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“Systematic Synthesis of a Metal Organic Framework Based on Triangular $\text{Cu}_3(\mu_3\text{-OH})$ Secondary Building Units: From a 0-D Complex, to an 1-D Chain and a 3-D Lattice”

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Abstract

Reactions of $\text{Cu}(\text{CF}_3\text{SO}_3)_2$ and pyrazole in methanolic solutions in the presence of stoichiometric amounts of py, py/4,4'-bpy, or 4,4'-bpy have yielded two new complexes $[\text{Cu}_3(\mu_3\text{-OH})(\mu\text{-pz})_3(\text{py})_3](\text{CF}_3\text{SO}_3)_2 \cdot 0.5\text{H}_2\text{O}$ (1) and $[\{\text{Cu}_3(\mu_3\text{-OH})(\mu\text{-pz})_3(\text{py})_2\}_2(\mu\text{-4,4'-bpy})](\text{CF}_3\text{SO}_3)_4$ (2), a one-dimensional coordination polymer, $\{[\text{Cu}_3(\mu_3\text{-OH})(\mu\text{-pz})_3(\text{py})(\mu\text{-4,4'-bpy})](\text{CF}_3\text{SO}_3)_2 \cdot 0.5\text{H}_2\text{O}\}_n$ (3), and a three-dimensional, eight-fold interpenetrated extended lattice, $\{[\text{Cu}_3(\mu_3\text{-OH})(\mu\text{-pz})_3(\mu\text{-4,4'-bpy})_{1.5}](\text{CF}_3\text{SO}_3)_2 \cdot 1.5\text{H}_2\text{O}\}_n$ (4).

INTRODUCTION

Metal organic frameworks (MOFs) have attracted the interest of chemists, physicists, and materials scientists due to their promising applications in catalysis, separations, optics, magnetism, host-guest chemistry and gas storage, as well as for the variety of their often esthetically pleasing, highly symmetric structures.¹ The synthesis of coordination polymers utilizing secondary building units (SBUs) – functional, pre-assembled clusters of atoms, capable of independent existence – allows the tailoring of the polymer properties via the introduction of SBU-derived functionalities.² Bulky SBUs, serving as large vertices joined by rigid organic links, favor the formation of interpenetrated extended frameworks.³

The trinuclear $\text{Cu}_3(\mu_3\text{-O(H)})$ moiety is a common cluster unit generated *in situ* from reactions of copper (II) and pyrazoles or triazoles.^{4, 5} The principal interest in the latter complexes has been their relevance to the active center of particulate Methane Monooxygenase (pMMO) and other multicopper oxidases.^{4d, 5c-e, 6} The investigation of the fundamental properties of these complexes have revealed interesting redox, magnetic, and spectroscopic properties.⁴⁻⁸ For example, we have shown that the rigid trinuclear metallacycle $[\text{Cu}(\mu\text{-pz})_3]$ supports the pH-controlled exchange of $\mu_3\text{-E}$ capping ligands from $\text{E} = \text{O}^{2-}$, to OH^- and Cl^- in basic, intermediate and acidic environment, respectively.^{4d} The 3-E ligand exchange is accompanied by a stepwise change from a strongly antiferromagnetic ($\text{E} = \text{O}^{2-}$), to weakly antiferromagnetic ($\text{E} = \text{OH}^-$), and ferromagnetic ($\text{E} = \text{Cl}^-$) exchange among the three Cu-centers.^{7a} In addition, the planar $[\text{Cu}_3(\mu_3\text{-O})]^{4+}$ species can be reversibly oxidized to its mixed-valence, delocalized, formally $\text{Cu}^{\text{II}}_2\text{Cu}^{\text{III}}$ analogue.⁶ Recently, several coordination polymers containing $\text{Cu}_3(\mu_3\text{-O(H)})$ -pyrazolate/triazolate SBUs, connected by carboxylate links have been reported and the field has been reviewed.^{9, 10}

