Electronic Supporting Information (ESI)

for

Structure modulation in two Cu^{II}-based MOFs by synergistic assembly of mixed-ligand synthetic strategy and solvent effect

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Experimental Section

Materials and methods.

All chemicals were commercially purchased and used as received.

Elemental analyses (C, H, and N) were performed on a Perkin-Elmer 240C analyzer (Perkin-Elmer, USA). The X-ray powder diffraction (XRPD) was recorded on a Rigaku D/Max-2500 diffractometer at 40 kV, 100 mA for a Cu-target tube and a graphite monochromator. Simulation of the XRPD spectra were carried out by the single-crystal data and diffraction-crystal module of the Mercury (Hg) program available free of charge *via* the Internet at http://www.iucr.org. IR spectrum was measured in the range of 400-4000 cm^{-1} on a Tensor 27 OPUS FT-IR spectrometer using KBr pellets (Bruker, German). Thermogravimetric analyses (TGA) were performed on a Rigaku standard TG-DTA analyzer with a heating rate of 10 °C·min^{-1}, with an empty Al_2O_3 crucible used as a reference in the range of 25 °C–700 °C. Gas adsorption studies were measured on an ASAP 2020 Surface Area and Porous Analyzer. Magnetic data were collected using crushed crystals of the sample on a Quantum Design MPMS-XL-7-SQUID magnetometer. The data were corrected using Pascal's constants to calculate the diamagnetic susceptibility, and an experimental correction for the sample holder was applied.

X-ray Crystallography.

The crystallographic data of **1** and **2** were collected on a Rigaku SCX-mini diffractometer at 298(2) K with Mo-Kα radiation (λ = 0.71073 Å). The crystal data were solved by direct methods and refined by a full-matrix least-square method on F^2 using the *SHELXL-97* crystallographic software package.[S1] Copper atoms in **1** and **2** were found from *E*-maps and other non-hydrogen atoms were located in successive difference Fourier syntheses. The final refinement was performed by full matrix least-squares methods with anisotropic thermal parameters for non-hydrogen atoms on F^2. The hydrogen atoms of organic ligands were added theoretically, riding on the concerned atoms and refined with fixed thermal factors. During the refinement of the compounds **2**, the command "omit -3 50" was used to omit some disagreeable reflections. The atoms C72, C81, C98, C101, O3w, O4w, O5w, and O6w in compound **2** were restrained using thermal restraints (isor) to sovle ADP or NDP alerts and make the displacement parameters more reasonable. The H atoms on OH^- groups and water molecules cannot be added in the calculated positions. Thus, the H atoms on OH^- groups and water molecules were directly included in the final molecular formula. Further details of crystal data and structure refinement for **1** and **2** were

summarized as follows in Table S1. Selected bond lengths of **1** and **2** were given in Table S2 and S3. Full crystallographic data for **1** and **2** have been deposited with the CCDC (999642 for **1**, and 999643 for **2**). These data can be obtained free of charge from The Cambridge Crystallographic Data Centre *via* www.ccdc.cam.ac.uk/data_request/cif.[S2]

References

S1 (a) G. M. Sheldrick, *SHELXL97, Program for Crystal Structure Refinement*; University of Göttingen: Göttingen, Germany, 1997; (b) G. M. Sheldrick, *SHELXS97, Program for Crystal Structure Solution*; University of Göttingen: Göttingen, Germany, 1997.

S2 The checkcif program available at: http://journals.iucr.org/services/cif/checkcif.html.

Crystal data for 1 and 2

Table S1. Crystal Data and Structure Refinement Parameters for Compounds 1–2.

compound	**1**	**2**
formula	$C_{52}H_{36}N_8O_8Cu_2$	$C_{168}H_{124}N_{16}O_{62}Cu_{16}$
Fw	1027.98	4375.59
λ/Å	0.71073	0.71073
T/K	298(2)	298(2)
crystal system	Monoclinic	Triclinic
space group	$P2_1/c$	P-1
a [Å]	13.931(3)	16.195(3)
b [Å]	18.433(4)	23.027(5)
c [Å]	22.377(7)	23.751(5)
α[°]	90	72.72(3)
β [°]	127.04(2)	75.60(3)
γ[°]	90	82.82(3)
V (Å ^{3})	4587(2)	8179(3)
Z	4	2
D_c/Mg·m^{-3}	1.489	1.776
F(000)	2104	4408
reflections collected/unique	39075/8075	69223/28674
R_{int}	0.0485	0.0930
data / restraints / parameters	8075/0/631	28674/48/2359
R_1/wR_2 [$I>2\sigma(I)$] [a]	0.0527/0.1038	0.0808/0.1433
R_1/wR_2 [(all data)] [a]	0.0578/0.1120	0.1541/0.1677
GOF on F^2	1.114	1.071

[a] $R_1 = \Sigma(||F_0| - |F_C||)/\Sigma|F_0|$ $wR_2 = [\Sigma w(|F_0|^2 - |F_C|^2)^2/(\Sigma w|F_0|^2)^2]^{1/2}$.

