). Site CO2B in Cu-1a·6.7CO2 is adjacent to a phenyl ring (O(1B)···Ph(C21−C26) centroid distance 3.07(5) Å) and has the lowest occupancy of the three sites. Site CO2B also accepts a weak supramolecular bond from a phenyl C–H donor (C(35)−H(35)···O(3B)CO2 distance 2.79(3) Å; angle 166(1)°). Potential favorable intermolecular C···O and C···H contacts exist between sites CO2A and CO2B (C(2A)···O(3B) and C(2B)···O(1A) distances ) 2.92(8) and 3.95(6) Å, respectively). Site CO2C, located in the small tetrahedral void in Cu-1a·6.7CO2, has a high occupancy comparable to that of CO2A on Cu(II) sites; it makes four equal interactions with the surrounding phenyl rings (O(1C)···Ph(C11−C12) centroid distance 3.56(1) Å). CD4 cannot form strong coordinate bonds, and thus in Cu-1a·6.1CD4, CD4A adjacent to Cu(II) (Cu(1)···C(1A) distance 2.62(5) Å) has the lowest occupancy of the three CD4 sites. CD4B adjacent to a single phenyl ring has an intermediate occupancy, while CD4C in the small tetrahedral void has the highest occupancy. The Cu-1a·6.1CD4 contains a broad band in this region, which does not appear to change significantly with increasing pressure. Therefore, the spectrum recorded at 0 bar of CO2 was used as a background to produce a free spectrum for Cu-1, showing changes as the pressure of CO2 was increased from 0 to 1 bar (Figure 4c). After background subtraction, spectra were obtained free of contributions from the host material and gas-phase CO2 (Figure 4d) and these showed two peaks assigned to the adsorbed CO2 phase. The band areas of the adsorbed phase were obtained (Figure 4d, inset), showing the change in CO2 uptake with pressure. These data were normalized such that the band areas at 1 bar have been set to 1; the same procedure was performed at 273 K, and the spectra obtained after subtraction of the gas phase are shown in Figure 4e. Two bands for adsorbed CO2 are observed at 195 and 147 K. Reitveld refinements of data measured at 10 K with loadings of 6 CO2, 18 CO2, and 6 CD4 molecules per Cu12 cage reveals three binding sites common to both CO2 and CD4 guests in the resultant structures Cu-1a·6.7CO2, Cu-1a·18.6CO2, and Cu-1a·6.1CD4 (Figure 5). Site occupancies for guests CO2A–C and CD4A–C were refined with globally fixed atomic displacement parameters, meaning that a valid
Cu(II) remains the most populated, reaching saturation, while the occupancies of CO₂ B and CO₂ C increase to similar values of 0.46(1) and 0.58(1), respectively. Thus, this study has afforded a sharp comparison of the MOP—gas binding between CO₂ and CH₄ at atomic resolution and represents the first example of such in an unpillared MOP material.¹³d

We also sought to understand the effect of Cu(II)-bound water on CO₂ binding from a structural perspective. An inspection of electron density maps and analysis using PLATON SQUEEZE for Cu-la-H₂O showed complete removal of free solvent from the large octahedral void and small tetrahedral void along with retention of coordinated water on both Cu(II) paddlewheel axial sites (Tables S4 and S5). The retention of coordinated water despite prolonged heating under vacuum reflects the difficulty of activating a large monolithic single crystal in contrast to microcrystalline powder.¹⁹

S₅). The retention of coordinated water despite prolonged removal of free solvent from the large octahedral void and small tetrahedral void is in a location found adjacent to the coordinated water in the large octahedral void (Figure 6) and at the center of the small tetrahedral void.

![Figure 6](https://dx.doi.org/10.1021/acs.inorgchem.0c01935)  
**Figure 6.** View of CO₂ binding environments at the copper paddlewheel in Cu-la-H₂O determined by in situ SCXRD at 120 K. Selected intermolecular distances are labeled in Å. Color code: carbon, black; oxygen, red; hydrogen, white; copper, teal; guest CO₂, yellow.

