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Supporting Information

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High H_2 Adsorption in a Microporous Metal-Organic Framework with Open-Metal Sites

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H_2 Data and Langmuir Fit for MOF-505 after 25 ºC, 70 ºC, and 120 ºC Activations

For H_2 at supercritical conditions only a very small initial portion of the isotherm is being measured, thus the utility of determining and interpreting K values only applies within each individual system in question.

25 °C Activation

Pressure (torr)	Uptake (mg/g)	P/N (torr/mg/g)	Regressed P/N
0.00	0.00	-	8.65
11.5	1.73	6.66	9.36
44.2	4.29	10.31	11.37
59.6	4.93	12.08	12.32
133.0	7.57	17.56	16.83
166.5	8.28	20.10	18.90
215.6	9.41	22.92	21.92
270.7	10.16	26.64	25.31
382.5	11.53	33.19	32.19
468.7	12.28	38.16	37.50
506.6	12.65	40.05	39.83
662.0	13.60	48.68	49.39
767.1	14.10	54.41	55.86

70 °C Activation

Pressure (torr)	Uptake (mg/g)	P/N (torr/mg/g)	Regressed P/N
0.00	0.00	-	6.32
10.0	1.99	5.03	6.76
49.6	6.22	7.97	8.51
55.6	6.57	8.46	8.77
128.4	10.38	12.37	11.98
161.2	11.34	14.22	13.42
242.5	13.59	17.84	17.00
308.1	14.77	20.85	19.89
452.2	16.85	26.83	26.23
459.1	17.02	26.97	26.54
642.7	18.72	34.33	34.62
770.8	19.72	39.09	40.26

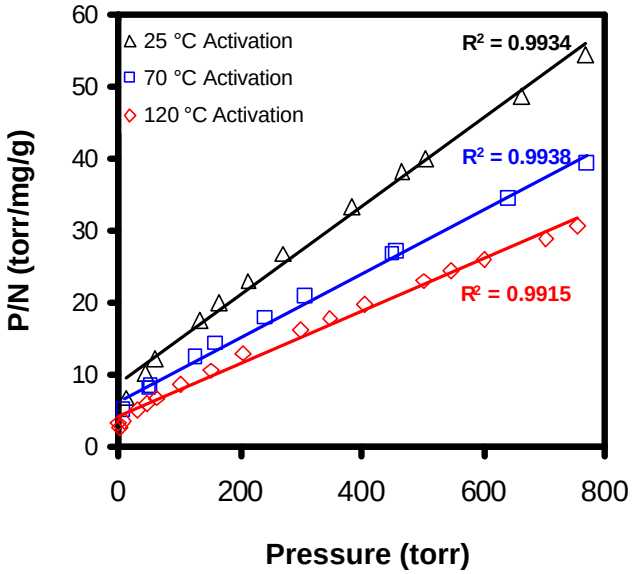
120 °C Activation

Pressure (torr)	Uptake (mg/g)	P/N (torr/mg/g)	Regressed P/N
0.00	0.00	-	4.23
0.995	0.31	3.26	4.26
4.689	1.69	2.78	4.40
9.600	2.77	3.47	4.58
32.3	6.25	5.17	5.40
48.4	8.11	5.97	5.99
62.6	9.20	6.80	6.51
101.7	11.77	8.64	7.93
152.3	14.28	10.66	9.78
205.3	15.96	12.86	11.71
300.7	18.49	16.26	15.18
350.3	19.62	17.85	16.99
405.1	20.47	19.79	18.98
502.9	21.95	22.91	22.54
548.5	22.61	24.26	24.20
603.1	23.20	26.00	26.19
702.6	24.27	28.96	29.82
753.8	24.70	30.52	31.68