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Herein, we present the rational, stepwise synthesis of a series of copper(II)-pyrazolato complexes, starting with the trinuclear complex $[\text{Cu}_3(\mu_3\text{-OH})(\mu\text{-pz})_3(\text{py})_3](\text{CF}_3\text{SO}_3)_2 \cdot 0.5\text{H}_2\text{O}$ ($\{\text{Cu}_3\}$, **1**), a discrete dimer-of-trinuclear units $[\{\text{Cu}_3(\mu_3\text{-OH})(\mu\text{-pz})_3(\text{py})_2\}_2(\mu\text{-4,4'-bpy})](\text{CF}_3\text{SO}_3)_4$ ($\{\text{Cu}_3\text{-bpy-Cu}_3\}$, **2**), a one-dimensional coordination polymer $[\{\text{Cu}_3(\mu_3\text{-OH})(\mu\text{-pz})_3(\text{py})(\mu\text{-4,4'-bpy})\}(\text{CF}_3\text{SO}_3)_2 \cdot 0.5\text{H}_2\text{O}]_n$ ($\{\text{-Cu}_3\text{-bpy-}\}_n$, **3**), leading finally to a three-dimensional coordination polymer $[\{\text{Cu}_3(\mu_3\text{-OH})(\mu\text{-pz})_3(\mu\text{-4,4'-bpy})_{1.5}\}(\text{CF}_3\text{SO}_3)_2 \cdot 1.5\text{H}_2\text{O}]_n$ ($\{\text{-Cu}_3\text{-bpy}_{1.5}\}_n$, **4**) (pz = pyrazolato anion, $\text{C}_3\text{H}_3\text{N}_2^-$; py = pyridine; 4,4'-bpy = 4,4'-bipyridine). Compounds **1** – **4** have been characterized by single crystal X-ray diffraction, elemental analysis and spectroscopic techniques.

Experimental Section

Materials and Methods

All commercially available reagents were used as received, except methanol, which was distilled prior to use. Infrared, ^1H -NMR and UV-Vis spectra were recorded at room temperature on a Bruker Tensor 27, Bruker Avance DPX-300 and Varian Cary 500 Scan, respectively. Thermogravimetric analyses (TGA) were performed with a Shimadzu TGA-50 analyzer, with the samples held for 1.0 min at 25.0 °C, heated from 25.0 °C to 800.0 °C at 10.0 °C/min, then held 1.0 min at 800.0 °C. Elemental Analyses were performed by Galbraith Laboratories, Inc., Knoxville, TN. Melting points were measured on an Electrothermal IA9100 apparatus and reported without correction. X-ray diffraction data were collected with a Bruker AXS SMART 1K CCD diffractometer,¹¹ using graphite-monochromated Mo-K α radiation at ambient temperature and were corrected for Lorentz and polarization effects.¹² The structures were solved employing the SHELXTL-direct methods program and refined by full-matrix least-squares on F^2 .¹³ For **3** and **4**, the high-angle data ($2\theta > 46^\circ$) were of poor quality and were eliminated from the final refinement. In the structure of **3**, three of the four triflate anions were refined with restrained bond lengths and angles. The structure of **4** contains large voids, occupied by apparently disordered solvent molecules, whose presence is evident from the TGA analysis. Modified structure factors of **4** were generated by the program SQUEEZE (part of the WinGX crystallographic package)¹⁴ for the final refinement cycle. Crystallographic details are summarized in Table 1. Selected bond lengths and angles for **1** – **4** are listed in Tables 2 – 5, respectively.

Synthesis

$[\text{Cu}_3(\mu_3\text{-OH})(\mu\text{-pz})_3(\text{py})_3](\text{CF}_3\text{SO}_3)_2 \cdot 0.5\text{H}_2\text{O}$ (1**)**—Complex **1** was synthesized in methanol similarly to a previously reported procedure.^{6b} $\text{Cu}(\text{CF}_3\text{SO}_3)_2$ (232.9 mg, 0.63 mmol), pzH (40.0 mg, 0.58 mmol), NaOH (35.3 mg, 0.88 mmol), and py (55 μL , 0.60 mmol) were stirred overnight in 10 mL of MeOH at ambient temperature. Crystals of the water solvate of **1** (165.9 mg, 90.0 %) suitable for X-ray diffraction were obtained from the reaction mixture by slow evaporation of the solvent in an open vessel. ^1H NMR (DMSO- d_6 , ppm): 39.65 (3H, $w_{1/2} = 50$ Hz); 33.61 (6H, $w_{1/2} = 80$ Hz); 19.77 (6H, $w_{1/2} = 375$ Hz); 11.51 (6H, $w_{1/2} = 100$ Hz); 8.56 (3H, $w_{1/2} = 35$ Hz). ESI-MS (CH_3CN , m/z) = 866 ($[\text{Cu}_3(\text{OH})^2(\text{pz})_3(\text{py})_2(\text{CF}_3\text{SO}_3)_2]^+$), 795 ($[\text{Cu}_3(\text{OH})(\text{pz})_3(\text{py})_3(\text{CF}_3\text{SO}_3)]^+$), 716 ($[\text{Cu}_3(\text{OH})(\text{pz})_3(\text{py})_2(\text{CF}_3\text{SO}_3)]^+$), 696 ($[\text{Cu}_3(\text{OH})(\text{pz})_3(\text{py})\text{H}_2\text{O}(\text{CF}_3\text{SO}_3)\text{CH}_3\text{CN}]^+$), 637 ($[\text{Cu}_3(\text{OH})(\text{pz})_3(\text{py})_2(\text{CF}_3\text{SO}_3)]^+$), 487 ($[\text{Cu}_3(\text{O})(\text{pz})_3(\text{py})]^+$), 449 ($[\text{Cu}_3(\text{O})(\text{pz})_3\text{CH}_3\text{CN}]^+$), 406 ($[\text{Cu}_3(\text{O})(\text{pz})_3]^+$); (MeOH, m/z) = 733 ($[\text{Cu}_3(\text{OH})(\text{pz})_3(\text{py})_2(\text{CF}_3\text{SO}_3)\text{H}_2\text{O}]^+$), 694 ($[\text{Cu}_3(\text{OH})(\text{pz})_2(\text{CF}_3\text{SO}_3)_2(\text{H}_2\text{O})_3]^+$), 636 ($[\text{Cu}_3(\text{OH})(\text{pz})_3(\text{py})(\text{CF}_3\text{SO}_3)]^+$), 553 ($[\text{Cu}_3(\text{OH})(\text{pz})_2(\text{py})(\text{CF}_3\text{SO}_3)]^+$), 485 ($[\text{Cu}_2(\text{pz})_3(\text{py})_2]^+$), 408 ($[\text{Cu}_2(\text{pz})_3(\text{py})]^+$). UV-Vis and IR data for **1** have been published previously.^{6b}

