An Ultramicroporous MOF with a High Concentration of Vacant Cu\(^{II}\) Sites

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Supporting Information

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Synthesis of $[\text{Cu}_3(\text{cdm})_4]$ 

K(cdm) was prepared according to a literature procedure.\(^1\) K(cdm) (240 mg, 1.63 mmol) was almost completely dissolved in methanol (30 mL) with the aid of sonication. To this was added a methanolic solution (3 mL) of anhydrous CuCl\(_2\) (216 mg, 1.61 mmol). Upon addition of the green CuCl\(_2\) solution, the remaining suspended K(cdm) was dissolved to give a deep orange solution. Dark orange crystals of solvated [Cu\(_3\)(cdm)\(_4\)] (173 mg, 0.252 mmol, 62% yield) formed on the walls of the reaction vessel over a period of two days. Elemental analysis calc. for Cu\(_3\)(C\(_4\)H\(_2\)N\(_3\)O)\(_4\)·2MeOH·1.5H\(_2\)O (C\(_{18}\)H\(_{19}\)N\(_{12}\)Cu\(_3\)O\(_{7.5}\)) : C, 30.28; H, 2.68; N, 23.54. Found: C, 29.99; H, 2.30; N, 23.59%. Powder diffraction confirms a phase-pure product (see powder diffraction section below). Thermogravimetric analysis (Figure S1) shows 12.5% weight loss before decomposition at ca. 230 °C, calculated 12.8% for loss of all solvent from Cu\(_3\)(C\(_4\)H\(_2\)N\(_3\)O)\(_4\)·2MeOH·1.5H\(_2\)O.

![Thermogravimetric plot](image.png)

**Figure S1:** Thermogravimetric plot of the as synthesized material.

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Single Crystal X-Ray Crystallography and Structure

A suitable single crystal was mounted on a fine glass fibre using viscous hydrocarbon oil. Data were collected using a Bruker X8 ApexII diffractometer equipped with graphite monochromated Mo-Kα radiation (\(\lambda = 0.71073\) Å). The data collection temperature was maintained at 123 K using an open-flow N₂ cryostream. Data reduction was carried out using the Bruker ApixII software suite.² The structure was solved by direct methods using SHELXS-2013.³ Refinement was carried out against \(F^2\) using SHELXL-2013.³ All non-hydrogen atoms were refined using an anisotropic model. Hydrogen atoms belonging to the amide group were placed in idealised X-ray positions and refined using a riding model. Solvent coordinated to the Cu(II) was modelled as 50:50 H₂O:MeOH. Due to the high symmetry and the constitutional disorder at this site the OH hydrogen atoms of the solvent could not be located and are not included in the model. TGA and microanalysis suggests the presence of interstitial solvent in the as-synthesised material. There is a small amount of residual unresolvable electron density in the small void spaces between the Cu(II) sites. This residual density could not be modelled or otherwise treated with crystallographic software.

Crystal data for [Cu₃(cdm)₄(H₂O)(MeOH)]: C₁₇H₁₃Cu₃N₁₂O₆, \(M = 672.01\), orange block, 0.140 × 0.120 × 0.120 mm³, \(P42d\) space group (No. 122), \(V = 2737.7(3)\) Å³, \(Z = 4\), \(D_c = 1.630\) g/cm³, \(F_{000} = 1336\), \(2\theta_{\text{max}} = 55.0^\circ\), 5238 reflections collected, 1561 unique (\(R_{\text{int}} = 0.0313\)). Final \(GooF = 1.119\), \(R1 = 0.0472\), \(wR2 = 0.1336\), \(R\) indices based on 1431 reflections with \(I > 2\sigma(I)\) (refinement on \(F^2\)), 90 parameters, 1 restraint, \(\mu = 2.363\) mm⁻¹.