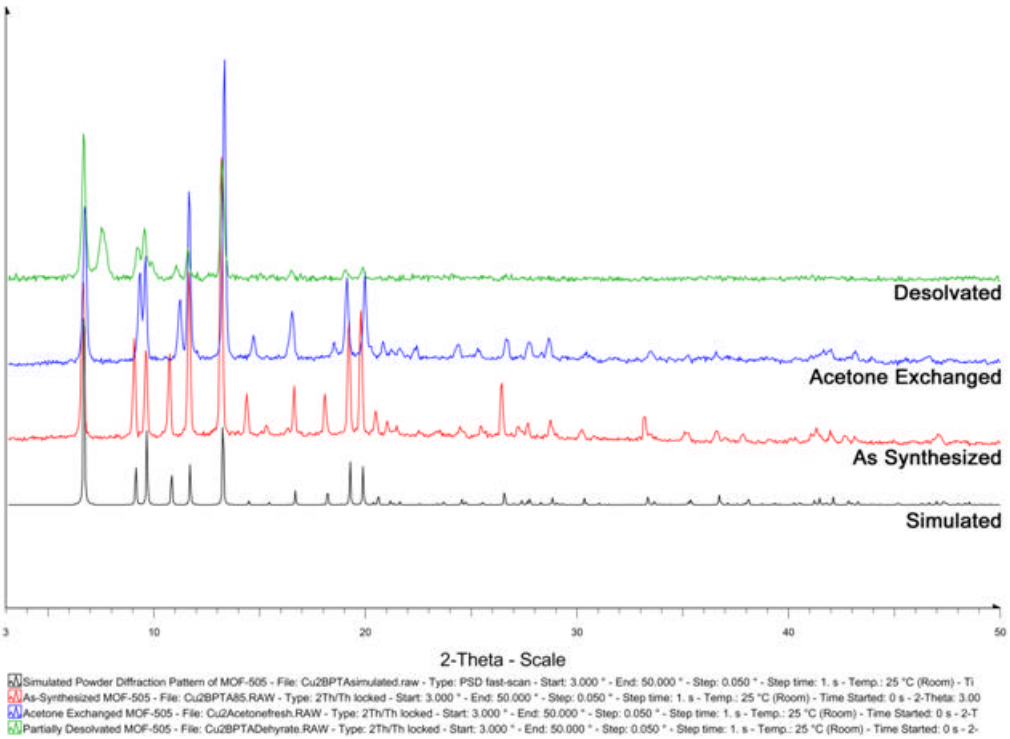
	K	N_m	R^2
25 °C	0.0071	16.2	0.9934
70 °C	0.0070	22.7	0.9938
120 °C	0.0086	27.5	0.9915

$$\frac{P}{N} = \frac{1}{N_m} P + \frac{1}{N_m * K}$$

$$K = \frac{1}{\text{intercept} * N_m} \qquad N_m = \frac{1}{\text{slope}}$$



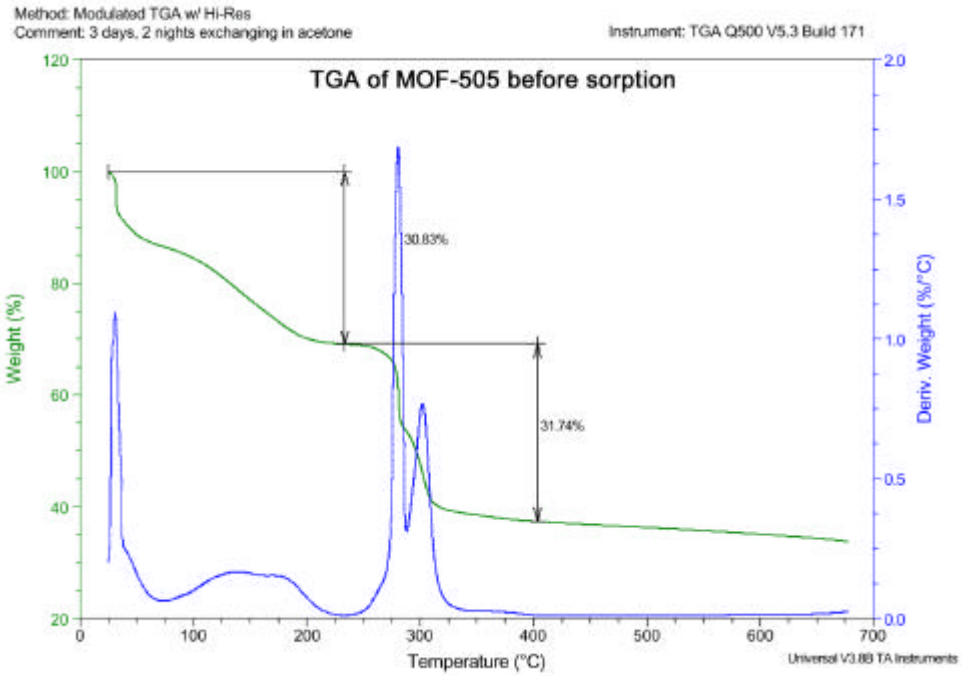
Powder X-ray Diffraction Studies on MOF-505:

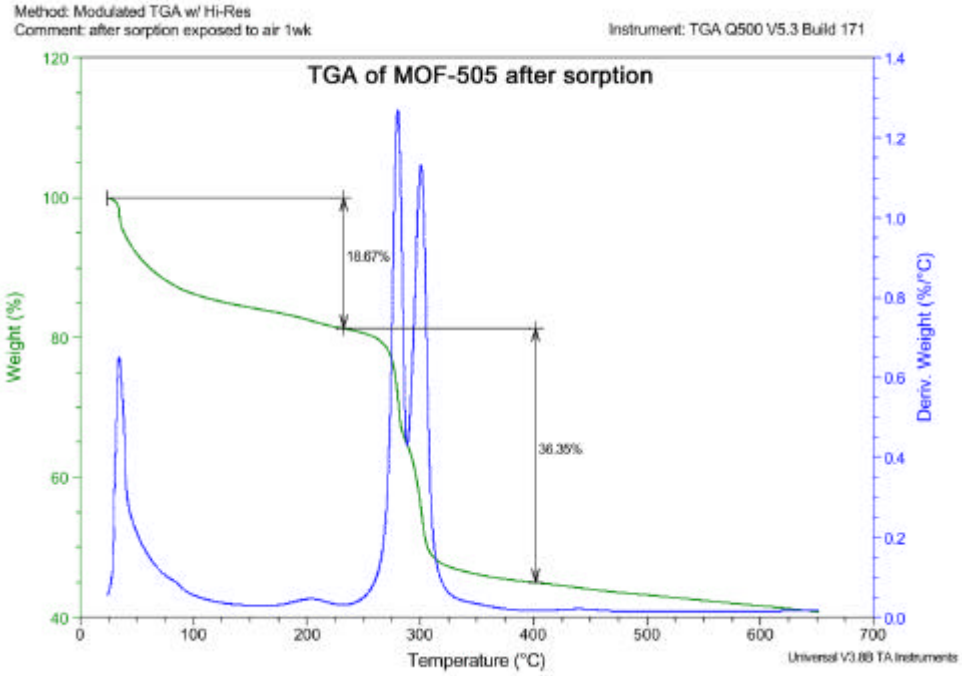


Observed PXRD		Simulated PXRD		Indices
2-Theta	**d**	**2-Theta**	**d**	**hkl**
6.526	13.5322	6.57	13.435	101
8.961	9.8605	9.03	9.781	012
9.530	9.2727	9.56	9.241	110
10.639	8.3084	10.73	8.238	003
11.568	7.6433	11.61	7.614	021
13.063	6.7718	13.17	6.717	202
14.289	6.1934	14.39	6.149	113
15.228	5.8136	15.36	5.764	104
16.529	5.3588	16.60	5.335	300
18.006	4.9226	18.12	4.891	024
19.101	4.6427	19.19	4.621	220
19.706	4.5016	19.81	4.478	033
20.391	4.3519	20.53	4.323	214
20.952	4.2366	21.11	4.205	205
21.384	4.1519	21.56	4.119	006
24.433	3.6402	24.49	3.632	321
25.416	3.5017	25.48	3.493	410
26.354	3.3792	26.52	3.359	404
28.711	3.1068	28.79	3.099	502

30.178	2.9590	30.30	2.948	235
33.160	2.6995	33.32	2.687	505
35.108	2.5540	35.34	2.538	603
36.570	2.4552	36.69	2.447	253
37.867	2.3740	38.08	2.361	0210
41.268	2.1859	41.46	2.176	526
41.952	2.1518	42.10	2.144	704
42.624	2.1194	42.83	2.110	437
47.083	1.9286	47.01	1.931	722