Figures in Supporting Information

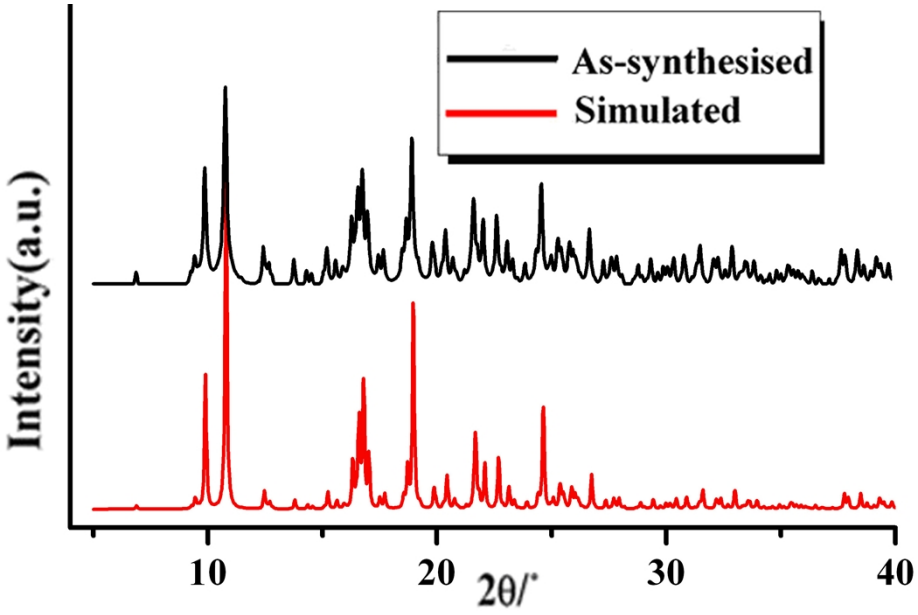

Fig. S1. XRPD patterns for **1**.

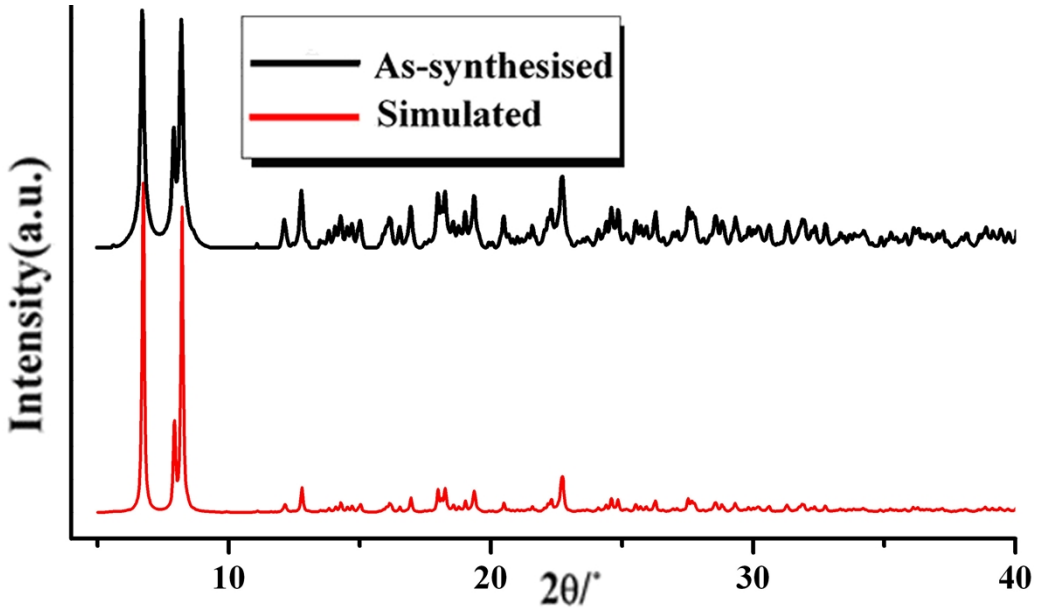

Fig. S2. XRPD patterns for **2**.