Figure S2: The network has a self-penetrating $(8^2.10)_4(8^3.10^3)_2(8^5.10)$ topology (three-connecting cdm = green; square planar Cu(II) = yellow; tetrahedral Cu(I) = pink).
Neutron powder diffraction data were collected on the high-intensity neutron diffractometer, Wombat (OPAL, ANSTO, Australia).\(^4\) Prior to neutron powder diffraction measurement and gas dosing, 1.119 g of desolvated \([\text{Cu}_3(\text{cdm})_4]\) was transferred to a cylindrical vanadium can (internal diameter of \textit{ca.} 6 mm) inside a helium-filled glovebox equipped with water and oxygen monitors. The sample cell was connected to a custom-designed gas-delivery centrestick and inserted into a top-loading cryofurnace. Temperature control at the sample was achieved using cartridge heaters and silicon-diode temperature sensors at the top and bottom of the cell. The gas-delivery line was also temperature-controlled in order to avoid freezing CO\(_2\) inside the tube, so that the sample could be left in place throughout the experiment without the requirement of warming the entire cryofurnace between gas doses. An initial diffraction pattern was collected on the evacuated sample at 15 K to be used as a structural reference point from which subsequent data for the CO\(_2\)-dosed sample could be analysed (Figure S3). The sample was then warmed to 300 K prior to dosing with a known amount of CO\(_2\), before being slowly cooled to the measurement temperature of 15 K, all the while ensuring that the temperature was kept above the boiling/sublimation point of CO\(_2\) at the current pressure. By 150 K the pressure reading was zero, indicating that all CO\(_2\) had been absorbed by the sample. No evidence of frozen CO\(_2\) was observed in the diffraction patterns. The total cooling time was approximately 1 hour, with the intention of ensuring diffusion of the CO\(_2\) molecules to their thermodynamic equilibrium positions and minimising random disorder of guest molecules prior to the diffraction measurement. 30 minutes of diffraction data were acquired for each dose using an area detector in the angular range 17° < 2\(\theta\) < 137° with an incident neutron wavelength of 2.4145(3) Å, determined using an Al\(_2\)O\(_3\) standard reference material (NIST SRM 676). A correction was applied to the Debye-Scherrer ring curvature before data reduction.

Structure Refinement from NPD data

Rietveld analysis and difference Fourier analysis of the diffraction data was carried out using GSAS & EXPGUI, with a pseudo-Voigt peak shape and 16-term shifted Chebyshev background function. VESTA was used for visualization of the crystal structure and nuclear density isosurfaces. Following refinement of the guest-free structure, this was used together with the data from the CO$_2$-loaded sample to generate Fourier difference maps of residual nuclear density. CO$_2$ molecules were introduced to the refinement in the locations and orientations suggested by both this residual density and the DFT calculations (see below). Initially, the cdm ligand was treated as a rigid body, and the CO$_2$ molecules were restrained to be linear with C-O bond lengths around 1.16 Å. After the refinement converged under these conditions, the constraints/restraints were progressively removed. The CO$_2$ molecules modelled at site A in the final refined structures were somewhat bent, presumably an artefact of the static disorder, with O-C-O angles of 154° and 159° for the first and second doses, respectively. The O atoms for the CO$_2$ at site B could not be satisfactorily refined, apparently due to disorder of the guest.

![Rietveld refinement](image)

Figure S3: Rietveld refinement (red) against NPD data (black) for guest-free [Cu$_3$(cdm)$_4$] at 15 K.

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**Figure S4:** Rietveld model for guest-free [Cu$_3$(cdm)$_4$] shown with the NPD data for [Cu$_3$(cdm)$_4$]·1CO$_2$ at 15 K, highlighting the residual intensity (blue) from which the Fourier nuclear density map was calculated.