The CO₂ site in the large octahedral void is in a location similar to that of CO₂ B found by NPD; however, it simultaneously takes part in three types of interactions: accepting a hydrogen bond from the coordinated water molecule (O(1)H₂O—O(1A)CO₂ distance 2.88(6) Å), interacting with the adjacent phenyl ring (O(3A)CO₂—Ph(C21—C26) centroid distance 3.49(6) Å), and making favorable C₅⁻—O⁻ contacts with symmetry-equivalent neighbors (C(2A)CO₂—O(1A)CO₂ distance 3.52(7) Å). The hydrogen atoms on the coordinated water molecule were not observed in the electron density map; the presence of a hydrogen bond is deduced from atomic positions and supported by DFT calculations (vide infra). This structure represents the first crystallographic evidence of the mechanism by which partial hydration of Cu(II)-containing MOFs may lead to enhanced CO₂ adsorption properties.

**DFT Calculations and Analysis of the Host—Guest Interaction**

DFT calculations have been used to probe further the CO₂ and CH₄ binding sites in Cu-la. Host environments analogous to sites CO₂ A-C and CD₄ A-C determined by NPD. Structures obtained by NPD were chosen as starting configurations, and positions of guest molecules were fully optimized. The calculated minimum energy configurations were found to be in a good agreement with the experimentally determined structures. Binding energies were then calculated for the guests in the optimized geometries. The results of DFT calculations are summarized in Table 2.

At the equivalent adsorption sites, binding energies of CO₂ molecules were found to be higher than those of CH₄ molecules. The values of −27.9 and −28.0 kJ/mol were predicted for the sites CO₂ Cu and CO₂ Ph, analogous to NPD sites CO₂ A and CO₂ B, while for the sites CH₄ Cu and CH₄ Ph, analogous to CD₄ A and CD₄ B, the binding energies were calculated to be −22.9 and −20.5 kJ/mol, respectively. For both guest molecules, the most energetically favorable adsorption configurations were found to be inside the small tetrahedral void with binding energies of −39.5 and −31.5 kJ/mol for CO₂ Tet and CH₄ Tet, respectively. It should be noted that experimentally determined sites CO₂ C and CD₄ C are centered on the crystallographic special points in the middle of the void. However, in the case of a CO₂ guest molecule the DFT calculations predict the lowest energy CO₂ Tet position to be shifted by 0.92 Å toward the void edge. The binding energy for the site CO₂ Tet in the middle of the void was calculated to be −32.9 kJ/mol, which is significantly smaller than the value found for the CO₂ Tet* site.

Further calculations were performed to investigate intermolecular interactions between guest molecules at close-lying binding sites determined from the diffraction experiments. In this context, the diffraction experiments are ambiguous, since it is uncertain whether adjacent partially occupied crystallographic sites are populated simultaneously. Three configurations of CO₂ Cu−−CO₂ Cu sites CO₂ Ph−−CO₂ Ph molecular pairs were considere...
Table 2. DFT Optimized Guest Geometries and Calculated Binding Energies for CO$_2$ and CH$_4$ in Local Fragments of Cu-1a