$[\{\text{Cu}_3(\mu_3\text{-OH})(\mu\text{-pz})_3(\text{py})_2\}_2(\mu\text{-4,4'-bpy})](\text{CF}_3\text{SO}_3)_4$ (2**)**— $\text{Cu}(\text{CF}_3\text{SO}_3)_2$ (221.3 mg, 0.60 mmol), pzH (40.1 mg, 0.58 mmol), NaOH (35.2 mg, 0.88 mmol) were stirred in 20 mL of

MeOH, and a solution of 4,4'-bpy (16.3 mg, 0.10 mmol) and py (35 μ L, 0.40 mmol) in 20 mL of MeOH was added dropwise. The reaction mixture was stirred for 24 h at ambient temperature. The mother liquor was filtered and the volume was reduced to 12 mL under reduced pressure. Suitable crystals for X-ray diffraction were obtained by MeOH evaporation after filtering the crystals and washing with chilled CH_2Cl_2 ; 164.0 mg (89.9 %) of product were obtained. Mp. (237.7–238.2) $^\circ\text{C}$. For $\text{C}_{52}\text{H}_{50}\text{Cu}_6\text{F}_{12}\text{N}_{18}\text{O}_{15}\text{S}_4$ (calcd, found %): C (32.79, 32.56); H (2.65, 2.57); N (13.24, 13.15). ^1H NMR (DMSO- d_6 , ppm): 39.64 (3H, $w_{1/2}$ = 20 Hz); 33.64 (6H, $w_{1/2}$ = 50 Hz); 21.18 (4H, $w_{1/2}$ = 50 Hz); 14.73 (2H, $w_{1/2}$ = 350 Hz); 12.05 (4H, $w_{1/2}$ = 70 Hz); 9.94 (2H, $w_{1/2}$ = 40 Hz), 8.68 (2H, $w_{1/2}$ = 20 Hz). IR (cm^{-1}): 3119 (br), 1608 (w), 1493 (w), 1451 (w), 1418 (w), 1379 (w), 1295 (sh), 1280 (m), 1243 (sh), 1217 (s), 1178 (m), 1158 (m), 1071 (m), 1023 (s), 818 (m), 783 (sh), 763 (m), 755 (sh), 700 (m), 634 (s), 576 (m), 518 (m), 489 (m), 465 (m), 435 (m). UV-Vis (MeOH, cm^{-1}): 15198 (br), 46083. ESI-MS (CH_3CN , m/z) = 783 ($[\text{Cu}_3(\text{OH})(\text{pz})_3(\text{py})(\text{bpy})(\text{CF}_3\text{SO}_3)]^+$), 715 ($[\text{Cu}_3(\text{O})(\text{pz})_2(\text{py})(\text{bpy})(\text{CF}_3\text{SO}_3)]^+$), 636 ($[\text{Cu}_3(\text{O})(\text{pz})_2(\text{bpy})(\text{CF}_3\text{SO}_3)]^+$), 486 ($[(\text{Cu}_3\text{O}(\text{pz})_3(\text{py}))^+]$), 449 ($[\text{Cu}_3\text{O}(\text{pz})_3(\text{MeCN})]^+$), 408 ($[\text{Cu}^3\text{O}(\text{pz})^3]^+$).