**Figure S5:** Rietveld refinement against NPD data for [Cu$_3$(cdm)$_4$]·1CO$_2$ at 15 K. Some of the intensity difference is presumed to relate to the O atoms of the CO$_2$ in site B, which could not be successfully refined.
## Tables of Neutron Refinement Parameters

**Table S1:** Expanded table of parameters from Rietveld refinements for guest-free and CO$_2$-loaded [Cu$_3$(cdm)$_4$].

<table>
<thead>
<tr>
<th>CO$_2$ dosed / CO$_2$: [Cu$_3$(cdm)$_4$]</th>
<th>Atom occupancy</th>
<th>Total CO$_2$ found / CO$_2$: [Cu$_3$(cdm)$_4$]</th>
<th>Nearest Cu…C distance / Å</th>
</tr>
</thead>
<tbody>
<tr>
<td>C O Avg. Site A Site B Site A Site B</td>
<td>C O</td>
<td>C O</td>
<td></td>
</tr>
<tr>
<td>0 0 0 0 0 0 0 0 0 0 0 0</td>
<td>0.35(5) 0.40(4) 0.37(6) 0.147(29) 1.04(13)</td>
<td>3.0465(5) 3.8788(4)</td>
<td></td>
</tr>
<tr>
<td>1.00</td>
<td>0.49(6) 0.37(5) 0.43(8) 0.55(6) 1.97(20)</td>
<td>3.0926(6) 3.8923(4)</td>
<td></td>
</tr>
</tbody>
</table>

**Table S2:** Details of the refined guest atoms in [Cu$_3$(cdm)$_4$]-1CO$_2$.

<table>
<thead>
<tr>
<th>Atom</th>
<th>Wyckoff position</th>
<th>Site occupancy</th>
<th>Fractional coordinates</th>
<th>Atomic displacement parameter (U$_{iso}$) / 10$^2$ Å$^2$</th>
</tr>
</thead>
<tbody>
<tr>
<td>C_A</td>
<td>8c</td>
<td>0.35(5)</td>
<td>x 0.5</td>
<td>0.1428(20) 2(2)</td>
</tr>
<tr>
<td>O_A</td>
<td>16e</td>
<td>0.40(4)</td>
<td>y 0.454(9)</td>
<td>0.1553(20) 6.5(26)</td>
</tr>
<tr>
<td>C_B</td>
<td>8d</td>
<td>0.147(29)</td>
<td>z 0.5067(23)</td>
<td>8.5(28)</td>
</tr>
</tbody>
</table>

**Table S3:** Details of the refined guest atoms in [Cu$_3$(cdm)$_4$]-2CO$_2$.

<table>
<thead>
<tr>
<th>Atom</th>
<th>Wyckoff position</th>
<th>Site occupancy</th>
<th>Fractional coordinates</th>
<th>Atomic displacement parameter (U$_{iso}$) / 10$^2$ Å$^2$</th>
</tr>
</thead>
<tbody>
<tr>
<td>C_A</td>
<td>8c</td>
<td>0.49(6)</td>
<td>x 0.5</td>
<td>0.1453(18) 1(2)</td>
</tr>
<tr>
<td>O_A</td>
<td>16e</td>
<td>0.37(5)</td>
<td>y 0.446(9)</td>
<td>0.1553(25) 11(6)</td>
</tr>
<tr>
<td>C_B</td>
<td>8d</td>
<td>0.55(6)</td>
<td>z 0.5342(32)</td>
<td>7(5)</td>
</tr>
</tbody>
</table>

**Table S4:** Unit cell parameters and Rietveld figures of merit for guest-free and CO$_2$-loaded [Cu$_3$(cdm)$_4$] at 15 K.

