

Supporting Information for

Oxygen and methanol mediated irreversible coordination polymer structural transformation from a 3D Cu(I)-framework to a 1D Cu(II)-chain

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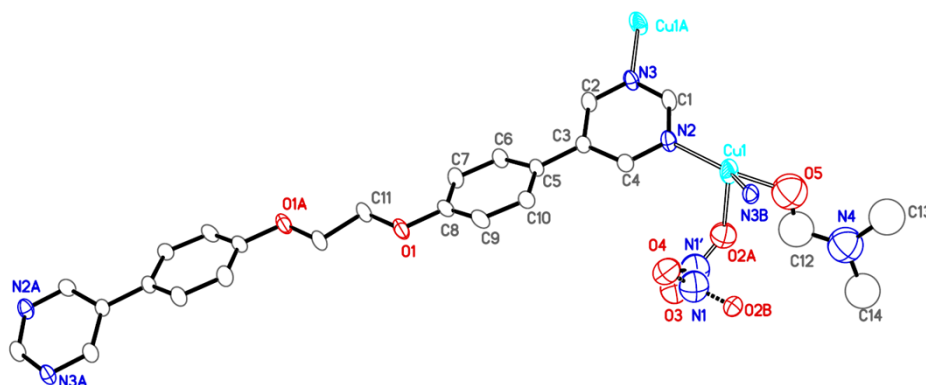


Fig. S1 The ORTEP figure of **1** (displacement ellipsoids drawn at the 30 % probability level).

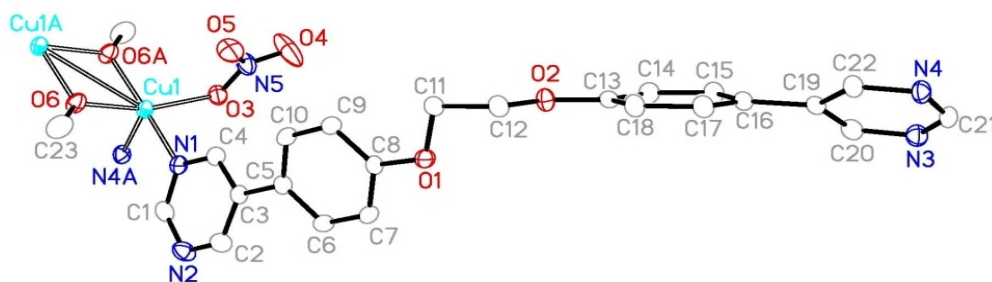


Fig. S2 The ORTEP figure of **2** (displacement ellipsoids drawn at the 30 % probability level).

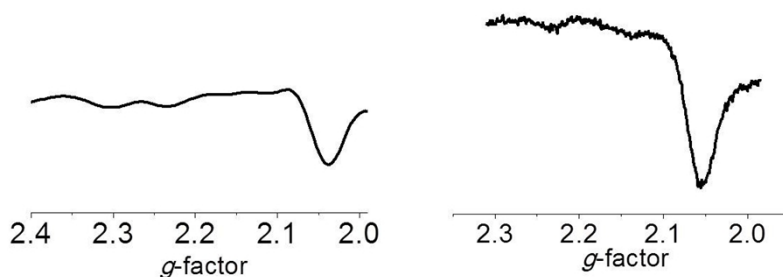


Fig. S3 The ESR spectra of **2** (left) and **1-1d** (right), which indicates the copper ions in **2** and **1-1d** are bivalent. However, compound **2** is ESR silent somehow and only a weak signal of monomeric impurities is observed. Such a diamagnetic and ESR-silent behavior was often observed in the reported literatures (ref. 10a in the main text) for other methoxo-bridged compounds.¹

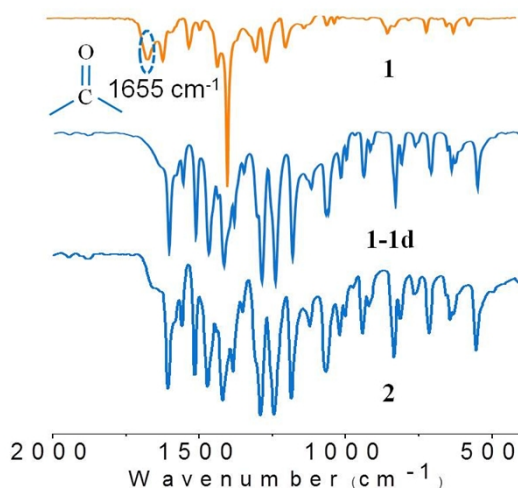


Fig. S4 IR spectra of **1**, **1-1d** and **2**. No $>C=O$ peak of DMF found in IR spectrum of **1-d**, which is the same as that of **2**.