$[\text{Cu}_3(\mu_3\text{-OH})(\mu\text{-pz})_3(\text{py})(\mu\text{-4,4'-bpy})](\text{CF}_3\text{SO}_3)_2 \cdot 0.5\text{H}_2\text{O}]_n$ (3)—A solution of py (17 μ L, 0.19 mmol) and 4,4'-bpy (37.8 mg, 0.24 mmol) in 20 mL of MeOH was added dropwise to a solution of $\text{Cu}(\text{CF}_3\text{SO}_3)_2$ (228.3 mg, 0.62 mmol), pzH (40.5 mg, 0.58 mmol), and NaOH (36.1 mg, 0.90 mmol) also dissolved in 20 mL of MeOH. The solution was stirred overnight at ambient temperature; a small amount of a blue solid formed and was removed by filtration. The volume of the filtrate was reduced to 10 mL under reduced pressure and blue crystals, suitable for X-ray diffraction, were grown by slow evaporation of the remaining MeOH solvent. The crystals of **3** lost crystallinity upon drying (blue solid, 155.3 mg, 86.7%). For $\text{C}_{26}\text{H}_{24}\text{Cu}_3\text{F}_6\text{N}_9\text{O}_8\text{S}_2$ (calcd, found %): C (32.6, 32.8); H (2.8, 2.5); N (13.1, 12.9). ^1H NMR (DMSO- d_6 , ppm): 39.60 (3H, $w_{1/2}$ = 30 Hz); 33.64 (6H, $w_{1/2}$ = 60 Hz); 26.0 (2H, $w_{1/2}$ = 740 Hz); 17.34 (4H, $w_{1/2}$ = 430 Hz); 13.76 (2H, $w_{1/2}$ = 100 Hz); 10.82 (4H, $w_{1/2}$ = 60 Hz); 9.00 (1H, $w_{1/2}$ = 20 Hz).

$[\text{Cu}_3(\mu_3\text{-OH})(\mu\text{-pz})_3(\mu\text{-4,4'-bpy})_{1.5}](\text{CF}_3\text{SO}_3)_2 \cdot 1.5\text{H}_2\text{O}]_n$ (4)—A solution of 4,4'-bpy (49.6 mg, 0.31 mmol) in 25 mL of MeOH was added dropwise to a solution of $\text{Cu}(\text{CF}_3\text{SO}_3)_2$ (225.2 mg, 0.60 mmol), pzH (38.6 mg, 0.56 mmol), and NaOH (37.6 mg, 0.94 mmol), also dissolved in 25 mL of MeOH. The mixture was stirred 24 h at ambient temperature. A brown solid was filtered out under, the filtrate volume was reduced to 10 mL, and the solution was filtered again. Suitable crystals for X-ray diffraction were grown from slow evaporation of the filtrate (163.0 mg, 92.8%). For $\text{C}_{26}\text{H}_{28}\text{Cu}_3\text{F}_6\text{N}_9\text{O}_{10}\text{S}_2$ (calcd, found %): C (31.37, 31.43); H (2.84, 2.72); N (12.67, 12.33). ^1H NMR (DMSO- d_6 , ppm): 39.60 (3H, $w_{1/2}$ = 50 Hz); 33.65 (6H, $w_{1/2}$ = 80 Hz); 15.69 (6H, $w_{1/2}$ = 280 Hz); 10.25 (6H, $w_{1/2}$ = 45 Hz).

Results and Discussion

In this work, nitrogen donor ligands — pyrazole and 4,4'-bipyridine -- were used to synthesize coordination polymers with a triangular $\text{Cu}_3(\mu_3\text{-OH})$ -SBU. The isolation of the complex $[\text{Cu}_3(\mu_3\text{-OH})(\mu\text{-pz})_3(\text{py})_3](\text{CF}_3\text{SO}_3)_2 \cdot 0.5\text{H}_2\text{O}$ (**1**), a trinuclear complex with three terminal pyridines, from methanolic solutions of pzH, py, base and $\text{Cu}(\text{CF}_3\text{SO}_3)_2$ suggested that a similar procedure, with bidentate 4,4'-bpy ligands instead of py, would be a viable synthetic method for the preparation of coordination polymers with $\{\text{Cu}_3(\mu_3\text{-OH})(\mu\text{-pz})_3\}$ SBUs. The systematic growth of such polymers, exemplified here by complexes **2**–**4**, was achieved using the stoichiometrically required ratio of py and 4,4'-bpy ligands. The amount of the monodentate pyridine ligand was decreased by one equivalent, as the amount of the bidentate, 4,4'-bpy, were increased by one-half equivalent in each step. This stepwise strategy allowed the control of products from a trinuclear discrete complex to a 3D-polymer in a facile reproducible manner.