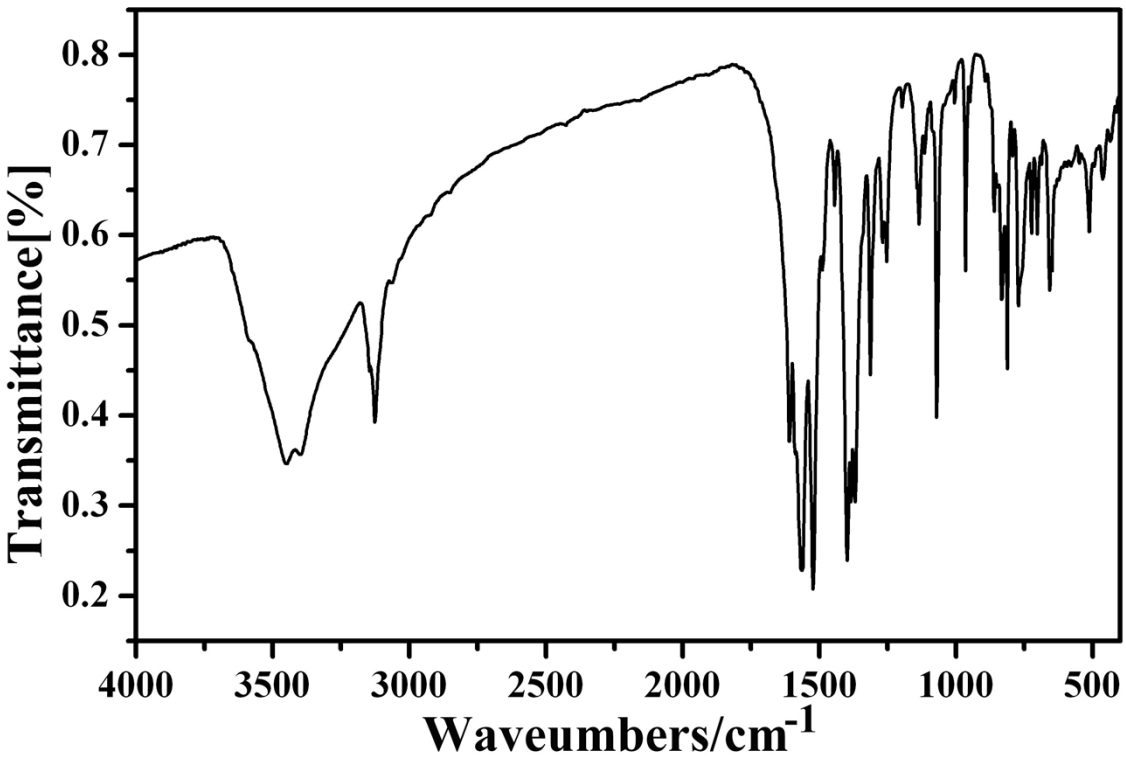

Fig. S3. IR spectrum of compound **1**.

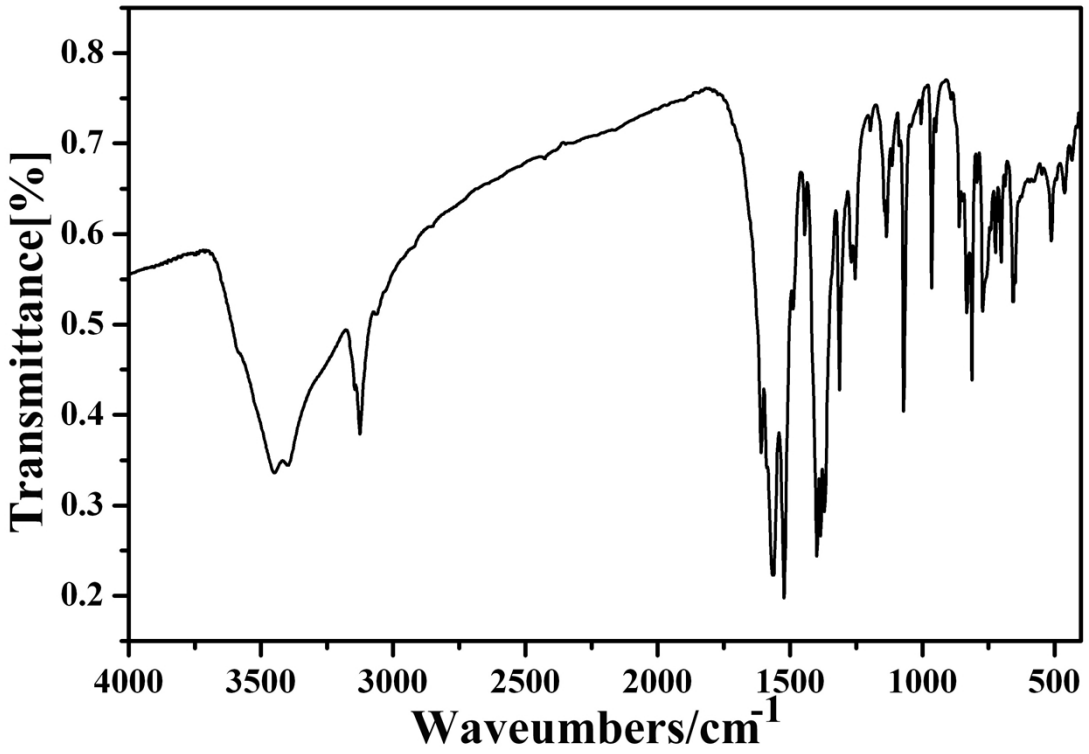

Fig. S4. IR spectrum of compound **2**.