| Single guest geometry optimizations$^a$ | Pairwise guest geometry optimizations$^b$ |
|---------------------------------------|-----------------------------------------|
| **Full Fragment** | **Local Environment** | **Binding Energy$^c$ (kJ/mol)** | **Full Fragment** | **Local Environment** | **Binding Energy$^d$ (kJ/mol)** |
| ![DFT: CO$_2$$^{Cu}$ (pink); NPD: CO$_2$$^A$ (blue)](image) | ![DFT: CO$_2$$^{Cu}$ (blue) and CO$_2$$^{Ph}$ (pink)](image) | -27.9 (CO$_2$$^{S\text{O}_{2}}$) | -32.0 (CO$_2$$^{P\text{H}^{21}}$) |
| ![DFT: CO$_2$$^{Ph}$ (pink); NPD: CO$_2$$^B$ (yellow)](image) | ![DFT: CO$_2$$^{Cu}$ (blue) and CO$_2$$^{Ph}$ (pink)](image) | -28.0 (CO$_2$$^{P\text{H}_{22}}$) | -33.3 (CO$_2$$^{P\text{H}^{22}}$) |
| ![DFT: CO$_2$$^{Tet}$ (pink); NPD: CO$_2$$^C$ (green)](image) | ![DFT: CO$_2$$^{Cu}$ (blue) and CO$_2$$^{Ph}$ (pink)](image) | -32.9 (CO$_2$$^{T\text{e}^{10}}$) | -29.1 (CO$_2$$^{P\text{H}^{32}}$) |
| ![DFT: CH$_4$$^{Tet}$ (pink)](image) | ![DFT: H$_2$O$^{Cu}$ (red) and CO$_2$$^{Ph}$ (pink)](image) | -31.5 (CD$_4$$^{10}$) | -41.0 (CO$_2$$^{P\text{H}^{38}}$) |

$^a$ coordinated water (the O$_{H2O}$$^--$O$_{CO2}$ distance is 2.96 Å, and the O$^--$H$\cdot\cdot\cdot$O$_{CO2}$ angle is 150.7$^\circ$).

**CONCLUSIONS**

We report a detailed investigation into the permanent porosities and gas adsorption properties of a family of three MOPs constructed from {Cu}$^2$ paddlewheels and tripodally disposed tris-carboxylate ligands. The formation of stable, permanently porous molecular solids from MOPs is rare, as the materials are prone to structural collapse upon removal of reaction solvent from their void spaces. The order of decreasing structural resilience to solvent removal for the MOPs (Cu-1a > Cu-1b > Cu-2) has been rationalized by using Hirshfeld surfaces to analyze the supramolecular interactions which mediate their molecular packing. The most stable material, Cu-1a, has the highest density of the three, and its molecular packing is exclusively mediated by large regions of weak van der Waals interactions with a notable absence of any stronger $\pi$--$\pi$ or edge-to-face stacking interactions. The high uptake of CO$_2$ and CH$_4$ in permanently porous Cu-1a has been probed using a combination of IR spectroscopy, *in situ* neutron and X-ray diffraction, and DFT modeling of the experimentally elucidated host–guest binding interactions. The different types of voids in Cu-1a present a platform for comparing the contrasting binding preferences of these industrially and environmentally important gases. CO$_2$
shows a roughly equal propensity to bind at either an open metal site or a small tetrahedral void enclosed by phenyl rings, while CD₄ shows a preference for the latter site. It is interesting to note that packing coefficients of 0.33 and 0.28, respectively, for CO₂ and CH₄ in the small tetrahedral void (molecular volumes: CO₂, 34.0 Å³; CH₄, 28.5 Å³; small void, 102 Å³) are the closest matches in the structure to the optimum packing coefficient of 0.55 ± 0.009 suggested by Mercozzi and Rebek for guest binding inside receptor cavities. The use of multiple analytical techniques to probe the host–guest interactions in Cu-1a gives a validated structural insight into design features used commonly used to target CO₂ and CH₄ adsorption in porous MOP materials.

■ ASSOCIATED CONTENT

Supporting Information
The Supporting Information is available free of charge at https://pubs.acs.org/doi/10.1021/acs.inorgchem.0c01935. Experimental details for single-crystal structure refinements, powder diffraction data, DFT calculations, and supporting figures and tables (PDF)

Accession Codes
CCDC 1516122–1516130 contain the supplementary crystallographic data for this paper. These data can be obtained free of charge via www.ccdc.cam.ac.uk/data_request/cif, or by emailing data_request@ccdc.cam.ac.uk, or by contacting The Cambridge Crystallographic Data Centre, 12 Union Road, Cambridge CB2 1EZ, UK; fax: +44 1223 336033.

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Notes
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