<table>
<thead>
<tr>
<th>Dose CO$_2$: [Cu$_3$(cdm)$_4$] /</th>
<th>Unit cell parameters</th>
<th>Residual (wRp)</th>
</tr>
</thead>
<tbody>
<tr>
<td>a / Å</td>
<td>c / Å</td>
<td>V / Å$^3$</td>
</tr>
<tr>
<td>0</td>
<td>11.21463(30)</td>
<td>21.5714(10)</td>
</tr>
<tr>
<td>1.00</td>
<td>11.2777(6)</td>
<td>21.3598(19)</td>
</tr>
<tr>
<td>2.00</td>
<td>11.2794(7)</td>
<td>21.337(22)</td>
</tr>
</tbody>
</table>
Figures of NPD Difference Maps and Refinements

**Figure S6:** Residual nuclear density found by difference Fourier analysis of NPD data for [Cu₃(cdm)₄]·1CO₂ (left) and [Cu₃(cdm)₄]·2CO₂ (right). In addition to the density at CO₂ adsorption sites A and B, some density is seen near the O atoms in a), but is too close to the O (< 1 Å) to be attributable to CO₂.

**Figure S7:** Rietveld refined structures of [Cu₃(cdm)₄]·1CO₂ (left) and [Cu₃(cdm)₄]·2CO₂ (right). Atom occupancies for the CO₂ molecules are reflected by the partially filled spheres.
Figure S8: Optimal CO$_2$ positions in [Cu$_3$(cdm)$_4$], determined by DFT energy minimisations. For comparison, shown in black are the atom positions experimentally determined from NPD of [Cu$_3$(cdm)$_4$]·CO$_2$. At site A, the distance between the CO$_2$ and the nearest Cu$^{ll}$ site is greater than that determined from NPD, presumably because no empirical correction was used to account for van der Waals interactions. The calculated orientation of the CO$_2$ at this site is highly consistent with the experimental results, with only a 9° difference in the rotation of the two orientations when viewed along the c axis. The calculated optimal CO$_2$ position at site B is centred exactly on the Rietveld-refined C atom.
Details of DFT Calculations of CO\textsubscript{2} Sites from NPD Data

All DFT calculations were performed using VASP 5.2 with the Perdew-Burke-Ernzerhof (PBE) generalised gradient approximation (GGA) functional, and Gaussian smearing of partial occupancies.

A constant temperature (NVT) molecular dynamics (MD) simulation was conducted at 200 K on one unit cell of Cu\textsubscript{3}(cdm)\textsubscript{4}·1CO\textsubscript{2} (with unit cell parameters taken from NPD results) with periodic boundary conditions, a plane wave energy cut-off of 300 eV, and a 1 fs time step. In the initial structure, three of the four CO\textsubscript{2} molecules in the unit cell were placed side-on to the Cu\textsuperscript{II} as indicated by the nuclear density found at adsorption site A in the NPD results. The fourth molecule was placed approximately end-on (C···O=C angle 147°; Cu···O distance 2.7Å), giving it the opportunity to adopt either arrangement. As the simulation proceeded, this end-on CO\textsubscript{2} molecule quickly adopted the side-on configuration, providing further evidence that this arrangement is the most stable. The simulation was then continued at 100 K for a further 25 ps (25 000 frames). The CO\textsubscript{2} molecules were observed to move back and forth between adsorption sites A and B with the atom positions at these sites very consistent with those determined using NPD. As they moved through the structure, the CO\textsubscript{2} molecules remained close to parallel to the channels, indicating the channels are too narrow for the molecules to flip end-over-end.

High precision energy minimisations were undertaken starting from the typical locations at the two sites that were observed in the MD simulation. A relatively high plane wave energy cut-off of 520 eV was used, together with a conjugate-gradient minimisation algorithm. The optimised positions of the CO\textsubscript{2} molecules at the two adsorption sites were found to be in good agreement with the experimental NPD results.

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**Gas Sorption Measurements**

Gas adsorption isotherms for pressures in the range of 0-1.2 bar were measured by a volumetric method using a Micromeritics ASAP 2420 instrument. Freshly prepared MOF samples were activated with scCO$_2$ at 40 and 150 Bar, with three filling and emptying cycles, the slow rate of these processes being paramount. The samples were then evacuated and held under a dynamic vacuum at $10^{-6}$ Torr for 24 h, and transferred to a pre-dried and weighed analysis tube contained in specially designed Schlenk glassware under a constant positive flow of argon atmosphere. Accurate sample masses were calculated using degassed samples. All adsorption measurements used ultra-high purity gases.