Thermal Gravimetric Analysis of MOF-505:





X-Ray Crystallography of MOF-505:

A blue block-shaped crystal (0.06 x 0.06 x 0.04 mm) of the title compound was mounted on a Bruker SMART APEX CCD diffractometer equipped with a normal focus Mo-target X-ray tube (λ = 0.71073Å) operated at 2000 W power (50kV, 40mA). The X-ray intensities were measured at 153(2) K. A total of 755 frames were collected with a scan width of 0.3º in ω and ϕ with an exposure time of 45 s/frame. The distance between the detector and crystal was 5.056 cm. The frames were integrated with the SAINT (v6.45A) software package with a narrow frame algorithm. The integration of the data in the rhombohedral cell yielded a total of 10057 reflections of which 2072 were unique and 1561 were greater than $2s(I)$. The range of q was from 1.00º to 27.58º and the final cell constants were based on the *xyz* centroids of 2794 reflections. Analysis of the data showed negligible decay during collection and absorption correction was performed using SADABS (v2.10). The structure was solved by direct methods and the subsequent difference Fourier syntheses and refined with the SHELXTL (v6.14) software package, using the rhombohedral space group R-3m with Z = 18. All non-hydrogen atoms of the extended structure except for solvent molecules were refined anisotropically. The structural model was refined with contributions from the disordered solvate molecules accounted for through use the SQUEEZE subroutine in the PLATON program suite. Final full matrix least-squares refinement on F^2 converged to $R1$ = 0.0361 ($F > 4sF$)) and wR2 = 0.0896 (all data) with GOF = 0.945.

Sheldrick, G. M. SHELXTL, v.6.10; Bruker Analytical X-ray, Madison, WI, 2000.

Sheldrick, G. M. SADABS. Program for empirical Absorption Correction of Area Detector Data, University of Göttingen: Göttignen, Germany, 1996.

SAINTPLUS, v.6.45A, Bruker Analytical X-ray, Madison, WI, 2003.

PLATON Van der Sluis, P.; Spek, A. L. *Acta Crystallogr., Sect. A: Found. Crystallogr.* **1990**, *A46*, 194-201.

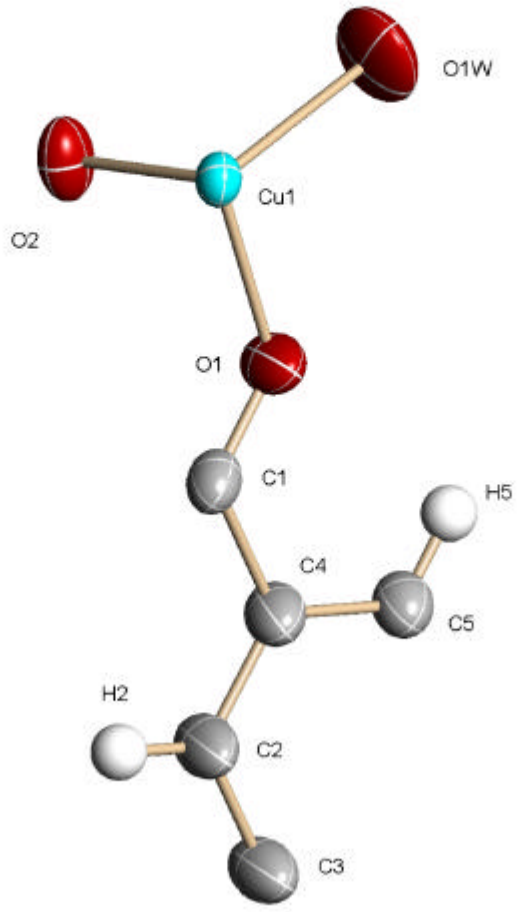
Special refinement and SQUEEZE details:

Difference electron density maps revealed the presence of disordered lattice solvate molecules which were ultimately modeled through the use of the SQUEEZE subroutine of the PLATON software suite. PLATON Reference: Spek, A. L. (1990), Acta Cryst.. A46, C-34. A sum total of 1 solvent accessible void per lattice was indicated comprising a total volume of 4416.8 $Å^3$ and contributing a total of 992 electrons. The void arises from diffuse scattering at -0.033, -0.025, -0.001 in the lattice and has been assigned as disordered dimethylformamide, ethanol, and water solvate molecules. These contributions have been included in all derived crystal quantities although the precise composition of the lattice solvate is somewhat speculative.