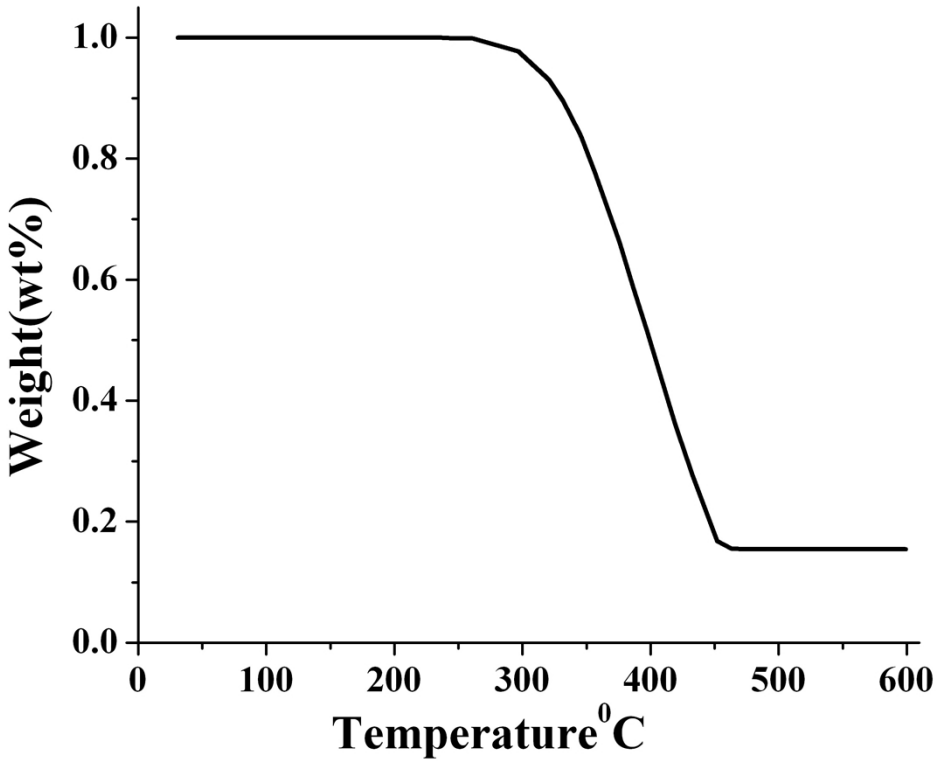

Fig. S5 Thermogravimetric curve of compound **1**.

