Electronic Supplementary Material (ESI) for CrystEngComm.

Desolvation Process in the Flexible Metal-Organic Framework [Cu(Me-4py-trz-ia)], Adsorption of Dihydrogen and Related Structure Responses

Supporting Information

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Contents

1. MOF Synthesis

Synthesis of **1a** was performed in a similar way as reported in [1]. A steel autoclave with a Teflon vessel (PARR) was loaded with 32.4 mg (0.1 mmol) of the protonated ligand, H_2(Me-4py-trz-ia), 25.0 mg (0.1 mmol) $CuSO_4 \cdot 5\ H_2O$ and 5 ml of a 1:1 mixture of water/acetonitrile. After addition of 1 drop of 6 $mol \cdot l^{-1}$ hydrochloric acid the autoclave was sealed, heated to 140 °C and kept at this temperature for five hours. After cooling the autoclave slowly to room temperature during a period of 60 hours blue crystals of **1a** were filtered off, washed with water/acetonitrile and stored in this solvent mixture. After drying at the air the yield was 49.3 mg blue crystals of **1a**.

Solvent exchange procedures:

For **1b:** After the synthesis of crystals of **1a** the solvent was exchanged with methanol 5 times over a period of 5 days. Then the crystals of **1b** were kept in methanol.

For **1c**: After the synthesis of crystals of **1a** the solvent was exchanged continuously by Soxhlet extraction with unhydrous methanol for 5 days. Then the crystals of **1c** were kept in methanol.

2. Single crystal structure data

Table SI-1. Single crystal structure data of **1a**, **1b**, **1c** and **1e**.

Compound	**1a**	**1b**	**1c**[*2]	**1e**
crystal size / mm	0.38 · 0.27 · 0.24	0.14 · 0.12 · 0.08	0.10 · 0.07 · 0.07	0.16 · 0.10 · 0.08
formula	$C_{16}H_{12}N_4O_5Cu$	$C_{16}H_{12}N_4O_5Cu$	$C_{33}H_{24}N_8O_9Cu_2$	$C_{16}H_{10}N_4O_4Cu$
M / g·mol^{-1}	403.84	403.84	803.68	385.82
temperature / K	213(2)	213(2)	150(2)	150(2)
diffractometer	STOE IPDS-1	STOE STADIVARI	STOE STADIVARI	STOE STADIVARI
wavelength / pm	71.073	154.186	154.186	154.186
crystal system	monoclinic	monoclinic	monoclinic	monoclinic
space group	$P2_1/c$ (no. 14)	$P2_1/c$ (no. 14)	Pc (no. 7)	$P2_1/c$ (no. 14)
unit cell parameters / pm, °	a = 1425.1(2) b = 1339.9(2) c = 1463.7(2) β = 93.001(11)	a = 1386.63(4) b = 1323.50(4) c = 1502.41(4) β = 93.199(2)	a = 1371.36(4) b = 1322.70(5) c = 1517.95(5) β = 93.415(3)	a = 1355.18(4) b = 1391.61(4) c = 1482.83(4) β = 90.716(3)
volume / 10^6 pm^3	2790.9(7)	2752.9(1)	2748.5(2)	2796.2(1)
Z	4	4	2	4
density / g·cm^3	0.961	0.974	0.971	0.916
absorption coefficient μ / mm^{-1}	0.804	1.326	1.313	1.262
θ range / °	2.5 – 27.0	4.4 – 70.0	4.4 – 70.0	4.4 – 70.5
number of measured reflections	23693	29057	24796	33399
number of independent reflections	6048	5133	6716	5258
number of observed reflections	3520	3605	5142	3932
R_{int}	0.0576	0.0456	0.0493	0.0502
parameters	244	244	473	229
R_1	0.0324*[1]	0.0556*[1]	0.0440*[1]	0.0593
wR_2	0.0740*[1]	0.1965*[1]	0.1166*[1]	0.1772
max. / min. residual e$^-$ density / 10^{-6} pm^{-3}	0.35 / -0.25	0.40 / -0.64	0.47 / -0.46	1.00 / -0.71

*[1] The PLATON/SQUEEZE-routine[4] was applied.

*[2] Refined as an inversion twin. Absolute structure parameter: 0.41(6).

3. Powder X-ray diffraction (PXRD)

The PXRD measurements were carried out on a STOE STADI-P diffractometer using Cu-$K_{\alpha 1}$ radiation (λ = 154.060 pm). The samples for these measurements were prepared in capillaries (outer diameter 0.5 mm). Activated samples were handled under inert conditions. The powder diffraction patterns were processed with WinXPow.[6] Indexing of the diffraction patterns was performed using EXPO2014 via the program N-TREOR09.[7] Subsequently, the selected unit cells were tested and refined with the Pawley method in TOPAS.[8]

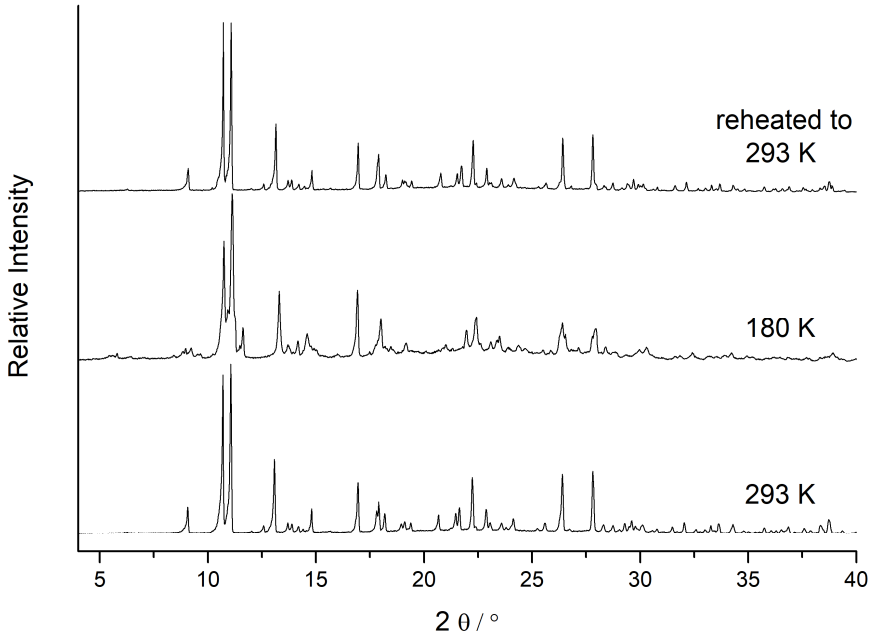


Figure SI-1. To demonstrate the influence of temperature powder diffraction patterns of an as-synthesized sample of **1a** were collected at 293 K, at 180 K and after warming up again to 293 K. Changes of the diffraction pattern at 180 K (e.g., peak splitting at 2Θ = 8°, additional peak at 2Θ = 11.5°) indicate reversible temperature-dependent structural changes of the as-synthesized material. This behaviour prevented a successful single crystal structure analysis at 180 K.

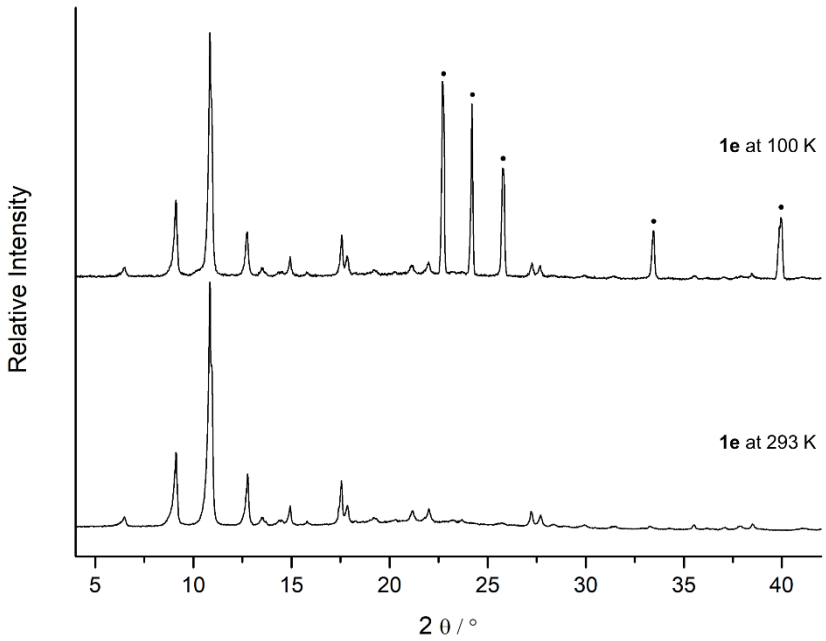


Figure SI-2. The PXRD pattern of the fully desolvated phase **1e** at 100 K is identical to that measured at room temperature, indicating no structural changes of the empty framework at lower temperatures. The additional peaks at 100 K (marked with black dots) belong to ice crystals that started to form at the outer wall of the glass capillary while cooling.