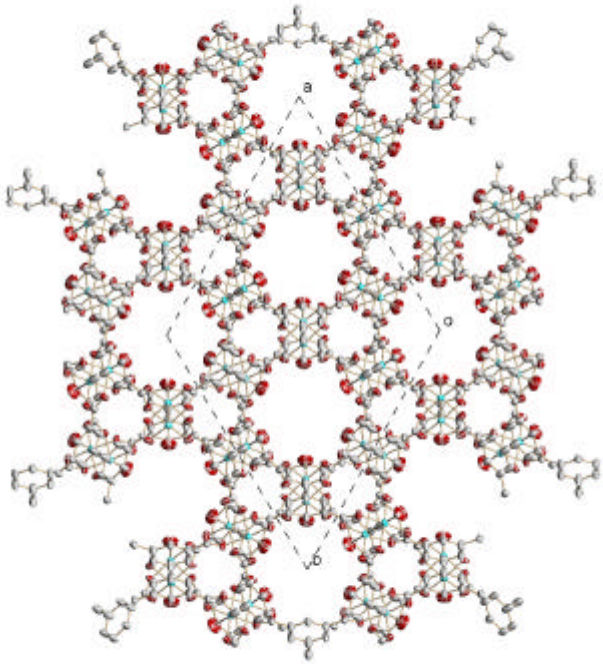
Refinement of F^2 against ALL reflections. The weighted R-factor wR and goodness of fit S are based on F^2, conventional R-factors R are based on F, with F set to zero for negative F^2.

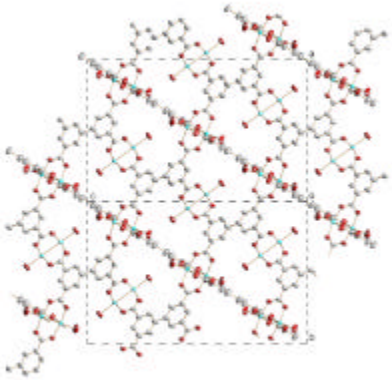
The threshold expression of $F^2 > 2\text{sigma}(F^2)$ is used only for calculating R-factors and is not relevant to the choice of reflections for refinement. R-factors based on F^2 are statistically about twice as large as those based on F, and R-factors based on ALL data will be even larger.

Asymmetric Unit of MOF-505 (50% thermal ellipsoids):



Packing of MOF-505 (50% thermal ellipsoids) hydrogen deleted for clarity:





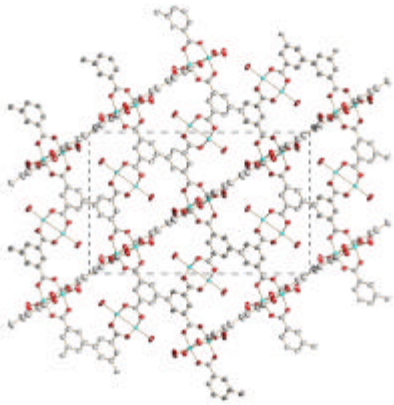


Table 1. Crystal data and structure refinement for MOF-505.