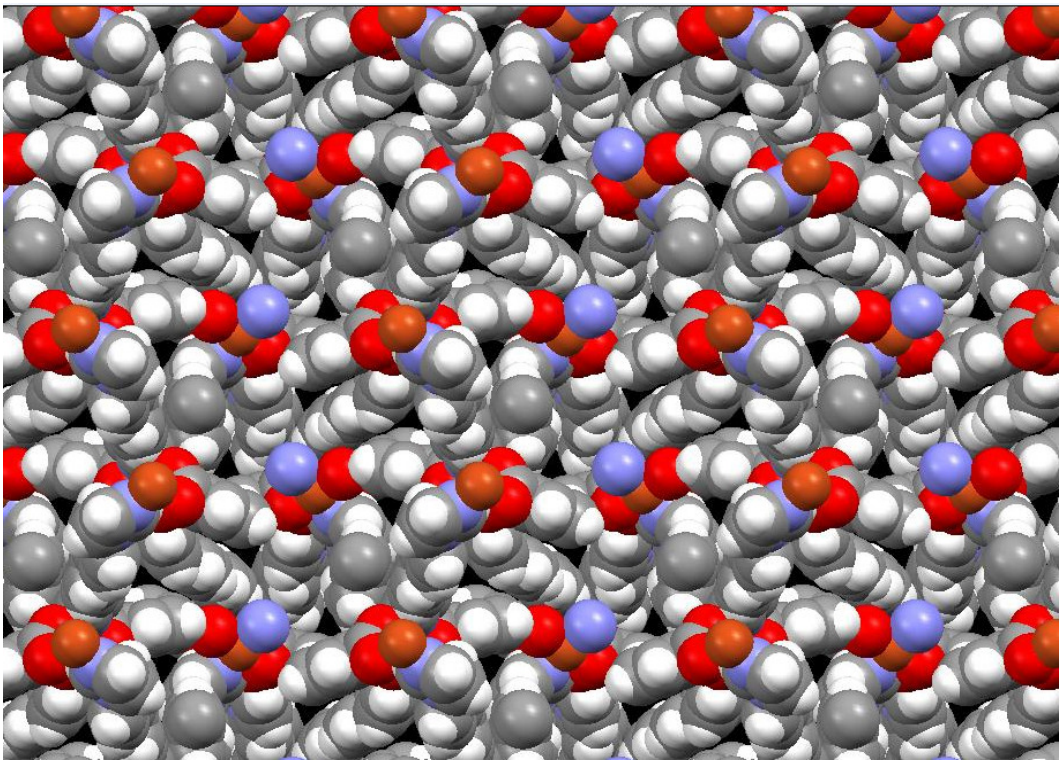

Fig. S6 Space filling view of compound **1**.

Gas adsorption measurements.

N_2 and H_2 sorption isotherms were carried out at 77 K to examine its gases loading capacity. As shown in Fig. S7, the compound **1** adsorbs a very limited amount of N_2 (*ca.* 4.44 $cm^3 \cdot g^{-1}$) and also little H_2 (*ca.* 26.34 $cm^3 \cdot g^{-1}$), respectively. These results illustrate that they are only surface absorption. This might be attributed to pore-size-exclusive effect, that is, the very small pore apertures of **1** (see Space filling view of Fig. S6 above) block the N_2 and H_2 molecules to enter the channels because their kinetic diameter is larger than the effective channel size.

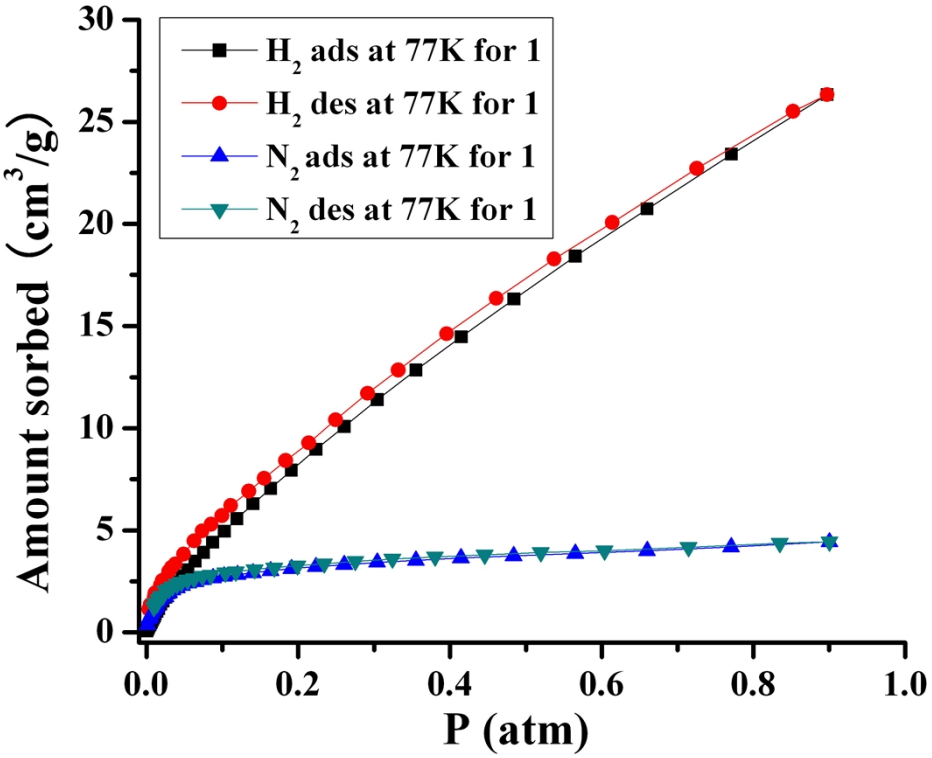

Fig. S7 N_2 and H_2 sorption isotherms for **1** at 77 K.

Table S2 The selected bond lengths [Å] and angles [º] of compound **1**.