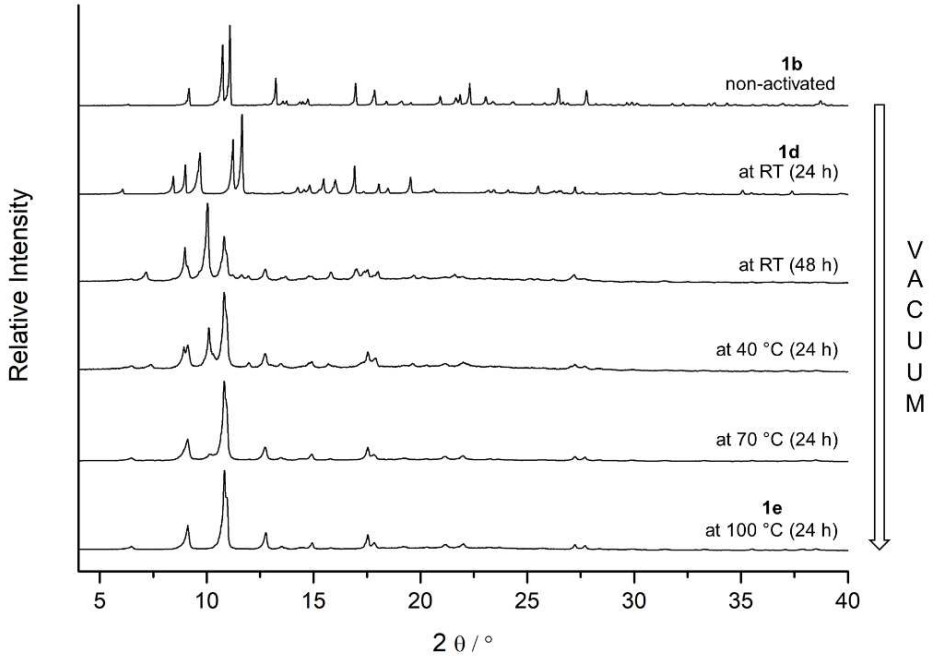


Figure SI-3. Room temperature X-ray powder diffraction patterns of sample **1b** (incomplete solvent exchange with methanol; pores are filled with methanol, two water molecules coordinating to Cu1) and after activation under vacuum at various temperatures or for different periods. The remaining water molecules at the Cu^{II} centres after removal of the non-coordinating solvent molecules from the pores cause the formation of the quite stable phase **1d** during activation in vacuum. Therefore, elevated temperatures or longer periods of activation are needed to obtain the fully desolvated phase **1e**. Since both **1a** and **1b** have to pass phase **1d**, they show similar structural transformations under vacuum. Such a behaviour is also observed for sample **1c** when exposed to humidity prior to activation.

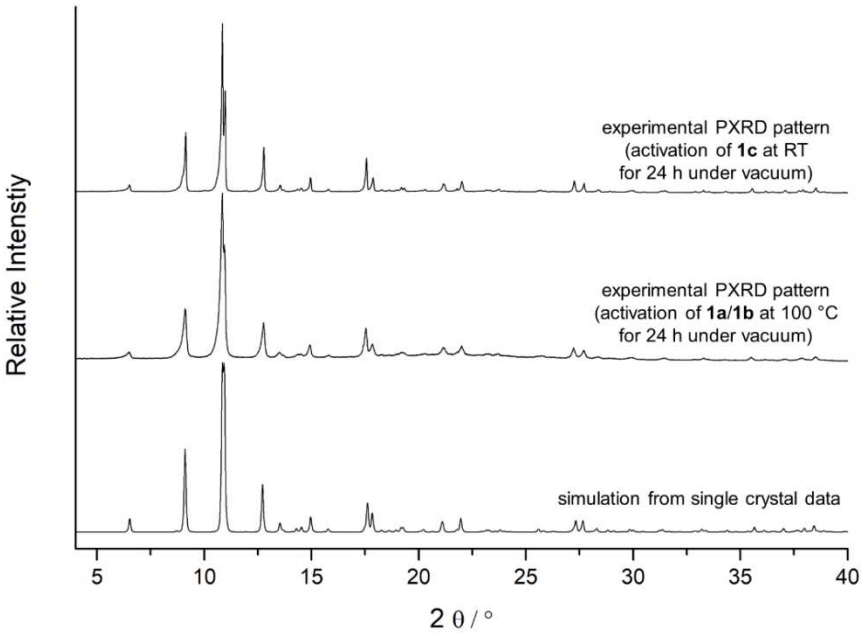


Figure SI-4. Comparison of the XRD pattern simulated from single crystal data of **1e** (a small crystal of **1e** was activated under vacuum at RT) (bottom) and experimental PXRD patterns of **1e** after activation of **1a**/**1b** for 24 h at 100 °C under vacuum (middle) and after activation of **1c** for 24 h at RT under vacuum (top). The peak at ca. 11° consists of two reflections, -1-11 and 111. Due to crystal fragmentation that occurs when activated along path A peaks are noticeably broader, -1-11 and 111 reflections are overlapping. When activated along path B (after Soxhlet extraction with methanol) the peaks are sharper and better resolved.

Table SI-2. Unit cell parameters and agreement factors of **1e** from indexing and subsequent Pawley refinement of PXRD pattern of an activated powder sample of **1b** (for 24 h under vacuum at 100 °C) and from single crystal structure analysis of an activated small crystal of **1e**.

Compound	**1e**	**1e**
Method	Pawley refinement	Single crystal analysis
Temperature	293 K	150 K
Space group	$P2_1/c$ (no. 14)	$P2_1/c$ (no. 14)
a / pm	1354.8(1)	1355.18(4)
b / pm	1383.9(1)	1391.61(4)
c / pm	1485.2(1)	1482.83(4)
β / °	90.928(3)	90.716(3)
V / 10^6 pm^3	2784.2(4)	2796.2(1)
Z	-	4
R_{int}	-	0.0502
R_1	-	0.0593
wR_2	-	0.1710
R_P	0.0322	-
R_{wp}	0.0422	-

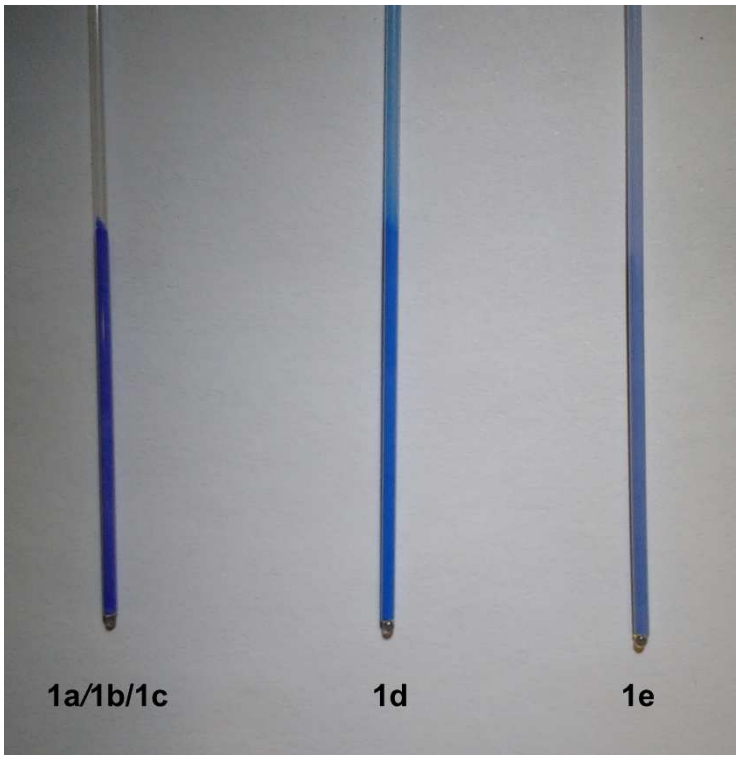


Figure SI-5. Comparison of the colours of the different samples of **1**. Air-dried samples **1a**, **1b** and **1c** showing the same shade of blue (left), partially activated **1d** (middle) and fully activated sample **1e** (right).

4. Structure determination of 1d from powder diffraction data

Space group determination and structure solution were performed with EXPO2014.[7] A reasonable structure model could be obtained by the simulated annealing approach in the space group $P2_1$ using the derived lattice parameters from the indexing procedure. Assuming symmetry reduction, for the starting structure model two linker molecules and two copper ions were given as fragments. Since the activation is obviously not completed at this stage two water molecules were added as fragments to the starting model. Torsion angles of the linker molecules were not restrained during this process. The obtained structure model was refined by the Rietveld method using TOPAS.[8] In the course of refinement the linker molecules were treated as rigid bodies using the Z-matrix notation allowing translation of the molecules and rotation of the phenyl and pyridine rings at the triazole group as well as the carboxylate groups at the phenyl ring (torsion angles to be refined freely). Atomic positions of the copper ions and the water molecules were not constrained/restrained during the refinement.

