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Supporting Information

Highly selective CO₂ vs. N₂ adsorption in the cavity of a molecular

coordination cage

James S. Wright, Alexander J. Metherell, William M. Cullen, Jerico R. Piper, Robert Dawson and Michael D. Ward

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S1. Single-crystal X-ray diffraction study of [Co₈(L^w)₁₂](BF₄)₁₆·CS₂·5H₂O

Crystals of **[Co₈(L^w)₁₂](BF₄)₁₆** (host cage B) were prepared as published previously.^{S1} Individual crystals were removed from the methanol mother liquor and soaked in neat CS₂ at 40 °C for 2 hours.

A suitable crystal was then removed from the CS₂, coated with oil, and transferred rapidly to a stream of cold N₂ on the diffractometer (Bruker APEX-2) to prevent any decomposition due to solvent loss. Data were collected at 100 K and corrected for absorption using empirical methods (SADABS), based on symmetry-equivalent reflections combined with measurements at different azimuthal angles.^{S2,S3} Crystal structures were solved and refined against all F^2 values, using the SHELXTL program suite.^{S4}

The asymmetric unit contains one half of the cage either side of the inversion centre. Twelve of the required sixteen anions could be located from the data. The other four are presumably too badly disordered to locate, or even entirely absent due to deprotonation of the hydroxy methyl groups, thereby reducing the charge of the cation such that fewer counter anions are required. Accordingly, the calculated formula does not match the reported formula in which all 16 anions are accounted for.

Atoms in the anions that could be identified, and water molecules, were refined isotropically. All other atoms (host cage and guest) were refined anisotropically. The anions and CS₂ molecules also needed weak DFIX restraints to fix their geometry. SADI and FLAT commands were applied to keep the disordered hydroxy methyl groups of the ligands in chemically sensible positions; several of these were modelled as two parts over different orientations. The aromatic rings of the ligands were fixed with AFIX restraints (AFIX 66 for pyridine rings, AFIX 56 for pyrazolyl rings and AFIX 116 for naphthyl groups). Weak global restraints were applied to all C, N, O atoms of the ligands to achieve a more chemically reasonable model which refined stably (SIMU and DELU commands).

Hydrogen atoms were placed in calculated positions and refined using idealised geometries (riding model) and assigned fixed isotropic displacement parameters. The hydrogen atoms of the water molecules were not located from the data, but were included in the reported formula.

After the cage, anions and solvent molecules were located, a large solvent accessible void remained, in which disordered anions and solvent molecules resided. This region of diffuse electron density was removed with the SQUEEZE command on PLATON. Solvent Accessible Volume = 11863 Å³; Electrons found in S.A.V. = 3503. As there are four complete cage molecules in the unit cell this corresponds to *ca.* 900 electrons per cage complex, accounting for the missing anions plus numerous solvent molecules.

Crystal data for $[Co_8(L^w)_{12}](BF_4)_{16} \cdot CS_2 \cdot 5H_2O$ are summarised in table S1 below.

Table S1. Data collection, structure solution and refinement parameters for crystal structure of
[Co ₈ (L ^w) ₁₂](BF ₄) ₁₆ ·CS ₂ ·5H ₂ O

	[Co ₈ (L ^w) ₁₂](BF ₄) ₁₆ ·CS ₂ ·5H ₂ O
Source	Μο(Κα)
Crystal habitat	Block
Crystal colour	Orange
Crystal size (mm)	0.31 x 0.22 x 0.21
Crystal system	Monoclinic
Space group, Z	C2/c
a (Å)	27.523(4)
<i>b</i> (Å)	39.478(5)
c (Å)	42.338(7)
α (°)	90
β (°)	106.279(7)
γ (°)	90
V (Å3)	44159(12)
Density (Mg m ⁻³)	1.217
Temperature (K)	100(2)
$\mu_{(Mo-Ka)} (mm^{-1})$	0.392
Reflns collected	57443
Independent reflns (R _{int})	12916 (0.0520)
Reflns used in refinement, n	12916
LS parameters, p	1934
Restraints, r	2551
<i>R</i> 1(<i>F</i>), <i>l</i> >2.0σ(<i>l</i>)	0.1637
$wR2(F^2)$, all data	0.5147

S2. Powder X-ray diffraction studies

Powder X-ray diffraction data was collected to determine the crystallinity of the dried samples of [Cd₈(L^o)₁₂]·16BF₄ (A)^{S5} and [Co₈(L^w)₁₂]·xBF₄ (B),^{S1} after allowing the samples to dry at room temperature for at least a month.

Data were recorded using Cu–K α 2 radiation on a Bruker D8 ADVANCE X-Ray powder diffractometer operating in capillary mode. The samples were packed in 0.7 mm borosilicate capillaries. The instrument was fitted with a focusing Göbel mirror optic and a high-resolution energy-dispersive Lynxeye XE detector. The sample capillary was spun about its axis at a rate of 30 rev min⁻¹ during data collection to even exposure of the sample to the X-rays.