Cu(1)-O(1)	1.959(3)	Cu(2)-O(8)#1	1.961(3)
Cu(1)-O(5)	1.986(3)	Cu(2)-O(4)	1.982(3)
Cu(1)-N(1)	2.004(3)	Cu(2)-N(5)	1.985(3)
Cu(1)-N(7)	2.015(3)	Cu(2)-N(4)#2	1.999(3)
O(1)-Cu(1)-O(5)	179.73(13)	O(8)#1-Cu(2)-O(4)	178.40(10)
O(1)-Cu(1)-N(1)	89.62(12)	O(8)#1-Cu(2)-N(5)	91.92(12)
O(5)-Cu(1)-N(1)	90.65(12)	O(4)-Cu(2)-N(5)	89.35(12)
O(1)-Cu(1)-N(7)	89.96(11)	O(8)#1-Cu(2)-N(4)#2	90.26(12)
O(5)-Cu(1)-N(7)	89.77(11)	O(4)-Cu(2)-N(4)#2	88.44(11)
N(1)-Cu(1)-N(7)	178.70(12)	N(5)-Cu(2)-N(4)#2	177.16(14)
Symmetry transformations used to generate equivalent atoms: #1: x-1, y, z; #2: x-2, -y+3/2, z-1/2.			

Table S3 The selected bond lengths [Å] and angles [º] of compound **2**.

Cu(1)-O(53)	1.906(6)	Cu(5)-O(26)	1.960(5)
Cu(1)-O(1)#1	1.962(5)	Cu(5)-O(14)	1.971(6)
Cu(1)-O(18)	1.990(6)	Cu(5)-O(2)	2.012(5)
Cu(1)-O(1)	2.013(5)	Cu(5)-O(22)	2.218(6)
Cu(2)-O(3)	1.936(5)	Cu(6)-O(2)#1	1.934(5)
Cu(2)-N(8)	1.948(7)	Cu(6)-N(1)#2	1.957(7)
Cu(2)-O(13)	1.989(6)	Cu(6)-O(20)	2.008(6)
Cu(2)-O(12)	2.023(6)	Cu(6)-O(25)#1	2.028(6)
Cu(2)-O(54)	2.183(6)	Cu(6)-O(23)#1	2.175(6)
Cu(3)-O(17)#1	1.945(6)	Cu(7)-O(24)	1.923(6)
Cu(3)-O(10)#1	1.946(6)	Cu(7)-O(33)	1.944(5)
Cu(3)-O(1)	1.995(5)	Cu(7)-O(5)	1.953(5)
Cu(3)-N(4)	2.006(7)	Cu(7)-O(4)	1.997(5)
Cu(3)-O(55)	2.289(5)	Cu(7)-O(27)	2.403(6)
Cu(4)-O(2)	1.925(5)	Cu(8)-N(5)	1.970(7)
Cu(4)-O(11)	1.951(6)	Cu(8)-O(5)#2	1.970(5)
Cu(4)-O(19)#1	1.973(6)	Cu(8)-O(34)#2	1.989(6)
Cu(4)-O(3)	2.026(5)	Cu(8)-O(28)#2	2.019(6)
Cu(4)-O(55)	2.229(6)	Cu(8)-O(30)	2.193(6)
Cu(5)-O(3)	1.943(5)	Cu(13)-O(7)	1.883(5)
Cu(9)-O(29)#3	1.899(6)	Cu(13)-O(42)	1.947(6)
Cu(9)-O(16)	1.954(5)	Cu(13)-O(38)	1.964(5)
Cu(9)-O(5)	1.975(5)	Cu(13)-O(49)	1.967(6)
Cu(9)-O(4)	1.984(5)	Cu(14)-O(6)	1.913(5)
Cu(10)-O(45)	1.941(5)	Cu(14)-N(16)#3	1.963(6)
Cu(10)-O(15)	1.954(5)	Cu(14)-O(36)	1.971(6)
Cu(10)-O(4)	1.975(5)	Cu(14)-O(37)	1.992(6)
Cu(10)-N(13)	1.988(7)	Cu(14)-O(49)	2.319(6)
Cu(10)-O(22)	2.334(5)	Cu(15)-O(8)	1.955(5)
Cu(11)-O(6)	1.885(5)	Cu(15)-N(12)#4	1.980(7)