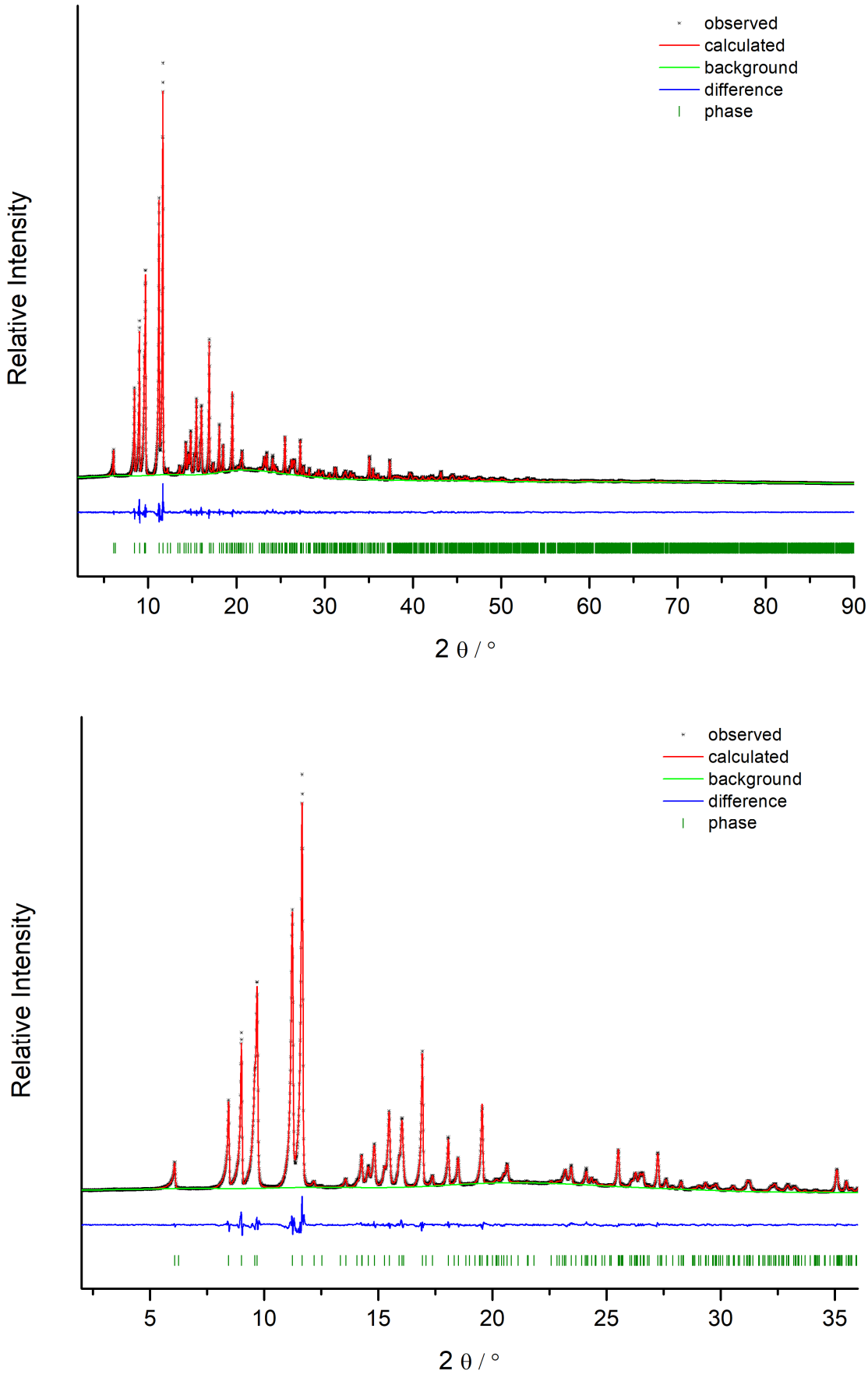
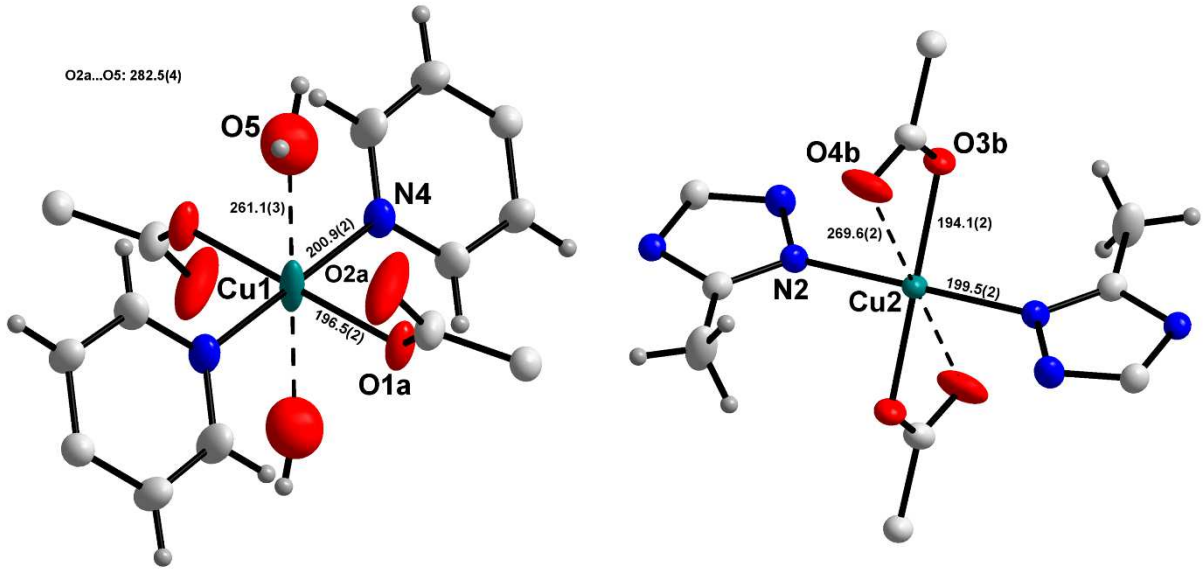
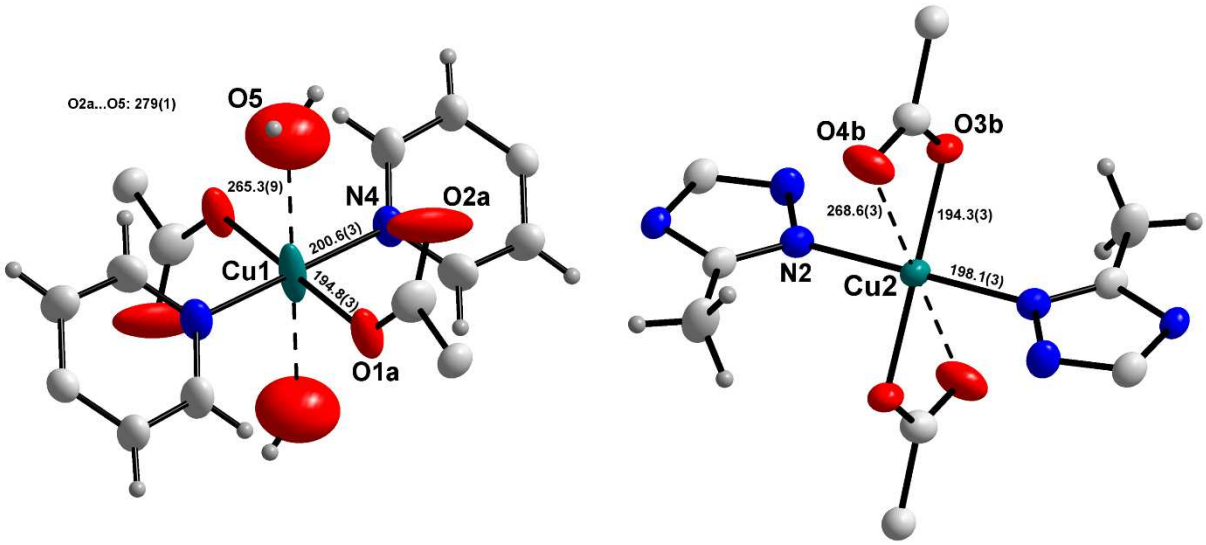


Figure SI-6. Rietveld refinement of phase **1b**. Space group $P2_1$ (no. 4); a = 1454.93(3) pm, b = 1193.95(1) pm, c = 1415.17(3) pm, β = 93.6939(5)°; Z = 2; V = 2453.20(7) 10^6 pm^3; R_p = 0.0286, R_{wp} = 0.0379).