The data were compared to calculated X-ray powder diffraction patterns derived from the observed single-crystal X-ray diffraction data for the as-synthesised cages [Co₈(L^w)₁₂]·16BF₄·xMeOH and [Co₈(L^o)₁₂]·16BF₄·xMeOH. Where sufficient crystallinity existed, the patterns were indexed using the TOPAS Academic programme,^{S6} and then TOPAS was also used for the Pawley fitting^{S7} of data using the unit cells found from indexing as a starting point.

2.1 Crystallinity check on dried [Cd₈(L^o)₁₂]·16BF₄

This compound was prepared as described earlier.^{S5} Scans were collected between 2.5-30° 20 using a step size of 0.015° and step time of 240 sec, giving a total exposure time of *ca.* 10 hours. The pattern was indexed using the TOPAS programme,^{S6} but a unit cell similar to that found from single-crystal X-ray diffraction on **[Co₈(L°)₁₂]·16BF₄·yMeOH** could not be found.^{S7} A phase change may have taken place upon desolvation, leading to a material whose unit cell could not be determined by powder X-ray diffraction: however NMR and mass spectrometry characterisation confirms the presence of the cage.^{S5}



Figure S2. Observed (blue) powder XRD profile for the dried [Cd₈(L^o)₁₂]·16BF₄.

2.2 Crystallinity check on dried [Co₈(L^w)₁₂]·xBF₄

Scans were collected between 2.5-30° 2 θ using a step size of 0.015° and step time of 240 sec, giving a total exposure time of *ca*. 10 hours.

The pattern was indexed using the TOPAS programme,^{S6} and a unit cell was found similar to that found from single-crystal X-ray diffraction on $[Co_8(L^w)_{12}]$ ·xBF₄·yMeOH.^{S1} A Pawley refinement^{S7} employing 951 parameters (7 background, 1 zero error, 5 profile, 4 cell, 934 reflections), resulted in final indices of fit Rwp = 2.012, Rwp' = 7.141. A reflection at *ca*. 2 θ = 9.5° was not completely described by the Pawley fit, and persisted in other samples of the dried $[Co_8(L^w)_{12}]$ ·xBF₄ analysed, whose purity and composition were confirmed by ¹H NMR spectroscopy and mass spectrometry.^{S1}

 $[[Co_8(L^w)_{12}] \cdot xBF_4, C2/c: a = 27.834 (4) \text{ Å, } b = 39.612 (10) \text{ Å, } c = 42.603 (4) \text{ Å, } \beta = 107.179 (7)^\circ, V = 44877 (13) \text{ Å}^3].$



Figure S3. Observed (blue) and calculated (red) powder XRD profiles and difference plot [I_{obs} - I_{calc}] (grey) of the Pawley refinement. 20 fitting range 3.60 – 30.0 °, $d_{min} = 2.94$ Å.

S3. NMR titration

A 0.2 mM solution of **[Co₈(L^w)₁₂](BF₄)₁₆** in D₂O was prepared according to the previously published method.^{S1} A ¹H NMR titration to measure the binding constant of CS₂ in cage **[Co₈(L^w)₁₂](BF₄)₁₆** in water was performed according to the previously published method.^{S1,S8}

Data from the NMR titration is shown below (Figure S4). The CS₂ guest is in fast exchange; changes in the chemical shift for three signals of the host, as guest is added, were plotted and fitted to a 1:1 host:guest binding model (Figure S5; fitting these curves to a 1:1 binding isotherm afforded a binding constant of $K = 2 \text{ M}^{-1}$).



Figure S4. Shifts in the some of the 1H NMR signals of cage B during addition of portions of CS2



conc / mM

Figure S5. Fitting of the changes in chemical shifts for some of the signals in Fig. S4 to a 1:1 binding isotherm.

S4. Volumetric gas sorption measurements

Gas sorption measurements were performed using a Micromeritics ASAP 2020 Plus (Micromeritics Instrument Corporation, Norcross, USA) with high purity gases. Samples of around 100 mg were heated to 120 °C for at least 12 hours under dynamic vacuum before each gas sorption measurement was performed. Carbon dioxide and nitrogen isotherms were collected at 298 and 273 K over a pressure range of 1 – 1000 mbar. CO_2/N_2 selectivities were calculated either using the Henry's law method from the quantity adsorbed at low pressures or as an ideal selectivity based on the uptakes at 1 bar.



Figure S6. Volumetric gas sorption profiles for CO₂ and N₂ at 273 K for (left) cage **B** and (right) cage **A**. Filled circles represent adsorption and hollow circles represent desorption. CO₂ uptake profiles shown in purple (left) or black (right), N₂ uptake is shown in green. Data recorded at 298K is shown in the main text.



Figure S7. Expansion of the low-pressure regions of the volumetric gas adsorption profiles for CO₂ and N₂ at 298 K for (left) cage **B** and (right) cage **A**, used for determination of Henry's law selectivity constants (see Table 1, main text). CO₂ uptake profiles are shown in black, N₂ uptake is shown in red.



Figure S8 Expansion of the low-pressure regions of the volumetric gas adsorption profiles for CO₂ and N₂ at 273 K for (left) cage **B** and (right) cage **A**, used for determination of Henry's law selectivity constants (see Table 1, main text). CO₂ uptake profiles are shown in black, N₂ uptake is shown in red.

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