Identification code	MOF-505
Empirical formula	C8 H3 Cu O5
Formula weight	242.64
Temperature	153(2) K
Wavelength	0.71073 Å
Crystal system, space group	Rhombohedral, R-3m
Unit cell dimensions	a = 18.4826(8) Å alpha = 90°
	b = 18.4826(8) Å beta = 90°
	c = 24.713(2) Å gamma = 120°
Volume	7311.2(8) $Å^3$

Z, Calculated density	18, 0.992 Mg/m^3
Absorption coefficient	1.338 mm^{-1}
F(000)	2160
Crystal size	0.06 x 0.06 x 0.04 mm
Theta range for data collection	1.52 to 27.58º
Limiting indices	-7<=h<=24, -23<=k<=17, -30<=l<=32
Reflections collected / unique	10057 / 2072 [R(int) = 0.0488]
Completeness to theta = 27.58	99.9 %
Absorption correction	empirical and multi-scan
Max. and min. transmission	0.9484 and 0.9240

Refinement method	Full-matrix least-squares on F^2
Data / restraints / parameters	2072 / 0 / 70
Goodness-of-fit on F^2	0.945
Final R indices [I>2 s(I)]	R1 = 0.0361, wR2 = 0.0861
R indices (all data)	R1 = 0.0517, wR2 = 0.0896
Largest diff. peak and hole	0.549 and -0.269 e.Å^{-3}

Table 2. Atomic coordinates (x 10^4) and equivalent isotropic displacement parameters (Å^2 x 10^3) for MOF-505.

U(eq) is defined as one third of the trace of the orthogonalized

Uij tensor.

	x	y	z	U(eq)
Cu(1)	8573(1)	1427(1)	1229(1)	25(1)
O(1)	8146(1)	382(1)	1624(1)	45(1)
O(2)	7445(1)	1069(1)	970(1)	43(1)
C(1)	7837(2)	265(2)	2089(1)	37(1)

C(2)	7149(2)	-780(2)	2829(1)	51(1)
C(3)	6920(3)	-1540(1)	3074(2)	55(1)
C(4)	7583(2)	-559(2)	2345(1)	44(1)
C(5)	7793(2)	-1103(1)	2098(2)	41(1)
O(1W)	8971(1)	1029(1)	539(1)	81(1)

Table 3. Bond lengths [Å] and angles [°] for MOF-505.

Cu(1)-O(1)	1.9442(16)
Cu(1)-O(1)#1	1.9442(16)
Cu(1)-O(2)#1	1.9535(16)
Cu(1)-O(2)	1.9536(16)
Cu(1)-O(1W)	2.130(3)
Cu(1)-Cu(1)#2	2.6519(7)
O(1)-C(1)	1.253(3)
O(2)-C(1)#3	1.255(3)
C(1)-O(2)#3	1.255(3)
C(1)-C(4)	1.491(3)
C(2)-C(4)	1.383(3)
C(2)-C(3)	1.388(3)
C(2)-H(2)	0.9500
C(3)-C(2)#4	1.388(3)
C(3)-C(3)#5	1.514(7)
C(4)-C(5)	1.388(3)
C(5)-C(4)#4	1.388(3)
C(5)-H(5)	0.9500
O(1)-Cu(1)-O(1)#1	88.83(11)

O(1)-Cu(1)-O(2)#1	167.82(7)
O(1)#1-Cu(1)-O(2)#1	89.63(8)
O(1)-Cu(1)-O(2)	89.63(8)
O(1)#1-Cu(1)-O(2)	167.82(7)
O(2)#1-Cu(1)-O(2)	89.33(11)
O(1)-Cu(1)-O(1W)	95.60(8)
O(1)#1-Cu(1)-O(1W)	95.60(8)
O(2)#1-Cu(1)-O(1W)	96.58(8)
O(2)-Cu(1)-O(1W)	96.58(8)
O(1)-Cu(1)-Cu(1)#2	83.43(5)
O(1)#1-Cu(1)-Cu(1)#2	83.44(5)
O(2)#1-Cu(1)-Cu(1)#2	84.39(5)
O(2)-Cu(1)-Cu(1)#2	84.39(5)
O(1W)-Cu(1)-Cu(1)#2	178.64(9)
C(1)-O(1)-Cu(1)	123.74(15)
C(1)#3-O(2)-Cu(1)	122.09(16)
O(1)-C(1)-O(2)#3	126.3(2)
O(1)-C(1)-C(4)	116.7(2)
O(2)#3-C(1)-C(4)	117.0(2)
C(4)-C(2)-C(3)	121.0(2)
C(4)-C(2)-H(2)	119.5
C(3)-C(2)-H(2)	119.5
C(2)-C(3)-C(2)#4	118.6(3)
C(2)-C(3)-C(3)#5	120.69(17)