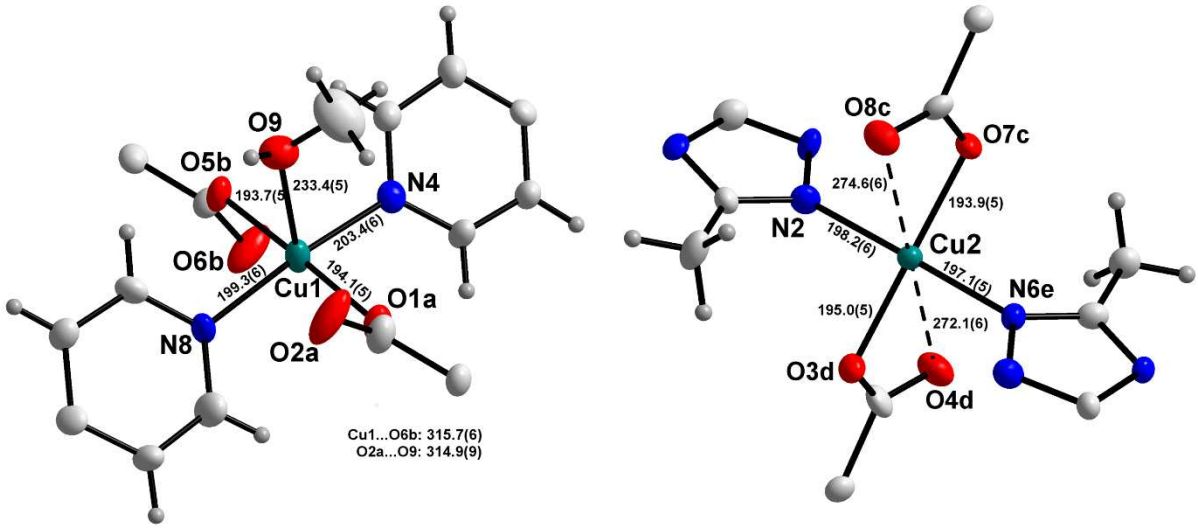
5. Coordination modes of the Cu^{2+} centres Cu1 and Cu2



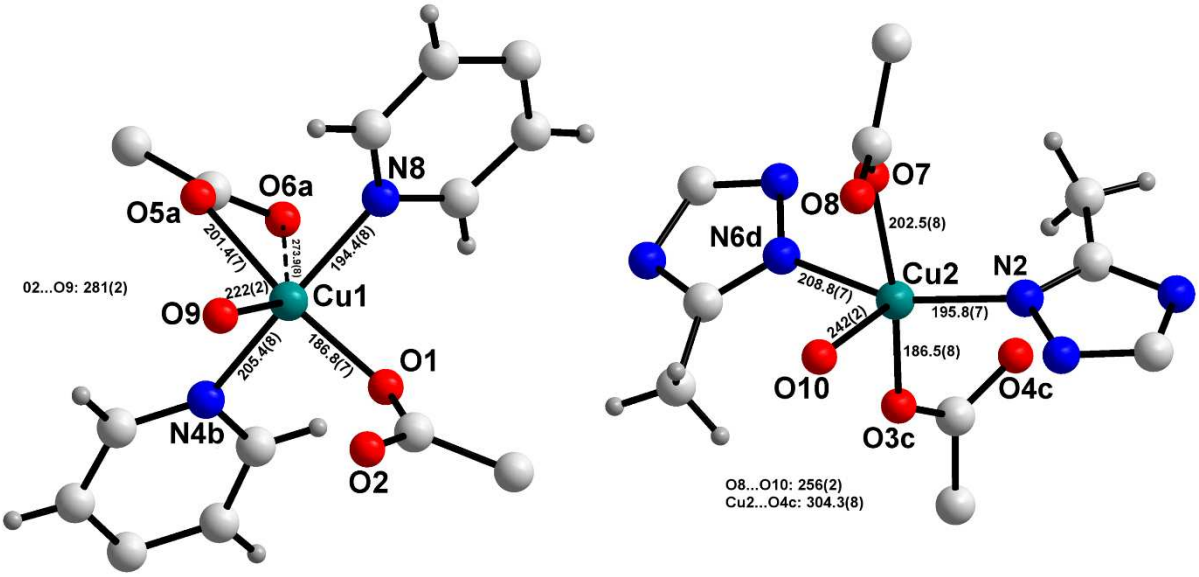
(a) **1a** (single crystal data). Symmetry codes: a: 1-x, -0.5+y, 0.5-z; b: -x, -0.5+y, 0.5-z.



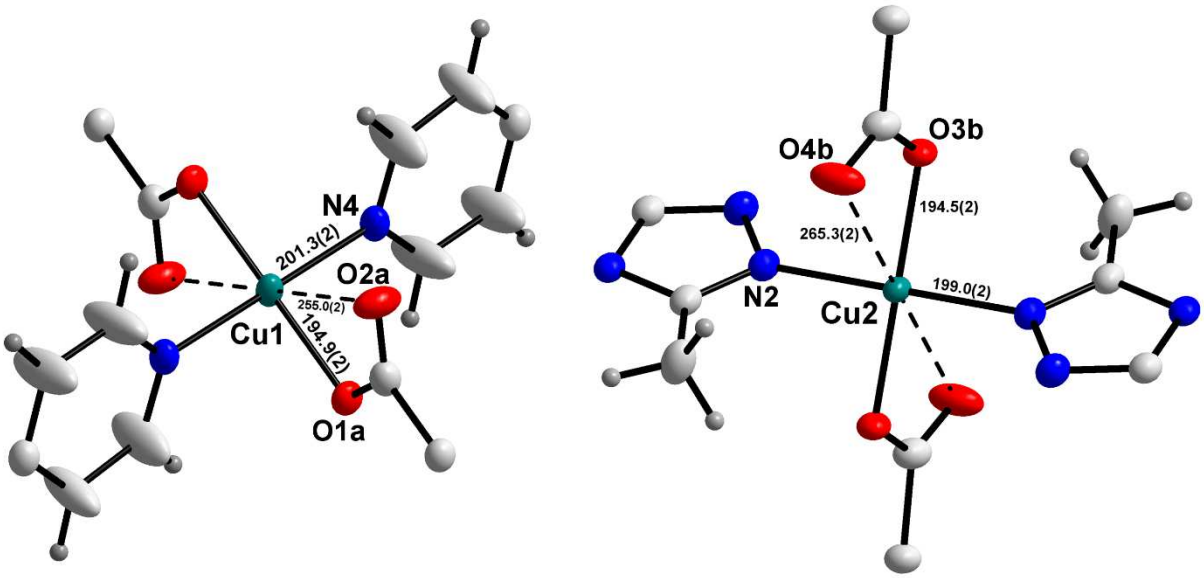
(b) **1b** (single crystal data). Symmetry codes: a: 1-x, -0.5+y, 0.5-z; b: -x, -0.5+y, 0.5-z.



(c) **1c** (single crystal data). Symmetry codes: a: x, 1-y, 0.5+z; b: x, -y, -0.5+z; c: -1+x, -y, -0.5+z; d: x, 1-y, -0.5+z; e: -1+x, y, -1+z.



(d) **1d** (powder data). Symmetry codes: a: -x, -0.5+y, 1-z; b: -x, -0.5+y, -z; c: 1-x, 0.5+y, -z; d: 1-x, 0.5+y, 1-z.



(e) **1e** (single crystal data). Symmetry codes: a: 1-x, -0.5+y, 0.5-z; b: -x, -0.5+y, 0.5-z.

Figure SI-7. Fragments of the crystals structures of **1a** -**1e** showing the coordination environment of the copper atoms. The ellipsoids drawn for the structures of **1a**, **1b**, **1c** and **1e** represent 50% probability.