Complex **1** was easily assembled in a one-pot procedure, while the slow dropwise addition of 4,4'-bpy or 4,4'-bpy/py to a methanolic solution containing $\text{Cu}(\text{CF}_3\text{SO}_3)_2$, pzH and NaOH allowed the isolation of **2** – **4**. Blue crystals were isolated after slow MeOH evaporation. The crystals of **3** – **4** become opaque when dried under vacuum, but no loss of crystallinity was observed during the collection of X-ray diffraction data, even though the crystals were exposed to the atmosphere at ambient conditions. Complexes **2** – **4** were only isolated from methanolic solutions, while the analogous trinuclear complex **1** was easily obtained from a wide variety of solvents including acetone, THF, and CH_2Cl_2 . **1** is well soluble in common organic solvents, while **2** is soluble in MeOH, DMF, DMSO, MeCN, and partially soluble in EtOH and acetone. Complexes **3** and **4** are insoluble in organic solvents with the exception of coordinating solvents, as DMSO and DMF.

The ^1H NMR in $\text{DMSO}-d_6$ of **1** – **4** showed paramagnetically shifted resonances for protons of the pyrazolate, pyridine and 4,4'-bpy ligands. The presence of only one set of signals for $\text{H}^{3/5}\text{-pz}$, as well as, the presence of only one set of signals for the $\text{H}^{1/6}\text{-}$, and $\text{H}^{2/4}\text{-py/bpy}$ protons indicate the magnetic equivalence of those pairs of protons in solution. Upon standing for one week in DMSO solutions, the complexes showed no change in their ^1H NMR spectra and no bands for free py or 4,4'-bpy ligands were observed in the 7–8 ppm range. Often, the NMR spectra of soluble coordination polymers correspond to metal-solvate/ligand complexes and free ligands.^{1e} Here, however, the ^1H NMR spectrum of a mixture of $(\text{PPN})_2[\text{Cu}_3(\mu_3\text{-O})(\mu\text{-pz})_3\text{Cl}_3]$ ^{4d} and 4,4'-bpy in $\text{DMSO}-d_6$, showed resonances at 9.44, 8.08, 7.69, and 7.53 ppm, different than those of **3** and **4** in $\text{DMSO}-d_6$ solutions, suggesting that either the polymeric, or oligomeric $[\text{Cu}_3(\mu\text{-bpy})]_n$ structures persist in solution (PPN = bis (triphenylphosphoranylidene) ammonium ion).

The thermal stability of **1** – **4** was tested from room temperature to 800.0 °C. Complexes **1** and **2** were stable up to 230°, **3** showed weight loss of 1.5% at 119°, corresponding to one water molecule, while **4** showed weight loss of 5.5% up to 260°, corresponding to the loss of three water molecules per formula weight. The continuous weight loss above ~250° corresponds to the decomposition of the organic ligands (SI).

Description of structures

The trinuclear complex **1** (Figure 1) contains a $\mu_3\text{-OH}$ group bridging unsymmetrically three copper atoms – the average Cu–OH bond length is 1.998(2) Å and the O-atom is 0.408 Å above the $[\text{Cu}(\text{pz})]_3\text{-plane}$ – while three terminal py ligands are on the opposite side of their *trans*- $\mu_3\text{-OH}$ and orthogonal to the $\text{Cu}_3\text{-plane}$. The $\text{Cu}\cdots\text{Cu}$ distances, Cu– N_{pz} , Cu– N_{bpy} bond lengths are within 3.346(1) – 3.378(2) Å, 1.947(3) – 1.960(2) Å, and 2.024(2) – 2.029(3) Å respectively. Two copper atoms are in square-pyramidal N_3O_2 -coordination environment, while the third one (Cu2) is in distorted N_3O_3 -coordination environment (taking into account the interactions with triflate anions at 2.380(2) – 3.415(5) Å). One triflate anion is in hydrogen bonding contact with the $\mu_3\text{-OH}$ group ($\text{O1}\cdots\text{O6}$) at a distance of 2.770 Å. Additional hydrogen bonding is formed within a water molecule (O8) occupying a cavity within two trinuclear units and one oxygen atom in a triflate anion ($\text{O8}\cdots\text{O6}$) at a distance of 2.93(1) Å.