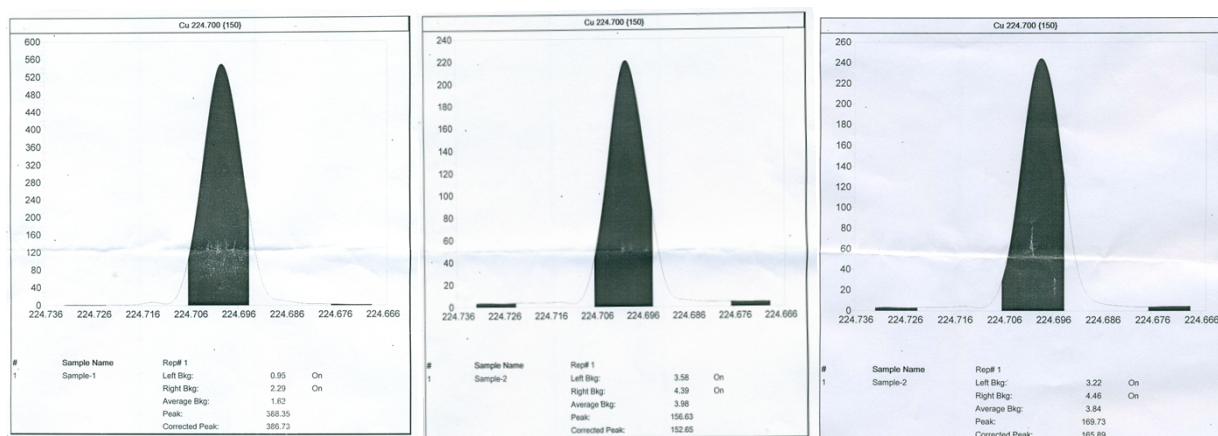



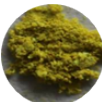





Fig. S5 The ICP-LC measurement indicates that the amount of copper in **1** is 18.1% (calcd is 18.2%) (left), in **2** is 11.9% (calcd is 12.1%) (middle) and in **1-1d** is 12.1% (right).

Table S1. Elemental analyses for **1**, **2** and **1-1d** (The calcd. values are shown in brackets).

	C	H	N
1	43.26 (43.32)	3.85 (3.65)	13.96 (14.23)
2	52.02 (52.42)	3.63 (4.02)	12.66 (13.29)
1-1d	51.41	3.39	12.39

Table S2. Structural transformation from **1** to **2** at different temperatures.

Temperature	30 °C	45 °C	60 °C
Original color ($t_0 = 0$)			
t_1	6h	2h	1.5h
Color ($t = t_1$)	 1-1a	 1-1a'	 1-1a''
t_2	36h	32h	26h
Color ($t = t_2$)	 1-1d	 1-1d'	 1-1d''