C(2)#4-C(3)-C(3)#5	120.68(17)
C(2)-C(4)-C(5)	119.9(2)
C(2)-C(4)-C(1)	120.6(2)
C(5)-C(4)-C(1)	119.6(2)
C(4)-C(5)-C(4)#4	119.7(3)
C(4)-C(5)-H(5)	120.2
C(4)#4-C(5)-H(5)	120.2

Symmetry transformations used to generate equivalent atoms:

#1 -y+1,-x+1,z #2 -x+5/3,-y+1/3,-z+1/3

#3 y+2/3,x-2/3,-z+1/3 #4 x,x-y-1,z

#5 -x+4/3,-y-1/3,-z+2/3

Table 4. Anisotropic displacement parameters (Å^2 x 10^3) for MOF-505.

The anisotropic displacement factor exponent takes the form:

-2 pi^2 [h^2 a*^2 U11 + ... + 2 h k a* b* U12]

	U11	U22	U33	U23	U13	U12
Cu(1)	27(1)	27(1)	28(1)	-1(1)	1(1)	17(1)
O(1)	63(1)	34(1)	48(1)	9(1)	17(1)	31(1)
O(2)	33(1)	56(1)	48(1)	-17(1)	-11(1)	27(1)
C(1)	34(1)	31(1)	51(1)	6(1)	5(1)	19(1)

C(2)	68(2)	37(2)	60(2)	16(1)	28(1)	35(1)
C(3)	73(3)	43(2)	60(2)	15(1)	30(2)	37(2)
C(4)	48(2)	33(1)	55(2)	11(1)	16(1)	25(1)
C(5)	41(2)	34(1)	50(2)	4(1)	9(2)	21(1)
O(1W)	111(2)	111(2)	51(2)	-17(1)	17(1)	77(2)

Table 5. Hydrogen coordinates (x 10^4) and isotropic displacement parameters (Å^2 x 10^3) for MOF-505.

	x	y	z	U(eq)
H(2)	7005	-406	2996	61
H(5)	8080	-960	1762	49

Table 6. Torsion angles [º] for MOF-505.

O(1)#1-Cu(1)-O(1)-C(1)	82.8(2)
O(2)#1-Cu(1)-O(1)-C(1)	0.0(5)
O(2)-Cu(1)-O(1)-C(1)	-85.2(2)
O(1W)-Cu(1)-O(1)-C(1)	178.3(2)
Cu(1)#2-Cu(1)-O(1)-C(1)	-0.77(19)
O(1)-Cu(1)-O(2)-C(1)#3	84.6(2)
O(1)#1-Cu(1)-O(2)-C(1)#3	1.8(5)
O(2)#1-Cu(1)-O(2)-C(1)#3	-83.3(2)
O(1W)-Cu(1)-O(2)-C(1)#3	-179.8(2)

Cu(1)#2-Cu(1)-O(2)-C(1)#3
1.12(19)
Cu(1)-O(1)-C(1)-O(2)#3
2.0(4)
Cu(1)-O(1)-C(1)-C(4) -
176.70(16)
C(4)-C(2)-C(3)-C(2)#4
1.1(7)
C(4)-C(2)-C(3)-C(3)#5 -
177.5(5)
C(3)-C(2)-C(4)-C(5)
0.2(5)
C(3)-C(2)-C(4)-C(1) -
179.1(3)
O(1)-C(1)-C(4)-C(2) -
172.4(3)
O(2)#3-C(1)-C(4)-C(2)
8.8(4)
O(1)-C(1)-C(4)-C(5)
8.4(4)
O(2)#3-C(1)-C(4)-C(5) -
170.4(3)
C(2)-C(4)-C(5)-C(4)#4
-1.5(6)

C(1)-C(4)-C(5)-C(4)#4

177.7(2)

Symmetry transformations used to generate equivalent atoms:

#1 -y+1,-x+1,z #2 -x+5/3,-y+1/3,-z+1/3

#3 y+2/3,x-2/3,-z+1/3 #4 x,x-y-1,z

#5 -x+4/3,-y-1/3,-z+2/3