Complex **2** consists of two triangular $[\text{Cu}_3(\mu_3\text{-OH})(\mu\text{-pz})_3]^{2+}$ units bridged by a 4,4'-bpy ligand, each unit has two pyridines at terminal positions (Figure 2). The $\mu_3\text{-OH}$ ligands reside in opposite sides of each other, each 0.487 Å above the $\text{Cu}_3\text{-plane}$. All copper atoms – $\text{Cu}\cdots\text{Cu}$ distances are of 3.333(1) – 3.363(1) Å – are in distorted square-planar N_3O -coordination sphere. The Cu– N_{py} and the Cu– N_{bpy} bond lengths are of 2.013(2) – 2.026(2) Å, and 2.048(2) Å, respectively. This arrangement holds the two trinuclear units, which are symmetry related by a two-fold rotation axis, at a distance of 11.185 Å.

The crystal structure of **3** is a one-dimensional zigzag polymer running along the crystallographic *b* axis with $[\text{Cu}_3(\mu_3\text{-OH})(\mu\text{-pz})_3]^{2+}$ units bridged by a 4,4'-bpy ligand (Figure 3). The asymmetric unit consists of two $[\text{Cu}_3(\mu_3\text{-OH})(\mu\text{-pz})_3]^{2+}$ units and four triflate anions. The $\mu_3\text{-OH}$ capping ligands are out of the plane by 0.520 – 0.539 Å towards different sides of the Cu_3 -plane. Dihedral angles among Cu_3 -planes are of 9.1, 12.2, and 29.2°. All copper atoms – $\text{Cu}\cdots\text{Cu}$ distances within 3.249(3) – 3.367(4) Å – are in distorted square-planar coordination environment. One copper atom bears a py ligand to endcap the polymer and prevents further polymerization to an additional dimension.

Structure **4** consists of a 3D net in which the tricopper cluster, $[\text{Cu}_3(\mu_3\text{-OH})(\mu\text{-pz})_3]^{2+}$, acts as a three-connected node. Figure 4 shows the 4,4'-bpy ligands providing the bridging among the cluster units. The central $\mu_3\text{-OH}$ capping ligands are out of the plane by 0.545 Å. $\text{Cu}\cdots\text{Cu}$ distances are within 3.254(3) – 3.371(3) Å while the dihedral angles among Cu_3 -planes are of 75.8°. The charge balance is satisfied by two triflate anions, which occupy the cavities in the structure together with one and a half water molecule per trinuclear unit. Each copper atom is in square-pyramid N_3O_2 -coordination environment if the long $\text{Cu}\cdots\text{O}$ interactions of 2.95(2) – 3.35(2) Å are taken into account. One triflate anion is in H-bonding contact with the $\mu_3\text{-OH}$ group ($\text{O1}\cdots\text{O9s}$) at a distance of 2.91(3) Å. Additional hydrogen bonding is formed between the water molecules (O1w and O2w , coordinated to copper atoms at 2.67(5) Å) and two oxygen atoms of triflate anions ($\text{O1w}\cdots\text{O8s}$, $\text{O2w}\cdots\text{O9s}$) at a distance of 2.55(3) – 2.76(2) Å (Figure 5). The network of H-bonds, involving the $\mu_3\text{-OH}$, coordinated and non-coordinated triflate ions, as well as coordinated and non-coordinated H_2O molecules, interlock the $\{[\text{Cu}_3(\mu_3\text{-OH})(\mu\text{-pz})_3(\mu\text{-4,4'-bpy})_{1.5}]\}_n$ nets providing sturdiness to the 3D structure.¹⁵