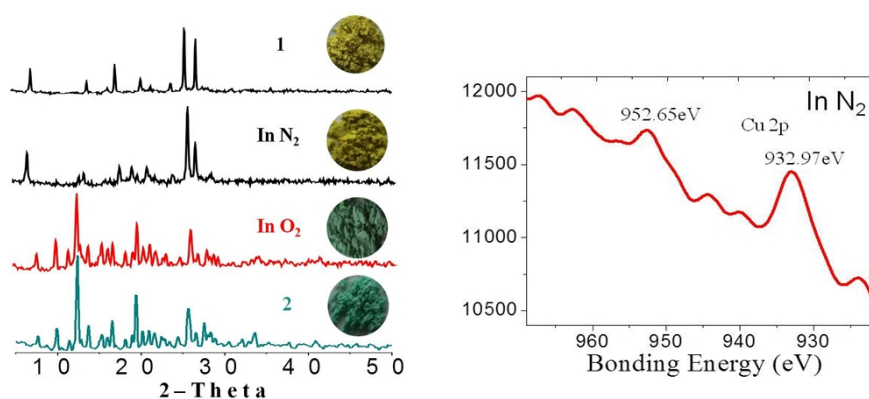


Fig. S6 The corresponding XRPD patterns (left) of **1** in MeOH under N_2 atmosphere, under O_2 atmosphere (22 h) and compounds **1-2**. XPS spectrum (right) also indicates that no structural transformation occurred in N_2 . The corresponding samples pictures are inserted.

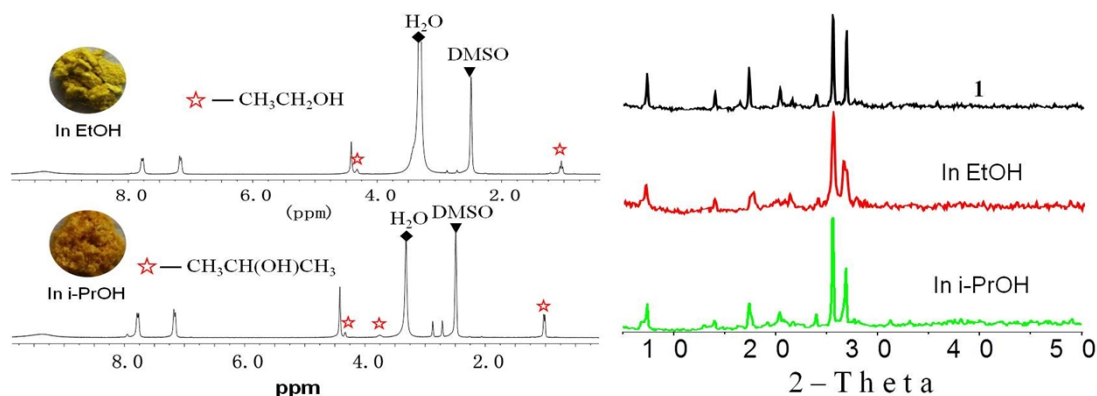


Fig. S7 ^1H NMR spectra ($\text{DMSO-}d_6$, left) of compound **1** in EtOH and *i*-PrOH, respectively, and their corresponding XRPD patterns (right). The samples pictures are inserted. The ^1H NMR spectra indicate that the coordinated DMF molecules in **1** are partly exchanged by the corresponding ROH solvent molecules, and corresponding XRPD patterns show that no structural transformation occurred in EtOH and *i*-PrOH.

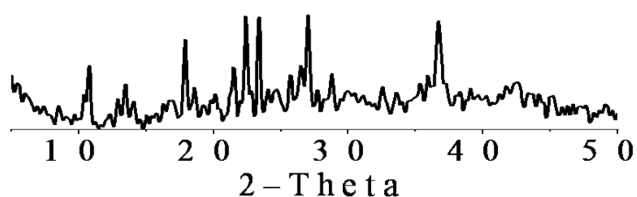


Fig. S8 The XRPD pattern of compound **1** in H_2O indicates that an unknown structure was generated.