6. Temperature dependent PXRD patterns

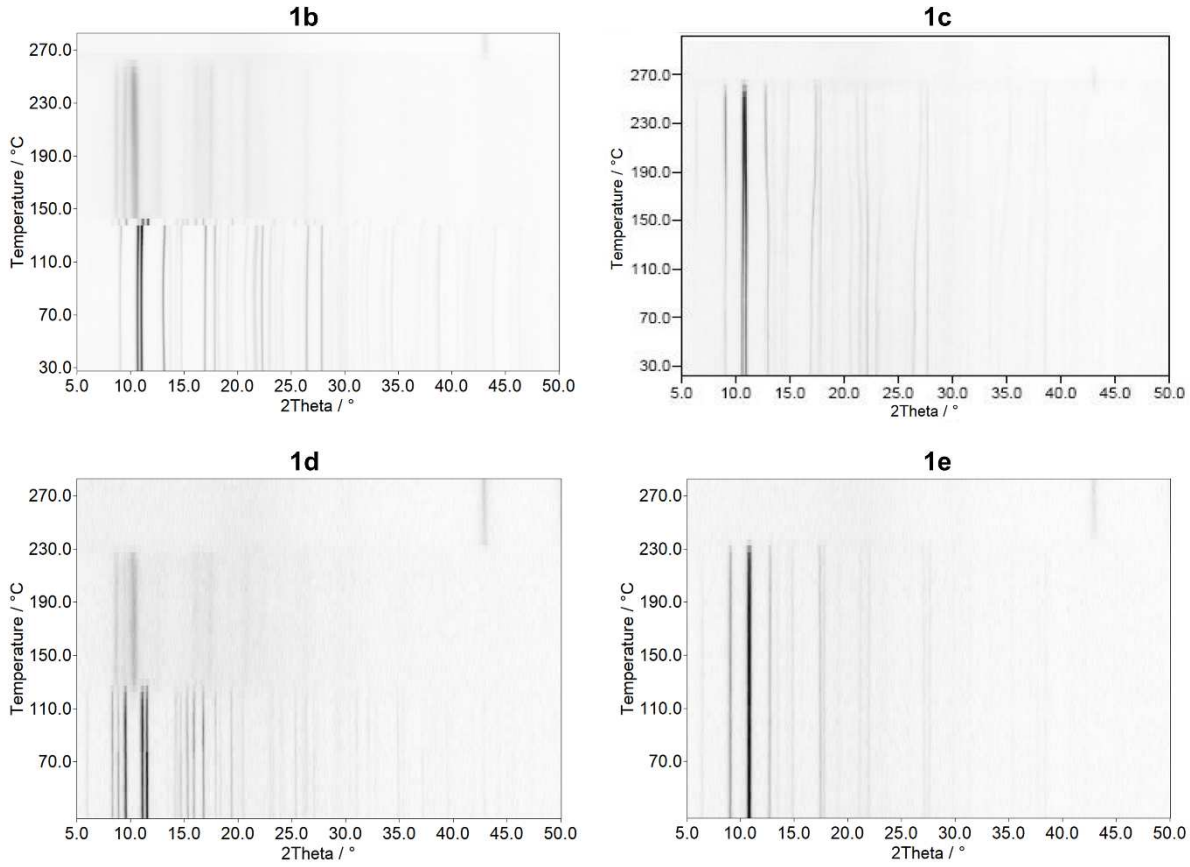


Figure SI-8. Temperature-dependent PXRD patterns of samples **1b**, **1c**, **1d** and **1e**. The diagram for **1b** indicates the formation of phase **1d** at ca. 140 °C, which quickly transforms to a high-temperature phase, while the diagram for **1c** shows a continuous cell transformation from **1c** to the fully desolvated material **1e**. This is in agreement with the observed behaviour under vacuum. [The reason for the higher thermal stabilities of samples **1b** and **1c** in comparison to that of **1d** and **1e** is not fully understood yet.]

7. DFT calculations

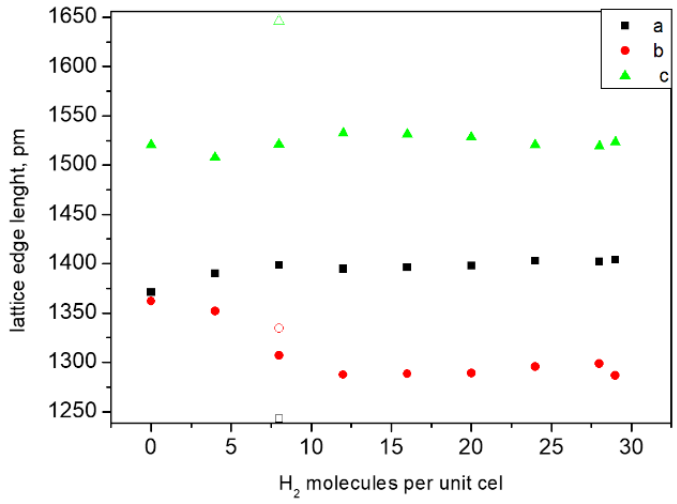


Figure SI-9. Unit cell parameter response (DFT simulations) upon H_2 loading (filled symbols) and H_2O chemisorbed at Cu1 and Cu2 sites (open symbols).

Table SI-3. Comparison of the unit cell parameters of the simulated structures.

	Simulated empty framework	Simulated structure with 2 H_2O at Cu1	Simulated structure with 2 H_2O each at Cu1 and Cu2	Simulated structure with 1 H_2O each at Cu1 and Cu2	Simulated structure with 1 H_2O each at Cu1 and Cu2	Simulated structure with 29 H_2 in unit cell
Space group	$P2_1/c$	$P2_1/c$	$P2_1/c$	$P2_1$	$P1$	$P1$
a / pm	1371.2	1389.6	1242.6	1484.2	1485.8	1404.0
b / pm	1361.9	1306.6	1334.3	1197.0	1196.5	1286.6
c / pm	1520.3	1541.4	1646.0	1396.1	1394.7	1523.2
α / °	-	-	-	-	90.00	90.00
β / °	92.31	94.00	93.39	94.26	94.27	93.29
γ / °	-	-	-	-	90.00	90.00
V / 10^6 pm^3	2836.9	2791.7	2724.5	2473.5	2472.5	2747.0

CIFs of simulated structures:

Simulated empty framework:

```
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_symmetry_space_group_name_H-M    'P2₁/c'
_symmetry_Int_Tables_number       14
_symmetry_cell_setting
monoclinic
loop_
_symmetry_equiv_pos_as_xyz
  x,y,z
  -x,y+1/2,-z+1/2
  -x,-y,-z
  x,-y+1/2,z+1/2
_cell_length_a                    13.7121
_cell_length_b                    13.6194
_cell_length_c                    15.2034
_cell_angle_alpha                 90.0000
_cell_angle_beta                  92.3109
_cell_angle_gamma                 90.0000
loop_
_atom_site_label
_atom_site_type_symbol
_atom_site_fract_x
_atom_site_fract_y
_atom_site_fract_z
Cu1 Cu 0.5 0 0.5
Cu2 Cu 0 0 0
O1 O 0.42225 0.41761 0.07864
O2 O 0.36956 0.56788 0.11997
O3 O 0.05991 0.42636 0.40359
O4 O 0.12695 0.57254 0.36656
N1 N 0.15422 0.18561 0.16648
N2 N 0.0882 0.06842 0.08655
N3 N 0.15305 0.02483 0.14308
N4 N 0.40289 0.02963 0.4004
C1 C 0.3649 0.47656 0.12069
C2 C 0.2863 0.42486 0.17087
C3 C 0.2598 0.32776 0.1495
C4 C 0.18281 0.28355 0.19252
C5 C 0.13336 0.33249 0.25833
C6 C 0.16176 0.4288 0.2814
C7 C 0.2366 0.47518 0.23632
C8 C 0.11307 0.48283 0.35555
C9 C 0.02236 0.23702 0.05292
C10 C 0.08734 0.16515 0.09973
C11 C 0.19426 0.09568 0.19204
C12 C 0.26762 0.07689 0.26286
C13 C 0.2983 0.14771 0.32585
C14 C 0.36515 0.12072 0.39323
C15 C 0.37574 0.96161 0.33952
C16 C 0.30845 0.98175 0.27064
H1 H 0.29859 0.28798 0.09925
H2 H 0.0741 0.29689 0.29214
H3 H 0.25616 0.55103 0.25244
H4 H 0.04609 0.31272 0.06696
H5 H 0.94733 0.22591 0.0748
H6 H 0.02246 0.22239 0.98169
H7 H 0.27053 0.22263 0.32425
H8 H 0.38915 0.1727 0.44431
H9 H 0.41022 0.88964 0.34717
H10 H 0.28701 0.92466 0.22331
```

Simulated structure with 2 H_2O at Cu1 in $P2_1/c$:

```
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_symmetry_Int_Tables_number       14
_symmetry_cell_setting
monoclinic
loop_
_symmetry_equiv_pos_as_xyz
  x,y,z
  -x,y+1/2,-z+1/2
  -x,-y,-z
  x,-y+1/2,z+1/2
_cell_length_a                    13.8955
_cell_length_b                    13.0655
_cell_length_c                    15.4143
_cell_angle_alpha                 90.0000
_cell_angle_beta                  93.9945
_cell_angle_gamma                 90.0000
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_atom_site_label
_atom_site_type_symbol
_atom_site_fract_x
_atom_site_fract_y
_atom_site_fract_z
Cu1 Cu 0.5 0 0.5
Cu2 Cu 0 0 0
O1 O 0.40386 0.44855 0.07927
O2 O 0.36655 0.5994 0.14375
O3 O 0.06057 0.4301 0.4038
O4 O 0.12645 0.58522 0.37726
N1 N 0.15641 0.19411 0.16481
N2 N 0.09038 0.07157 0.08524
N3 N 0.15446 0.02634 0.14294
N4 N 0.40728 0.03423 0.39857
C1 C 0.35676 0.50502 0.13069
C2 C 0.28077 0.44714 0.1776
C3 C 0.25629 0.34639 0.15255
C4 C 0.1827 0.29605 0.19303
C5 C 0.13406 0.34254 0.25913
C6 C 0.16063 0.44214 0.28604
C7 C 0.23271 0.49459 0.24414
C8 C 0.11291 0.49259 0.36098
C9 C 0.0275 0.24759 0.04791
C10 C 0.09031 0.17255 0.09728
C11 C 0.19559 0.10044 0.19172
C12 C 0.26942 0.08156 0.26265
C13 C 0.29512 0.15328 0.32866
C14 C 0.36381 0.12636 0.39528
C15 C 0.38452 0.96518 0.33528
C16 C 0.31618 0.98533 0.2668
H1 H 0.29429 0.30887 0.10164
H2 H 0.07704 0.30219 0.29051
H3 H 0.25139 0.57287 0.26361
H4 H 0.02998 0.23242 0.9778
H5 H 0.05067 0.32643 0.063
H6 H 0.95255 0.23613 0.06538
H7 H 0.26238 0.22895 0.32988
H8 H 0.38642 0.17922 0.44767
H9 H 0.42327 0.89243 0.34108
H10 H 0.29871 0.9276 0.21699
Ow O 0.55584 0.19207 0.48934
H1w H 0.607 0.22916 0.52173
H2w H 0.58574 0.16497 0.43662
```