Cu(11)-O(47)	1.960(5)	Cu(15)-O(43)	1.980(6)
Cu(11)-O(35)	1.961(6)	Cu(15)-O(40)#5	2.021(6)
Cu(11)-O(31)#3	1.972(6)	Cu(15)-O(51)	2.158(6)
Cu(12)-O(7)	1.918(5)	Cu(16)-O(52)#5	1.899(6)
Cu(12)-O(41)	1.972(6)	Cu(16)-O(44)	1.929(5)
Cu(12)-N(9)	1.976(7)	Cu(16)-O(8)	1.964(5)
Cu(12)-O(48)	1.983(6)	Cu(16)-O(8)#5	1.966(5)
Cu(12)-O(31)#3	2.318(6)	Cu(16)-O(39)#5	2.421(6)
O(53)-Cu(1)-O(1)#1	170.3(3)	O(26)-Cu(5)-O(14)	87.0(2)
O(53)-Cu(1)-O(18)	92.1(2)	O(3)-Cu(5)-O(2)	81.3(2)
O(1)#1-Cu(1)-O(18)	94.9(2)	O(26)-Cu(5)-O(2)	93.9(2)
O(53)-Cu(1)-O(1)	94.1(2)	O(14)-Cu(5)-O(2)	144.2(3)
O(1)#1-Cu(1)-O(1)	80.8(2)	O(3)-Cu(5)-O(22)	88.2(2)
O(18)-Cu(1)-O(1)	164.3(2)	O(26)-Cu(5)-O(22)	92.5(2)
O(3)-Cu(2)-N(8)	170.5(3)	O(14)-Cu(5)-O(22)	105.5(2)
O(3)-Cu(2)-O(13)	93.7(2)	O(2)-Cu(5)-O(22)	110.1(2)
N(8)-Cu(2)-O(13)	90.1(3)	O(2)#1-Cu(6)-N(1)#2	170.5(3)
O(3)-Cu(2)-O(12)	84.6(2)	O(2)#1-Cu(6)-O(20)	94.0(2)
N(8)-Cu(2)-O(12)	87.4(3)	N(1)#2-Cu(6)-O(20)	90.4(3)
O(13)-Cu(2)-O(12)	145.8(3)	O(2)#1-Cu(6)-O(25)#1	84.6(2)
O(3)-Cu(2)-O(54)	91.8(2)	N(1)#2-Cu(6)-O(25)#1	86.8(3)
N(8)-Cu(2)-O(54)	95.7(3)	O(20)-Cu(6)-O(25)#1	143.4(3)
O(13)-Cu(2)-O(54)	105.2(3)	O(2)#1-Cu(6)-O(23)#1	92.3(2)
O(12)-Cu(2)-O(54)	109.0(2)	N(1)#2-Cu(6)-O(23)#1	94.5(3)
O(17)#1-Cu(3)-O(10)#1	158.3(3)	O(20)-Cu(6)-O(23)#1	107.1(3)
O(17)#1-Cu(3)-O(1)	90.6(2)	O(25)#1-Cu(6)-O(23)#1	109.4(2)
O(10)#1-Cu(3)-O(1)	92.6(2)	O(24)-Cu(7)-O(33)	93.0(2)
O(17)#1-Cu(3)-N(4)	86.6(3)	O(24)-Cu(7)-O(5)	174.2(2)
O(10)#1-Cu(3)-N(4)	90.4(3)	O(33)-Cu(7)-O(5)	92.1(2)
O(1)-Cu(3)-N(4)	177.1(3)	O(24)-Cu(7)-O(4)	94.2(2)
O(17)#1-Cu(3)-O(55)	85.8(2)	O(33)-Cu(7)-O(4)	166.7(2)
O(10)#1-Cu(3)-O(55)	115.8(2)	O(5)-Cu(7)-O(4)	81.3(2)
O(1)-Cu(3)-O(55)	87.7(2)	O(24)-Cu(7)-O(27)	87.7(2)
N(4)-Cu(3)-O(55)	91.3(2)	O(33)-Cu(7)-O(27)	105.4(2)
O(2)-Cu(4)-O(11)	175.2(2)	O(5)-Cu(7)-O(27)	88.4(2)
O(2)-Cu(4)-O(19)#1	96.9(2)	O(4)-Cu(7)-O(27)	86.1(2)
O(11)-Cu(4)-O(19)#1	87.6(2)	N(5)-Cu(8)-O(5)#2	175.3(3)
O(2)-Cu(4)-O(3)	81.4(2)	N(5)-Cu(8)-O(34)#2	87.5(3)
O(11)-Cu(4)-O(3)	94.2(2)	O(5)#2-Cu(8)-O(34)#2	88.5(2)
O(19)#1-Cu(4)-O(3)	142.3(2)	N(5)-Cu(8)-O(28)#2	91.9(3)
O(2)-Cu(4)-O(55)	87.9(2)	O(5)#2-Cu(8)-O(28)#2	92.8(2)
O(11)-Cu(4)-O(55)	92.4(2)	O(34)#2-Cu(8)-O(28)#2	150.1(2)
O(19)#1-Cu(4)-O(55)	105.1(2)	N(5)-Cu(8)-O(30)	95.6(3)
O(3)-Cu(4)-O(55)	112.4(2)	O(5)#2-Cu(8)-O(30)	84.6(2)
O(3)-Cu(5)-O(26)	175.1(2)	O(34)#2-Cu(8)-O(30)	122.7(2)
O(3)-Cu(5)-O(14)	97.5(2)	O(28)#2-Cu(8)-O(30)	87.1(2)