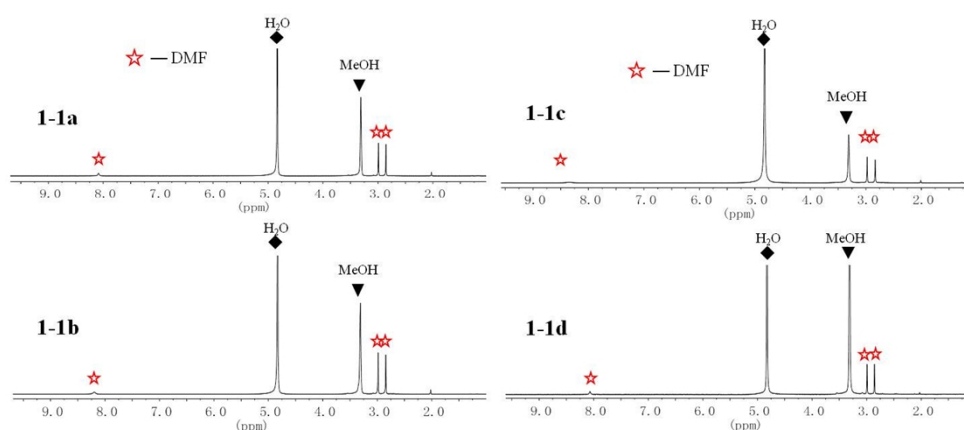
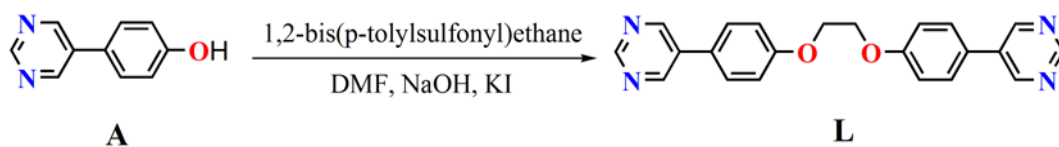


Fig. S9 ^1H NMR spectra (MeOD) performed on mother liquors of **1** in MeOH in air. **1-1a**, **1-1b**, **1-1c**, **1-1d** means that the mother liquors obtained at 6, 12, 24, and 36 h, respectively. No ligand signals are detected during the transformation process, which means the **1** to **2** might be a solid state structural transformation.

Experimental Section. $\text{Cu}(\text{NO}_3)_2$ (Acros) was used as obtained without further purification. Infrared (IR) samples were prepared as KBr pellets, and spectra were obtained in the 400–4000 cm^{-1} range using a Perkin-Elmer 1600 FTIR spectrometer. Elemental analyses were performed on a Perkin-Elmer model 2400 analyzer. ^1H NMR data were collected using an AM-300 spectrometer. Chemical shifts are reported in δ relative to TMS. Thermogravimetric analyses were carried out using a TA Instrument SDT 2960 simultaneous DTA-TGA under flowing nitrogen at a heating rate of 10 $^\circ\text{C}/\text{min}$. XRD patterns were obtained on a D8 ADVANCE X-ray powder diffractometer (XRD) with $\text{Cu K}\alpha$ radiation ($\lambda = 1.5405 \text{ \AA}$). ICP-LC was performed on an IRIS Interpid II XSP and NU AttoM. XPS spectra were obtained from THI5300 (PE). EPR spectra were obtained from Bruker A300-10/12/S-LC.

Synthesis of L.



A mixture of **A** (0.52 g, 3.00 mmol) and 1,2-bis(p-tolylsulfonyl)ethane (0.53 g, 1.43 mmol) and sodium hydroxide (0.24 g, 3 mmol) in anhydrous N,N-dimethylformamide (6 mL) was stirred for 6 h at 85 $^\circ\text{C}$ and monitored by thin-layer chromatography (TLC). After removal of the solvent, the residue was purified on silica gel by a column using $\text{CH}_2\text{Cl}_2:\text{CH}_3\text{OH} = 30:1$ as the eluent to afford **L** as a colorless crystalline solid (0.41 g; yield, 78%). IR (KBr pellet cm^{-1}): 3440 (br), 2936 (w), 1610 (m), 1555 (w), 1516 (s), 1415 (vs), 1285 (m), 1242 (vs), 1192 (s), 1055 (m), 800 (w), 628 (w). ^1H NMR (300MHz, DMSO, 25 $^\circ\text{C}$, TMS, ppm): 9.12–9.10 (d, 4H, $-\text{C}_4\text{H}_3\text{N}_2$),

7.79–7.76 (d, 4H, $-\text{C}_6\text{H}_4$), 7.17–7.15 (d, 4H, $-\text{C}_6\text{H}_4$), 4.42 (s, 4H, $-\text{CH}_2$). Elemental analysis (%) calcd for $\text{C}_{22}\text{H}_{18}\text{O}_2\text{N}_4$: C 71.34, H 4.89, N 15.13. Found: C 71.85, H 4.11, N 14.85.