Simulated structure with 2 H_2O at Cu1 and Cu2 in $P2_1/c$:

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data_simulation_2H2O_at_Cu1andCu2_inP21/c
_symmetry_space_group_name_H-M    'P21/C'
_symmetry_Int_Tables_number       14
_symmetry_cell_setting
monoclinic
loop_
_symmetry_equiv_pos_as_xyz
  x,y,z
  -x,y+1/2,-z+1/2
  -x,-y,-z
  x,-y+1/2,z+1/2
_cell_length_a                    12.4263
_cell_length_b                    13.3432
_cell_length_c                    16.4603
_cell_angle_alpha                 90.0000
_cell_angle_beta                  93.3873
_cell_angle_gamma                 90.0000
loop_
_atom_site_label
_atom_site_type_symbol
_atom_site_fract_x
_atom_site_fract_y
_atom_site_fract_z
Cu1 Cu 0.5 -2.83186E-33 0.5
Cu2 Cu 0 0 0
O1 O 0.39669 0.44117 0.07092
O2 O 0.37422 0.58263 0.14594
O3 O 0.07028 0.41491 0.41619
O4 O 0.16088 0.55767 0.38955
N1 N 0.14699 0.18487 0.17304
N2 N 0.08483 0.06905 0.08946
N3 N 0.14937 0.02225 0.14702
N4 N 0.39808 0.0281 0.4056
C1 C 0.35713 0.49245 0.12927
C2 C 0.28158 0.43276 0.17972
C3 C 0.24877 0.33628 0.15527
C4 C 0.17638 0.28374 0.20141
C5 C 0.136 0.32431 0.27199
C6 C 0.17087 0.42057 0.29709
C7 C 0.24272 0.47442 0.25062
C8 C 0.13206 0.46914 0.37355
C9 C 0.02155 0.24492 0.05611
C10 C 0.0825 0.16705 0.10414
C11 C 0.18816 0.09253 0.19807
C12 C 0.26168 0.07278 0.26942
C13 C 0.32667 0.14756 0.30804
C14 C 0.39342 0.12226 0.37614
C15 C 0.33779 0.9548 0.36917
C16 C 0.26854 0.97439 0.30107
H1 H 0.28054 0.30266 0.10111
H2 H 0.0796 0.28282 0.3078
H3 H 0.26831 0.54944 0.26992
H4 H 0.95932 0.20985 0.01507
H5 H 0.07655 0.28856 0.01953
H6 H 0.98287 0.29709 0.09734
H7 H 0.3278 0.22438 0.28588
H8 H 0.44551 0.17772 0.40777
H9 H 0.34542 0.88059 0.39765
H10 H 0.21988 0.91426 0.27283
Ow O 0.61705 0.20975 0.48477
H1w H 0.67214 0.26215 0.47939
H2w H 0.62417 0.16726 0.43628
Ow O 0.79322 0.15148 0.96549
H3w H 0.79889 0.10426 0.92055
H4w H 0.19371 0.61166 0.48397
```

Simulated structure with 1 H_2O at Cu1 and Cu2 in $P2_1$

```
data_simulation_1H2O_at_Cu1andCu2_inP21
_symmetry_space_group_name_H-M    'P21'
_symmetry_Int_Tables_number       4
_symmetry_cell_setting
monoclinic
loop_
_symmetry_equiv_pos_as_xyz
  x,y,z
  -x,y+1/2,-z
_cell_length_a                    14.8415
_cell_length_b                    11.9701
_cell_length_c                    13.9614
_cell_angle_alpha                 90.0000
_cell_angle_beta                  94.2569
_cell_angle_gamma                 90.0000
loop_
_atom_site_label
_atom_site_type_symbol
_atom_site_fract_x
_atom_site_fract_y
_atom_site_fract_z
Cu53 Cu 0.43499 0.97105 0.74624
Cu54 Cu 0.93339 0.1622 0.24734
O55 O 0.39085 0.7943 0.78046
O56 O 0.8514 0.32232 0.24178
O65 O 0.47564 0.43305 0.34606
O66 O 0.45499 0.62121 0.3551
O67 O 0.1235 0.61488 0.63071
O68 O 0.25591 0.71142 0.64062
O69 O 0.63984 0.5483 0.16074
O70 O 0.72094 0.40375 0.10516
O71 O 0.99706 0.69344 0.86661
O72 O 0.9528 0.51146 0.87271
N57 N 0.15572 0.29692 0.40477
N58 N 0.0436 0.20517 0.3317
N59 N 0.08809 0.13206 0.39219
N60 N 0.34487 0.03017 0.64176
N61 N 0.8136 0.89852 0.10216
N62 N 0.85052 0.05497 0.17484
N63 N 0.78659 0.08047 0.10446
N64 N 0.53893 0.97159 0.84928
C1 C 0.43357 0.52268 0.37135
C2 C 0.3482 0.49915 0.42142
C3 C 0.2957 0.40485 0.39461
C5 C 0.21279 0.38962 0.4345
C6 C 0.1824 0.46398 0.50229
C8 C 0.23636 0.55638 0.53141
C9 C 0.31843 0.57468 0.48961
C11 C 0.2038 0.6346 0.60724
C12 C 0.05747 0.40628 0.28096
C16 C 0.08366 0.30472 0.33773
C17 C 0.1567 0.18709 0.43709
C18 C 0.22201 0.1362 0.5082
C19 C 0.227 0.01854 0.51445
C21 C 0.289 0.96905 0.58184
C23 C 0.3409 0.14254 0.63642
C25 C 0.28081 0.19877 0.57165
C27 C 0.7054 0.50634 0.11705
C28 C 0.76791 0.59272 0.07813
C29 C 0.76245 0.70434 0.10888
C31 C 0.81975 0.7839 0.07266
C32 C 0.88272 0.75567 0.00663
C34 C 0.88744 0.64443 0.97511
C35 C 0.83047 0.5632 0.01162
C37 C 0.95101 0.61092 0.8989
C38 C 0.92953 0.88224 0.24362
C42 C 0.86716 0.94541 0.17521
C43 C 0.76302 0.98556 0.05971
C44 C 0.68906 0.97754 0.98427
C45 C 0.66688 0.87987 0.93066
C47 C 0.59155 0.88084 0.86421
C51 C 0.63401 0.07286 0.96625
C49 C 0.56007 0.06603 0.89888
H4 H 0.3196 0.34544 0.34278
```

```
H7 H 0.1176 0.45134 0.533
H10 H 0.3592 0.64823 0.50955
H13 H 0.07371 0.48221 0.32327
H14 H 0.09457 0.40924 0.21533
H15 H 0.98462 0.40235 0.25974
H20 H 0.18294 0.96676 0.46671
H22 H 0.29403 0.87822 0.58867
H24 H 0.38891 0.18796 0.68492
H26 H 0.28113 0.28974 0.57145
H30 H 0.71306 0.72786 0.15945
H33 H 0.92733 0.81889 0.97928
H36 H 0.8347 0.47689 0.9869
H39 H 0.89235 0.81576 0.27881
H40 H 0.98411 0.84429 0.2054
H41 H 0.95983 0.94036 0.2978
H46 H 0.70624 0.80334 0.94003
H48 H 0.57086 0.80718 0.82179
H50 H 0.51483 0.13689 0.88406
H52 H 0.64867 0.15014 0.00599
H73 H 0.35347 0.75483 0.73042
H74 H 0.34811 0.81929 0.82785
H75 H 0.80603 0.29268 0.28433
H76 H 0.81653 0.34263 0.18163
```

Simulated structure with 1 H_2O at Cu1 and Cu2 in *P*1