An analysis of the topology of the structure with Systre¹⁶ revealed it has srs topology (related to the SrSi_2 structure).^{2a} The Schläfli and vertex symbols are 10^3 and $10_5\cdot10_5\cdot10_5$, respectively.¹⁷ The large pore size of ~27 Å accounts for the high eight-fold interpenetration encountered in the structure (Figure 6). Eight-fold is the largest degree of interpenetration that has been observed in this topology,¹⁸ however, much more extensive interpenetration has been reported for other systems.¹⁹ An analysis of the interpenetration using PLATON¹⁴ revealed it is a class IIIb system consisting of eight nets; Figure 7 shows the eight homochiral interpenetrating nets. The importance of homochiral MOFs in catalysis has been highlighted in a recent review.²⁰ To the best of our knowledge, compound **4** is only the third reported example of class IIIb interpenetration with the srs topology.^{9h, 18a,b} One of those three examples is the $[\{\text{Cu}_3(\mu_3\text{-OH})\}\{\text{Cu}_3(\mu_3\text{-O})\}(\mu_4\text{-btrz})_3(\text{H}_2\text{O})_4(\text{OH})_2\text{Cl}_6]\text{Cl}\cdot0.5\text{H}_2\text{O}$ polymer,^{9th} containing 4,4'-bi(1,2,4-triazole) ligands bridging between $\text{Cu}_3(\mu_3\text{-O(H)})$ -units, while chlorides occupied terminal positions. In contrast, **4** has been expanded by the introduction of bridging 4,4'-bpy ligands between $[\text{Cu}_3(\mu_3\text{-OH})(\mu\text{-pz})_3]$ -units. In addition, the directional H-bonding between the $\mu_3\text{-OH}$ - and $\mu_3\text{-O}$ -moieties in $[\{\text{Cu}_3(\mu_3\text{-OH})\}\{\text{Cu}_3(\mu_3\text{-O})\}(\mu_4\text{-btrz})_3(\text{H}_2\text{O})_4(\text{OH})_2\text{Cl}_6]\text{Cl}\cdot0.5\text{H}_2\text{O}$ provided a very dense packing of 2.311 g/cm^{−1} in comparison with the less dense packing of 1.753 g/cm^{−1} in **4**. Table 3 lists important bond lengths and angles for **1** – **4**.

Conclusions

We have here exploited the strong preferences of the Cu^{II} -pyrazolates to form triangular complexes and of their Cu^{II} -centers to be square planar in the systematic, stoichiometrically-controlled synthesis of **1** – **4**. The success of this approach now suggests that a variety of $[\text{Cu}_3(\mu_3\text{-OH})(\mu\text{-pz}^*)_3]^{2+}$ -SBUs, where pz^* is a substituted pyrazole ring, can be used for the systematic synthesis of new $[\text{Cu}_3(\mu_3\text{-OH})(\mu\text{-pz}^*)_3]^{2+}$ -based MOFs. The fundamental hypothesis of research into the use of SBUs in the synthesis of MOFs has been the proposed introduction of the physicochemical functionalities of an individual SBU to the properties of the resulting MOF. Here we have achieved the synthesis of a MOF containing a chemically functional trinuclear SBU. We are currently investigating whether the known redox and

magnetic properties, manifested upon chemical manipulation of that SBU,^{4d, 6, 7} will persist in the corresponding MOFs.

Supplementary Material

Refer to Web version on PubMed Central for supplementary material.

Acknowledgments

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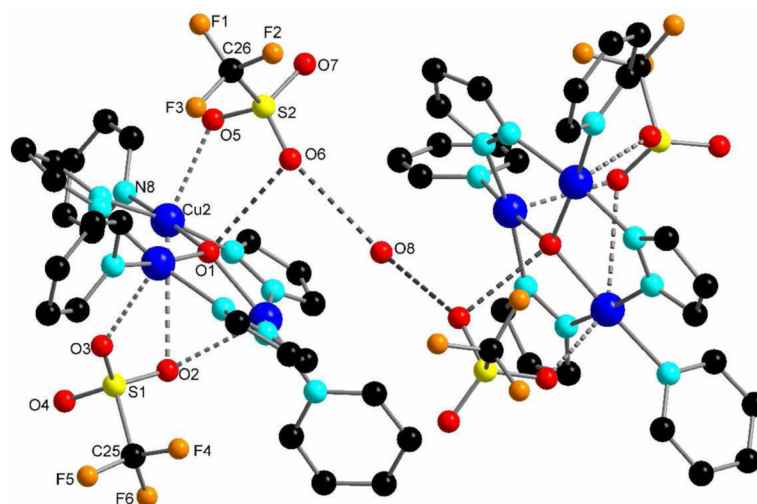


Figure 1. Crystal structure [Cu₃(μ₃-OH)(μ-pz)₃(py)₃](CF₃SO₃)₂·0.5H₂O (**1**) showing the hydrogen bonding among oxygen O1, O6, and O8. Hydrogen bonding and copper-oxygen interactions are represented by dashed lines. Hydrogen atoms are not shown.

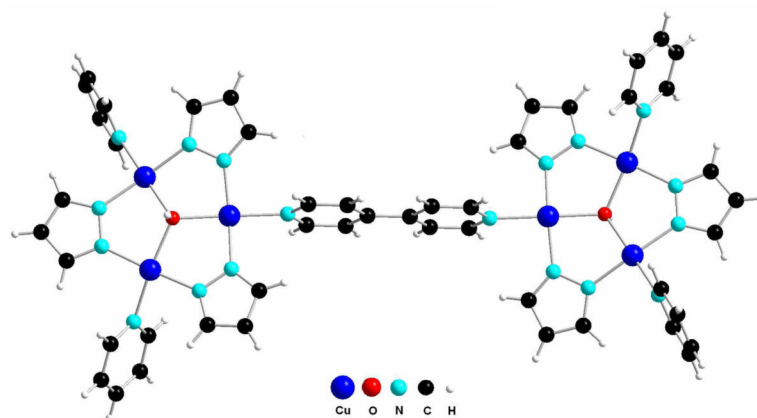


Figure 2. Crystal structure of $[\{Cu_3(\mu_3-OH)(\mu-pz)_3(py)_2\}_2(\mu-4,4'-bpy)](CF_3SO_3)_4$ (**2**). Triflate anions are omitted for clarity.