Synthesis of 1. **L** (3.70 mg, 0.01 mmol), $\text{Cu}(\text{NO}_3)_2$ (4.83 mg, 0.02 mmol), DMF (2 mL) and a few drops of acetonitrile were sealed in a 5 mL glass tube. The mixture was heated at 90 °C for 3 days under autogenous pressure and then cooled to room temperature at a rate of 5°C/h. Orange crystals (4.54 mg) were isolated from the tube. Yield, 65% (based on **L**). IR (KBr pellet cm^{-1}): 3461 (br), 1655 (m), 1604 (m), 1515 (w), 1384 (vs), 1288 (w), 1251 (m), 1186 (w), 838 (w), 704 (w). ^1H NMR (300MHz, DMSO, 25 °C, TMS, ppm) δ : 9.47 (br, 6H, $-\text{C}_4\text{H}_3\text{N}_2$), 7.96 (d, 4H, $-\text{C}_6\text{H}_4$), 7.79–7.76 (d, 4H, $-\text{C}_6\text{H}_4$), 7.18–7.15 (d, 4H, $-\text{C}_6\text{H}_4$), 4.42 (s, 4H, $-\text{CH}_2$), 2.87 (s, 3H, $-\text{CH}_3$), 2.81 (s, 3H, $-\text{CH}_3$), 2.06 (s, 3H, $-\text{CH}_3$). Elemental analysis (%) calcd for $\text{C}_{12.6}\text{H}_{12.65}\text{O}_{4.5}\text{N}_{3.55}\text{Cu}$: C 43.32, H 3.65, N 14.23. Found: C 43.26, H 3.85, N 13.96.

Synthesis of 2. A solution of $\text{Cu}(\text{NO}_3)_2$ (14.49 mg, 0.06 mmol) in CH_3OH (8 mL) was carefully layered onto a solution of **L** (11.10 mg, 0.03 mmol) in DMF (8 mL). The solutions were left for about three days at room temperature, and green-blue crystals (10.75 mg) of **2** were obtained. Yield, 68% (based on **L**). IR (KBr pellet cm^{-1}): 3425 (br), 2927 (w), 2791 (w), 1606 (m), 1559 (w), 1515 (m), 1471 (m), 1384 (m), 1290 (s), 1244 (s), 1185 (m), 1064 (m), 941 (w), 834 (m), 643 (w). ^1H NMR (300MHz, DMSO, 25 °C, TMS, ppm): 9.41 (br, 6H, $-\text{C}_4\text{H}_3\text{N}_2$), 7.78–7.75 (d, 4H, $-\text{C}_6\text{H}_4$), 7.17–7.14 (d, 4H, $-\text{C}_6\text{H}_4$), 4.42 (s, 4H, $-\text{CH}_2$), 4.08–4.07 (d, 1H, R–OH), 3.17–3.15 (d, 3H, $-\text{CH}_3$). Elemental analysis (%) calcd for $\text{C}_{23}\text{H}_{21}\text{O}_6\text{N}_5\text{Cu}$: C 52.42, H 4.02, N 13.29; Found: C 52.02, H 3.63, N 12.66.

Structural transformation of 1 to 2. The orange crystals of **1** (10 mg) were taken in a glass bottle (25 mL) containing CH_3OH (8 mL), which was left at room temperature in air. Over a

period of 6h, 12h, 24h and 36h, the distinct changes in color of the crystals from orange to dark yellow (**1-1a**), yellow-green (**1-1b**), green (**1-1c**) and green-blue (**1-1d**) were observed.

DMPO-trapped EPR. The DMPO trapped EPR spectra were carried out at a Bruker A300-10/12/S-LC electron paramagnetic resonance spectroscopy, which was operated at X-field with a centre field at 3511.520G. And the sweep width is 200G. The microwave frequency is 9.862008GHz, and power is 19.85 mW. Sweep time of the signal channel is 20.48 s, with a 3.56×10^5 gain at the receiver. 11 μL DMPO (purchased from J&K, 11 μL DMPO + 500 μL water) was dropped into 8mL CH_3OH solvent, in which **1** (10 mg) was suspended. After stirring for 36 h, the mother liquor was transferred to a 100 μL capillary tube, which then was immediately fixed in the resonant cavity of the spectrometer. The mother liquor (100 μL) was transferred to a glass tube (1 mL) and 80 μL SOD (purchased from Sigma S7571, diluted by water, 2000 U mL^{-1}) was injected into it immediately. The final solution was transferred to a 100 μL capillary tube, which then fixed in the resonant cavity of the spectrometer.