High pressure (100 bar) isotherms were undertaken on a PCTPro instrument using similar activation procedures, but did not reveal significant adsorption of hydrogen.

![Graph](image-url)

**Figure S9:** Comparison of adsorption kinetics of CO$_2$ at 273 K of [Cu(pma)$_2$], which has a typical adsorption profile for a Cu-based MOF, and [Cu$_3$(cdm)$_4$] highlighting the slow kinetics of [Cu$_3$(cdm)$_4$] resulting from the narrow channels.

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**Figure S10:** CO₂ adsorption enthalpy as calculated by the Van’t Hoff method. Oscillations can be related to the unusual adsorption mechanisms found in the material as a result of the ultramicroporosity.

**Figure S11:** (Left) Full low pressure isotherms for [Cu₃(cdm)₄]. (Right) The step-wise sorption at low pressure for methane, which prevents the determination of experimental enthalpy.
**Cavity Size and Uptake Calculations**

The static cavity size distribution was calculated using the geometric sizing algorithm using atomic coordinates from the single crystal data.\(^{10}\) There is a dominant cavity size of around 3.9 Å that represents the main channels. Using Molecular Dynamics (MD) with generic UFF the flexibility of the channel size was investigated over one nanosecond at 123 K with fixed cell volume. The window size was defined as the maximum size of a spherical probe allowed to pass through the structure.\(^ {11}\) Over the simulation time, the window size fluctuated around 3.5 Å, suggesting a size sieving mechanism between CO\(_2\) (kinetic diameter 3.3 Å) and CH\(_4\) (kinetic diameter 3.87 Å).

Hydrogen, methane and carbon dioxide adsorption isotherms were predicted using the GCMC routine with generic UFF force fields within the RASPA package, see snapshots in Figure S12. The shape, size and charge composition of CO\(_2\) is more favorable for adsorption within the cavity channels, resulting in twice as many CO\(_2\) molecules than CH\(_4\).

![Simulation snapshots](image)

**Figure S12**: Simulation snapshots during the gas loading of methane (left) and carbon dioxide (right).

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\(^{11}\) Haranczyk, M.; Rycroft, C. H.; Martin, R. L.; Willems, T. F. Zeo++ 0.1.0, 2012, Lawrence Berkeley National Laboratory, Berkeley.
Hydrogen, due to its light weight, is subject to quantum effects at low temperatures and sub-nm cavities. The Feynman-Hibbs correction term was added to the Lennard-Jones force field function for hydrogen which depends on temperature and molecular mass.\textsuperscript{12} As shown in Figure S13, quantum effects significantly reduce the uptake due to additional repulsive forces between hydrogen and the framework.

![Graph showing comparison of predicted H\textsubscript{2} uptake at 77 K with and without the consideration of the quantum Feynman-Hibbs potential.](image)

**Figure S13:** Comparison of predicted H\textsubscript{2} uptake at 77 K with and without the consideration of the quantum Feynman-Hibbs potential.

Experimental single gas isotherms were fitted with the dual Langmuir expression and then incorporated within the Ideal Adsorbed Solution Theory (IAST) to predict mixed gas isotherms of various compositions, see Figure S14.

Figure S14: a) Single gas isotherms at 273 K fitted with the dual Langmuir model for CO\textsubscript{2} (red) and CH\textsubscript{4} (blue). b) IAST predictions for mixed gas isotherms for various molar ratios CO\textsubscript{2}:CH\textsubscript{4}. b/c) Mixed gas CO\textsubscript{2}/CH\textsubscript{4} selectivity predictions calculated using IAST based on experimental single gas isotherms for various compositions found in industrial applications.