```
data_simulation_1H2O_at_Cu1andCu2_inP1
_symmetry_space_group_name_H-M    'P1'
_symmetry_Int_Tables_number       1
_symmetry_cell_setting            triclinic
loop_
_symmetry_equiv_pos_as_xyz
  x,y,z
_cell_length_a                    14.8578
_cell_length_b                    11.9649
_cell_length_c                    13.9468
_cell_angle_alpha                 90.0000
_cell_angle_beta                  94.2697
_cell_angle_gamma                 90.0000
loop_
_atom_site_label
_atom_site_type_symbol
_atom_site_fract_x
_atom_site_fract_y
_atom_site_fract_z
Cu53 Cu 0.4352 0.97123 0.74617
Cu54 Cu 0.93358 0.16209 0.2473
O55 O 0.39107 0.79434 0.78032
O56 O 0.85132 0.32204 0.24095
O65 O 0.47533 0.43336 0.34602
O66 O 0.45471 0.62162 0.35504
O67 O 0.12325 0.61534 0.63045
O68 O 0.25562 0.71171 0.64076
O69 O 0.63977 0.54822 0.16086
O70 O 0.72031 0.40346 0.10477
O71 O 0.99705 0.69304 0.8669
O72 O 0.95268 0.511 0.87273
N57 N 0.1558 0.29712 0.4044
N58 N 0.04377 0.20513 0.33151
N59 N 0.08849 0.13204 0.3919
N60 N 0.34538 0.03047 0.64139
N61 N 0.81361 0.89827 0.10237
N62 N 0.85067 0.05476 0.17506
N63 N 0.78663 0.0803 0.10477
N64 N 0.5389 0.97152 0.8496
C1 C 0.43329 0.52305 0.37127
C2 C 0.34796 0.49954 0.42128
C3 C 0.29555 0.40519 0.39437
C5 C 0.21268 0.38997 0.43416
C6 C 0.18223 0.46437 0.50196
C8 C 0.23611 0.55681 0.5312
C9 C 0.31814 0.57511 0.48948
C11 C 0.20354 0.63499 0.60713
C12 C 0.05716 0.40644 0.28083
C16 C 0.08363 0.30481 0.33751
C17 C 0.15704 0.18721 0.43669
C18 C 0.2225 0.13641 0.50773
C19 C 0.2274 0.01871 0.51417
C21 C 0.28941 0.96927 0.58161
C23 C 0.34156 0.14289 0.6358
C25 C 0.28147 0.19907 0.57096
C27 C 0.70504 0.50612 0.11689
C28 C 0.76758 0.59244 0.07797
C29 C 0.76222 0.70409 0.10883
C31 C 0.81965 0.78361 0.07277
C32 C 0.88265 0.75531 0.00681
C34 C 0.88725 0.64404 0.97515
C35 C 0.83013 0.56286 0.01147
C37 C 0.9509 0.61049 0.89902
C38 C 0.92959 0.88189 0.24384
C42 C 0.86727 0.94515 0.17539
C43 C 0.76298 0.98535 0.06002
C44 C 0.68895 0.97735 0.98465
C45 C 0.66714 0.87993 0.93044
C47 C 0.59184 0.88096 0.86397
C51 C 0.63354 0.07246 0.96727
C49 C 0.55966 0.06569 0.89984
H4 H 0.3195 0.34571 0.34257
H7 H 0.11747 0.45171 0.53264
H10 H 0.35886 0.6487 0.50948
H13 H 0.07264 0.48233 0.32356
H14 H 0.0947 0.41016 0.2155
H15 H 0.98452 0.40188 0.25905
H20 H 0.18326 0.96684 0.46657
H22 H 0.29431 0.87841 0.58862
H24 H 0.3897 0.18836 0.68413
H26 H 0.28192 0.29008 0.57055
H30 H 0.71285 0.72769 0.15939
H33 H 0.92738 0.81848 0.97963
H36 H 0.83427 0.47653 0.98664
H39 H 0.89237 0.81564 0.27929
H40 H 0.98392 0.8436 0.20551
H41 H 0.96013 0.94006 0.2979
H46 H 0.70679 0.80358 0.93934
H48 H 0.57147 0.80753 0.82104
H50 H 0.51414 0.13637 0.88549
H52 H 0.64789 0.14952 0.00753
H73 H 0.35358 0.75493 0.7303
H74 H 0.34852 0.81931 0.82792
H75 H 0.8061 0.29255 0.28374
H76 H 0.81634 0.34208 0.18075
Cu53 Cu 0.5648 0.47121 0.25382
Cu54 Cu 0.06642 0.6621 0.75271
O55 O 0.60894 0.29432 0.21967
O56 O 0.14868 0.82204 0.75906
O65 O 0.52468 0.93338 0.65398
O66 O 0.5453 0.12164 0.64497
O67 O 0.87675 0.11535 0.36956
O68 O 0.74438 0.2117 0.35924
O69 O 0.36023 0.04823 0.83914
O70 O 0.27971 0.90347 0.89524
O71 O 0.00295 0.19303 0.13311
O72 O 0.04731 0.01099 0.12726
N57 N 0.84422 0.79714 0.5956
N58 N 0.95624 0.70516 0.66849
N59 N 0.91153 0.63207 0.60809
N60 N 0.65463 0.53047 0.3586
N61 N 0.18637 0.39825 0.89763
N62 N 0.14932 0.55475 0.82494
N63 N 0.21337 0.58028 0.89522
N64 N 0.46109 0.47149 0.15039
C1 C 0.56672 0.02307 0.62873
C2 C 0.65205 0.99956 0.57873
C3 C 0.70446 0.90522 0.60564
C5 C 0.78733 0.89 0.56584
C6 C 0.81778 0.96438 0.49804
C8 C 0.7639 0.05682 0.46881
C9 C 0.68187 0.07513 0.51053
```

```
C11 C 0.79647 0.135 0.39287
C12 C 0.94284 0.90646 0.71919
C16 C 0.91637 0.80484 0.6625
C17 C 0.84297 0.68724 0.5633
C18 C 0.77751 0.63643 0.49226
C19 C 0.77261 0.51873 0.48582
C21 C 0.71061 0.46928 0.41838
C23 C 0.65845 0.64289 0.36419
C25 C 0.71854 0.69909 0.42902
C27 C 0.29496 0.00613 0.88312
C28 C 0.23242 0.09244 0.92204
C29 C 0.23776 0.20409 0.89117
C31 C 0.18033 0.28359 0.92722
C32 C 0.11733 0.25529 0.99318
C34 C 0.11275 0.14403 0.02486
C35 C 0.16988 0.06286 0.98855
C37 C 0.04909 0.11047 0.10098
C38 C 0.07036 0.38188 0.75618
C42 C 0.1327 0.44514 0.82461
C43 C 0.23701 0.48533 0.93997
C44 C 0.31105 0.47732 0.01534
C45 C 0.33284 0.37992 0.06956
C47 C 0.40814 0.38094 0.13602
C51 C 0.36648 0.57242 0.0327
C49 C 0.44036 0.56565 0.10013
H4 H 0.68052 0.84574 0.65744
H7 H 0.88254 0.95173 0.46736
H10 H 0.64115 0.14871 0.49052
H13 H 0.92734 0.98235 0.67647
H14 H 0.9053 0.91018 0.78452
H15 H 0.01548 0.90193 0.74097
H20 H 0.81676 0.46688 0.53342
H22 H 0.70571 0.37842 0.41138
H24 H 0.61031 0.68836 0.31586
H26 H 0.7181 0.79009 0.42943
H30 H 0.28713 0.22769 0.84061
H33 H 0.07259 0.31846 0.02035
H36 H 0.16576 0.97653 0.01339
H39 H 0.10757 0.31562 0.72072
H40 H 0.01604 0.3436 0.7945
H41 H 0.03983 0.44004 0.70211
H46 H 0.29317 0.30357 0.06067
H48 H 0.42849 0.30751 0.17896
H50 H 0.48589 0.63632 0.11446
H52 H 0.35214 0.64947 0.99243
H73 H 0.64643 0.25492 0.26969
H74 H 0.6515 0.3193 0.17207
H75 H 0.1939 0.79256 0.71627
H76 H 0.18367 0.84208 0.81926
```

Simulated structure with 29 H_2 in unit cell in *P*1

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data_simulation_29H2_in_unit_cell_inP1
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_symmetry_Int_Tables_number       1
_symmetry_cell_setting            triclinic
loop_
_symmetry_equiv_pos_as_xyz
  x,y,z
_cell_length_a                    14.0400
_cell_length_b                    12.8660
_cell_length_c                    15.2321
_cell_angle_alpha                 89.99996
_cell_angle_beta                  93.29066
_cell_angle_gamma                 89.99978
loop_
_atom_site_label
_atom_site_type_symbol
_atom_site_fract_x
_atom_site_fract_y
_atom_site_fract_z
Cu1 Cu 0.50011 -1.62175E-4 0.49981
Cu2 Cu 8.3861E-5 3.5056E-5 -2.57229E-4
O1 O 0.4164 0.43358 0.08231
O2 O 0.38057 0.59196 0.13822
O3 O 0.07021 0.43633 0.40523
O4 O 0.12029 0.59696 0.36538
N1 N 0.15693 0.19125 0.16618
N2 N 0.08815 0.06873 0.08713
N3 N 0.14951 0.02079 0.14544
N4 N 0.40146 0.02803 0.40117
C1 C 0.36804 0.49656 0.13028
C2 C 0.28872 0.44284 0.17683
C3 C 0.26234 0.34065 0.15346
C4 C 0.18598 0.29407 0.19342
C5 C 0.13652 0.34542 0.25762
C6 C 0.16457 0.44665 0.28266
C7 C 0.23927 0.49584 0.24099
C8 C 0.11495 0.5009 0.35594
C9 C 0.03275 0.24975 0.0483
C10 C 0.09138 0.17131 0.09847
C11 C 0.19234 0.09511 0.19389
C12 C 0.26453 0.07501 0.2653
C13 C 0.288 0.14721 0.3328
C14 C 0.35603 0.12021 0.39921
C15 C 0.38025 0.95836 0.33666
C16 C 0.3121 0.97816 0.26839
H1 H 0.30062 0.299 0.10397
H2 H 0.07731 0.30777 0.28854
H3 H 0.25944 0.57547 0.25875
H4 H 0.06611 0.32702 0.05357
H5 H 0.96112 0.2524 0.07454
H6 H 0.02488 0.22568 0.9789
H7 H 0.25424 0.22326 0.33531
H8 H 0.37516 0.17326 0.45328
H9 H 0.42003 0.88539 0.34049
H10 H 0.29588 0.91958 0.21788
H11 H 0.56096 0.19724 0.47871
H12 H 0.53727 0.21782 0.51841
H13 H 0.89532 0.19831 0.77257
H4 H 0.89038 0.24688 0.74498
H15 H 0.52527 0.30473 0.74505
H16 H 0.49188 0.2737 0.71472
H17 H 0.71403 0.64464 0.50917
H18 H 0.76554 0.635 0.52308
H19 H 0.80452 0.45298 0.04138
H20 H 0.77739 0.4272 0.00342
H21 H 0.26783 0.69957 0.37299
H22 H 0.31676 0.72362 0.37608
H23 H 0.55387 0.65617 0.64942
H24 H 0.58929 0.6124 0.65171
Cu1 Cu 0.5001 0.50008 -1.42322E-4
Cu2 Cu 9.82329E-5 0.49998 0.4998
O1 O 0.58365 0.93338 0.41724
O2 O 0.61947 0.09186 0.36153
O3 O 0.92995 0.93652 0.09443
O4 O 0.87998 0.09714 0.13443
N1 N 0.84331 0.69137 0.33352
N2 N 0.91211 0.56875 0.41241
N3 N 0.8506 0.5209 0.3542
N4 N 0.59849 0.52843 0.09867
C1 C 0.632 0.99645 0.36933
C2 C 0.71135 0.94282 0.32275
C3 C 0.7378 0.84066 0.34613
C4 C 0.81428 0.79419 0.30628
C5 C 0.86379 0.8456 0.24214
C6 C 0.83566 0.94679 0.21707
C7 C 0.76085 0.99589 0.25865
C8 C 0.88528 1.00107 0.1438
C9 C 0.96773 0.74969 0.45127
C10 C 0.90894 0.67134 0.40113
C11 C 0.80775 0.59529 0.30584
C12 C 0.73545 0.57531 0.23452
C13 C 0.71209 0.64749 0.16697
C14 C 0.64403 0.62053 0.10058
C15 C 0.61957 0.45881 0.16324
```