Single-Crystal Structure Determination. Suitable single crystal of **1** and **2** were selected and mounted in air onto thin glass fibers. X-ray intensity data of **1** and **2** were measured at 123(2) K and 298(2) K, respectively, on a Bruker SMART APEX CCD-based diffractometer (Mo $K\alpha$ radiation, $\lambda = 0.71073 \text{ \AA}$). The raw frame data were integrated into SHELX-format reflection files and corrected for Lorentz and polarization effects using SAINT.² Corrections for incident and diffracted beam absorption effects were applied using SADABS.² None of the crystals showed evidence of crystal decay during data collection. All structures were solved by a combination of direct methods and difference Fourier syntheses and refined against F^2 by the full-matrix least-squares technique.³

$\text{Cu}_2\text{L}(\text{NO}_3)_2(\text{DMF})_{0.4}$ (**1**) crystallizes in the Monoclinic system. The space group $C2/c$ was assumed and confirmed by successful solution and refinement of the data. The asymmetric unit consist of 0.5 independent Cu centers, which is located on a crystallographic inversion center, one L ligand, one nitrate ion and 0.2 DMF molecule. These species were refined anisotropically beside the DMF molecule, and the nitrate ion and DMF molecule were refined as disordered. Total 35 restraints were used to model the nitrate ion and DMF molecule. The presence of the largest residual electron density peak ($1.34\text{e}^-/\text{\AA}^3$) in this area reflects further unresolved disorder.

Crystal data, data collection parameters, and refinement statistics are listed in Table S3-4. Relevant interatomic bond distances and bond angles for **1-2** are given in Tables S5-6. Crystallographic data (excluding structure factors) for the structure reported in this paper have been deposited with the Cambridge Crystallographic Data Center as supplementary publication no CCDC 984134-984135. Copies of the data can be obtained free of charge on application to CCDC, 12 Union Road, Cambridge CB2 1EZ, UK (fax: (+44)1223-336-033; e-mail: deposit@ccdc.cam.ac.uk).

Table S3. Crystal data and structure refinement for **1**.

Identification code	1	
Empirical formula	$\text{C}_{23.20}\text{H}_{20.80}\text{Cu}_2\text{N}_{6.40}\text{O}_{8.40}$	
Formula weight	650.74	
Temperature	123(2) K	
Wavelength	0.71073 Å	
Crystal system, space group	Monoclinic, $C2/c$	
Unit cell dimensions	$a = 24.119(2)$ Å	$\alpha = 90^\circ$
	$b = 10.2056(7)$ Å	$\beta = 91.640(6)^\circ$
	$c = 10.8193(7)$ Å	$\gamma = 90^\circ$

Volume	2662.0(3) Å ³
Z, Calculated density	4, 1.624 Mg/m ³
Absorption coefficient	1.659 mm ⁻¹
F(000)	1320
Crystal size	0.38 x 0.08 x 0.07 mm
Theta range for data collection	1.69 to 25.50 deg
Reflections collected / unique	6881 / 2467 [R(int) = 0.0385]
Completeness to theta = 25.50	99.7 %
Goodness-of-fit on F ²	1.127
Final R indices [I>2sigma(I)]	R1 = 0.0920, wR2 = 0.2582

Table S4. Crystal data and structure refinement for **2**.