O(29)#3-Cu(9)-O(16)	89.5(2)	O(42)-Cu(13)-O(38)	83.3(2)
O(29)#3-Cu(9)-O(5)	96.0(2)	O(7)-Cu(13)-O(49)	92.6(2)
O(16)-Cu(9)-O(5)	169.5(2)	O(42)-Cu(13)-O(49)	175.2(3)
O(29)#3-Cu(9)-O(4)	177.0(2)	O(38)-Cu(13)-O(49)	92.7(2)
O(16)-Cu(9)-O(4)	93.6(2)	O(6)-Cu(14)-N(16)#3	165.1(3)
O(5)-Cu(9)-O(4)	81.0(2)	O(6)-Cu(14)-O(36)	87.7(2)
O(45)-Cu(10)-O(15)	155.5(3)	N(16)#3-Cu(14)-O(36)	89.7(3)
O(45)-Cu(10)-O(4)	92.4(2)	O(6)-Cu(14)-O(37)	88.6(2)
O(15)-Cu(10)-O(4)	90.5(2)	N(16)#3-Cu(14)-O(37)	89.5(3)
O(45)-Cu(10)-N(13)	92.7(3)	O(36)-Cu(14)-O(37)	162.6(3)
O(15)-Cu(10)-N(13)	86.0(3)	O(6)-Cu(14)-O(49)	88.3(2)
O(4)-Cu(10)-N(13)	174.3(2)	N(16)#3-Cu(14)-O(49)	106.6(3)
O(45)-Cu(10)-O(22)	120.0(2)	O(36)-Cu(14)-O(49)	104.8(2)
O(15)-Cu(10)-O(22)	84.5(2)	O(37)-Cu(14)-O(49)	92.1(2)
O(4)-Cu(10)-O(22)	86.4(2)	O(8)-Cu(15)-N(12)#4	173.7(2)
N(13)-Cu(10)-O(22)	88.8(2)	O(8)-Cu(15)-O(43)	88.4(2)
O(6)-Cu(11)-O(47)	166.9(2)	N(12)#4-Cu(15)-O(43)	87.3(3)
O(6)-Cu(11)-O(35)	91.3(2)	O(8)-Cu(15)-O(40)#5	93.6(2)
O(47)-Cu(11)-O(35)	83.8(2)	N(12)#4-Cu(15)-O(40)#5	92.6(3)
O(6)-Cu(11)-O(31)#3	93.0(2)	O(43)-Cu(15)-O(40)#5	143.9(3)
O(47)-Cu(11)-O(31)#3	93.1(2)	O(8)-Cu(15)-O(51)	85.6(2)
O(35)-Cu(11)-O(31)#3	173.3(3)	N(12)#4-Cu(15)-O(51)	93.4(3)
O(7)-Cu(12)-O(41)	88.1(2)	O(43)-Cu(15)-O(51)	126.1(3)
O(7)-Cu(12)-N(9)	167.2(3)	O(40)#5-Cu(15)-O(51)	90.0(2)
O(41)-Cu(12)-N(9)	88.9(3)	O(52)#5-Cu(16)-O(44)	91.0(2)
O(7)-Cu(12)-O(48)	89.5(2)	O(52)#5-Cu(16)-O(8)	173.8(3)
O(41)-Cu(12)-O(48)	160.5(3)	O(44)-Cu(16)-O(8)	91.4(2)
N(9)-Cu(12)-O(48)	89.1(3)	O(52)#5-Cu(16)-O(8)#5	95.0(2)
O(7)-Cu(12)-O(31)#3	85.5(2)	O(44)-Cu(16)-O(8)#5	169.3(2)
O(41)-Cu(12)-O(31)#3	105.9(3)	O(8)-Cu(16)-O(8)#5	81.8(2)
N(9)-Cu(12)-O(31)#3	107.3(3)	O(52)#5-Cu(16)-O(39)#5	93.4(2)
O(48)-Cu(12)-O(31)#3	93.2(2)	O(44)-Cu(16)-O(39)#5	107.4(2)
O(7)-Cu(13)-O(42)	91.8(2)	O(8)-Cu(16)-O(39)#5	91.4(2)
O(7)-Cu(13)-O(38)	168.9(2)	O(8)#5-Cu(16)-O(39)#5	81.1(2)

Symmetry transformations used to generate equivalent atoms: #1: -x, -y+1, -z; #2: x, y+1, z-1; #3: x, y-1, z+1; #4: -x+1, -y+1, -z+1; #5: -x+1, -y, -z+2.