C16 C 0.68772 0.47856 0.23152
H1 H 0.69949 0.79892 0.39555
H2 H 0.92308 0.80803 0.21127
H3 H 0.74066 0.07552 0.24091
H4 H 0.93461 0.82708 0.44581
H5 H 0.03942 0.75201 0.42516
H6 H 0.97538 0.72577 0.52072
H7 H 0.74598 0.72346 0.16437
H8 H 0.62498 0.67355 0.04647
H9 H 0.57969 0.3859 0.15943
H10 H 0.70385 0.42 0.28208
H11 H 0.4389 0.69674 0.02061
H12 H 0.46269 0.71662 0.98071
H13 H 0.10498 0.69802 0.72734
H4 H 0.10986 0.74663 0.75488
H15 H 0.47451 0.80675 0.7553
H16 H 0.50778 0.77614 0.78605
H17 H 0.283 0.15099 0.98676
H18 H 0.23167 0.13891 0.97385
H19 H 0.19598 0.95107 0.45889
H20 H 0.22369 0.92582 0.49678
H21 H 0.73378 0.2014 0.12773
H22 H 0.68527 0.22644 0.12466
H23 H 0.44909 0.15298 0.85743
H24 H 0.41264 0.11025 0.85402
O1 O 0.58384 0.56644 0.91739
O2 O 0.61952 0.408 0.86149
O3 O 0.92985 0.56346 0.59434
O4 O 0.88002 0.4028 0.63438
N1 N 0.84338 0.80854 0.83345
N2 N 0.91211 0.93118 0.91238
N3 N 0.85064 0.97901 0.85412
N4 N 0.59867 0.97146 0.59848
C1 C 0.63215 0.50338 0.86942
C2 C 0.71151 0.55701 0.82286
C3 C 0.73796 0.65918 0.84622
C4 C 0.81434 0.70571 0.80626
C5 C 0.86377 0.65433 0.74205
C6 C 0.83566 0.55313 0.71702
C7 C 0.76093 0.50398 0.75869
C8 C 0.88525 0.49887 0.64373
C9 C 0.96771 0.75025 0.95129
C10 C 0.90897 0.82859 0.9011
C11 C 0.80784 0.90461 0.80573
C12 C 0.73562 0.92461 0.73434
C13 C 0.71225 0.85239 0.66682
C14 C 0.64419 0.87933 0.60042
C15 C 0.61981 0.04113 0.66299
C16 C 0.68796 0.0214 0.73127
H1 H 0.69972 0.70087 0.89572
H2 H 0.92298 0.69194 0.7111
H3 H 0.74073 0.42436 0.74093
H4 H 0.93455 0.67289 0.94589
H5 H 0.0394 0.74786 0.92518
H6 H 0.97537 0.77424 0.02072
H7 H 0.74609 0.7764 0.6643
H8 H 0.62511 0.82629 0.54634
H9 H 0.57996 0.11406 0.65916
H10 H 0.70412 0.07998 0.7818
H11 H 0.43936 0.80257 0.52111
H12 H 0.46306 0.78196 0.48143
H13 H 0.10511 0.80196 0.22743
H4 H 0.11 0.75335 0.25497
H15 H 0.47506 0.69528 0.25437
H16 H 0.50856 0.72635 0.28456
H17 H 0.28628 0.35523 0.49065
H18 H 0.23477 0.36484 0.47674
H19 H 0.19615 0.54905 0.9588
H20 H 0.22381 0.57431 0.99672
H21 H 0.73309 0.29949 0.62721
H22 H 0.68433 0.27503 0.62412
H23 H 0.4461 0.34343 0.34993
H24 H 0.41065 0.38717 0.34785
O1 O 0.41664 0.06646 0.58238
O2 O 0.38074 0.90809 0.63825
O3 O 0.07001 0.06369 0.90497
O4 O 0.12032 0.90308 0.86531
N1 N 0.15709 0.30878 0.66609
N2 N 0.08817 0.43133 0.58719
N3 N 0.14962 0.47924 0.64543
N4 N 0.40164 0.47189 0.90108
C1 C 0.36827 0.0035 0.63037
C2 C 0.28898 0.05725 0.67694
C3 C 0.26261 0.15944 0.65355
C4 C 0.18612 0.20596 0.69334
C5 C 0.13652 0.15457 0.75743
C6 C 0.16459 0.05337 0.78254
C7 C 0.23941 0.00423 0.74101
C8 C 0.11489 -8.68627E-4 0.85578
C9 C 0.03274 0.25031 0.54833
C10 C 0.09145 0.32874 0.59846
C11 C 0.19254 0.40489 0.69378
C12 C 0.2648 0.42493 0.76514
C13 C 0.2882 0.35273 0.83266
C14 C 0.35619 0.37972 0.8991
C15 C 0.38053 0.54152 0.83653
C16 C 0.31243 0.52175 0.76821
H1 H 0.30098 0.20114 0.60414
H2 H 0.07721 0.19218 0.78824
H3 H 0.25956 0.92459 0.75877
H4 H 0.06603 0.17301 0.55366
H5 H 0.96111 0.24776 0.57458
H6 H 0.02489 0.27432 0.47892
H7 H 0.25438 0.27672 0.8352
H8 H 0.37525 0.32669 0.9532
H9 H 0.42034 0.61447 0.84038
H10 H 0.29627 0.58032 0.71768
H11 H 0.56147 0.3034 0.97919
H12 H 0.53769 0.28351 0.01909
H13 H 0.89554 0.30156 0.27265
H4 H 0.89062 0.25299 0.24506
H15 H 0.52685 0.19402 0.24449
H16 H 0.4937 0.22476 0.21373
H17 H 0.71754 0.84899 0.01258
H18 H 0.76881 0.86118 0.02562
H19 H 0.80459 0.04713 0.54125
H20 H 0.77738 0.07284 0.50329
H21 H 0.2667 0.79919 0.8723
H22 H 0.31521 0.77415 0.87547
H23 H 0.55216 0.84771 0.14202
H24 H 0.58889 0.89016 0.14556
H25 H 0.49824 0.48401 0.47865
H26 H 0.50392 0.51853 0.51835

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