Identification code	2
Empirical formula	C ₂₃ H ₂₁ CuN ₅ O ₆
Formula weight	526.99
Temperature	298(2) K
Wavelength	0.71073 Å
Crystal system, space group	Monoclinic, <i>P2(1)/n</i>
Unit cell dimensions	a = 8.281(3) Å alpha = 90° b = 15.288(6) Å beta = 96.566(5)° c = 18.093(7) Å gamma = 90°
Volume	2275.6(16) Å ³
Z, Calculated density	4, 1.541 Mg/m ³
Absorption coefficient	1.011 mm ⁻¹
F(000)	1088
Crystal size	0.21 x 0.20 x 0.18 mm
Theta range for data collection	1.75 to 25.50°
Reflections collected / unique	11593 / 4218 [R(int) = 0.0305]
Completeness to theta = 25.50	99.8 %

Max. and min. transmission	0.834 and 0.809
Goodness-of-fit on F ²	0.965
Final R indices [<i>I</i> > 2σ(<i>I</i>)]	R1 = 0.0411, wR2 = 0.1123

Table S5. Interatomic Distances (Å) and Bond Angles (°) with esds () for **1**.

Cu(1)-O(5)	1.909(10)	Cu(1)-N(3)#3	1.955(5)
Cu(1)-N(2)	1.965(5)	Cu(1)-O(3)#4	2.160(11)
Cu(1)-O(2A)	2.240(15)		
O(5)-Cu(1)-N(3)#3	92.7(17)	O(5)-Cu(1)-N(2)	134.7(17)
N(3)#3-Cu(1)-N(2)	132.6(2)	O(5)-Cu(1)-O(3)#4	37.2(18)
N(3)#3-Cu(1)-O(3)#4	100.3(3)	N(2)-Cu(1)-O(3)#4	117.4(4)
O(5)-Cu(1)-O(2A)	65(2)	N(3)#3-Cu(1)-O(2A)	108.8(4)
N(2)-Cu(1)-O(2A)	94.7(4)	O(3)#4-Cu(1)-O(2A)	96.9(5)

Symmetry transformations used to generate equivalent atoms:

#1 -x+2,-y+1,-z+3	#2 -x+1,y,-z+3/2
#3 -x+3/2,y-1/2,-z+3/2	#4 x,-y+1,z-1/2
#5 -x+3/2,y+1/2,-z+3/2	#6 x,-y+1,z+1/2

Table S6. Interatomic Distances (Å) and Bond Angles (°) with esds () for **2**.

Cu(1)-O(6)	1.934(2)	Cu(1)-O(3)	2.030(2)
Cu(1)-O(6)#1	1.937(2)	Cu(1)-N(4)#2	2.333(3)
Cu(1)-N(1)	2.024(3)	Cu(1)-Cu(1)#1	3.0356(12)
O(6)-Cu(1)-O(6)#1	76.72(9)	O(6)-Cu(1)-N(1)	94.79(9)
O(6)#1-Cu(1)-N(1)	169.64(10)	O(6)-Cu(1)-O(3)	162.30(10)
O(6)#1-Cu(1)-O(3)	93.49(9)	N(1)-Cu(1)-O(3)	93.12(10)
O(6)-Cu(1)-N(4)#2	106.78(9)	O(6)#1-Cu(1)-N(4)#2	91.87(10)
N(1)-Cu(1)-N(4)#2	96.32(10)	O(3)-Cu(1)-N(4)#2	88.01(9)
O(6)-Cu(1)-Cu(1)#1	38.39(6)	O(6)#1-Cu(1)-Cu(1)#1	38.33(6)
N(1)-Cu(1)-Cu(1)#1	132.92(8)	O(3)-Cu(1)-Cu(1)#1	130.23(7)
N(4)#2-Cu(1)-Cu(1)#1	101.82(7)		

Symmetry transformations used to generate equivalent atoms:

#1 $-x+1, -y+1, -z$ #2 $x+1, y, z-1$ #3 $x-1, y, z+1$

Reference

(1) a) G. A. van Albada, M. T. Lakin, N. Veldman, A. L. Spek, J. Reedijk, *Inorg. Chem.*, 1995, 34, 4910. b) G. A. van Albada, W. J.J. Smeets, A. L. Spek, J. Reedijk, *Inorg. Chim. Acta*, 1997, 260, 151.

(2) SMART Version 5.625, SAINT+ Version 6.22 and SADABS Version 2.05. Bruker Analytical X-ray Systems, Inc., Madison, Wisconsin, USA, 2001.

(3) Sheldrick, G. M. SHELXTL Version 6.1; Bruker Analytical X-ray Systems, Inc., Madison, Wisconsin, USA, 2000.