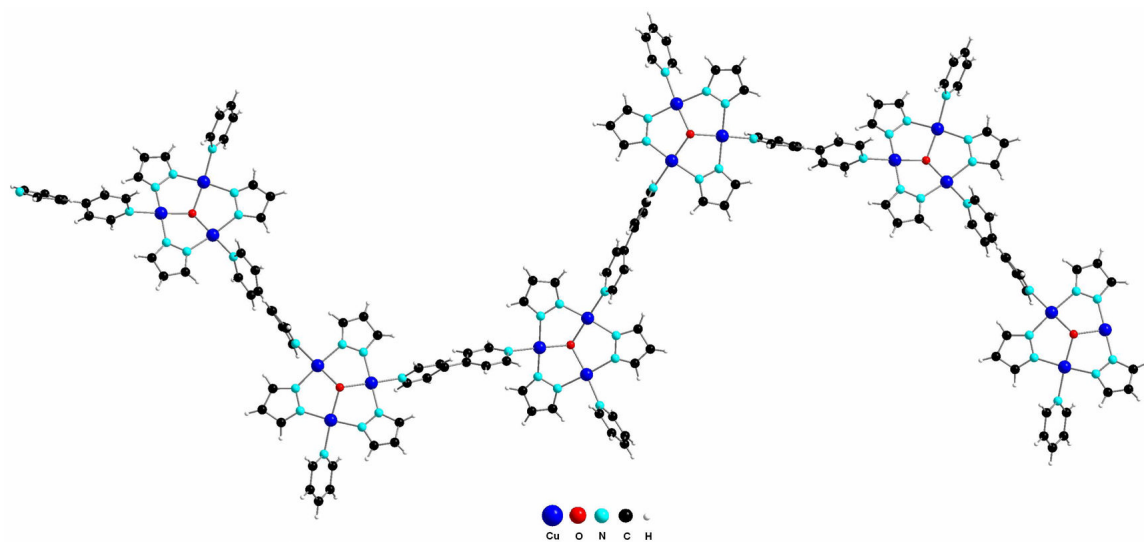


Figure 3.
Structure of the polymeric chain of $\{[\text{Cu}_3(\mu_3\text{-OH})(\mu\text{-pz})_3(\text{py})(\mu\text{-4,4'-bpy})](\text{CF}_3\text{SO}_3)_2 \cdot 0.5\text{H}_2\text{O}\}_n$ (**3**). Water molecules and counter anions are omitted for clarity. Hydrogen atoms in $\mu_3\text{-OH}$ are omitted.

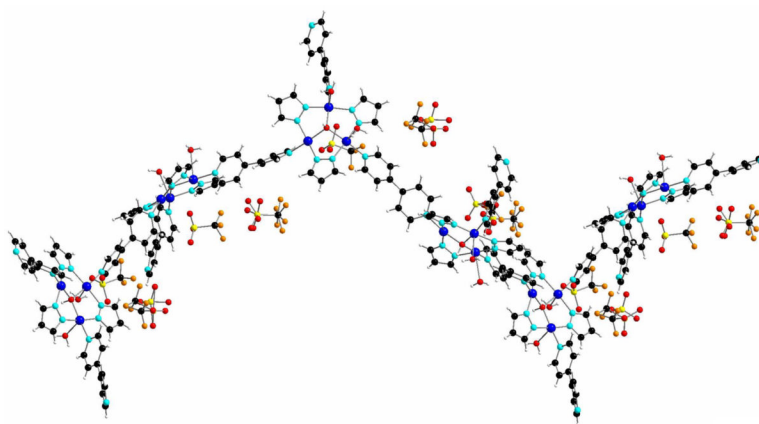


Figure 4.
Structure of the polymeric chain of $\{[\text{Cu}_3(\mu_3\text{-OH})(\mu\text{-pz})_3(\text{py})(\mu\text{-4,4'-bpy})](\text{CF}_3\text{SO}_3)_2 \cdot 0.5\text{H}_2\text{O}\}_n(\mathbf{4})$.

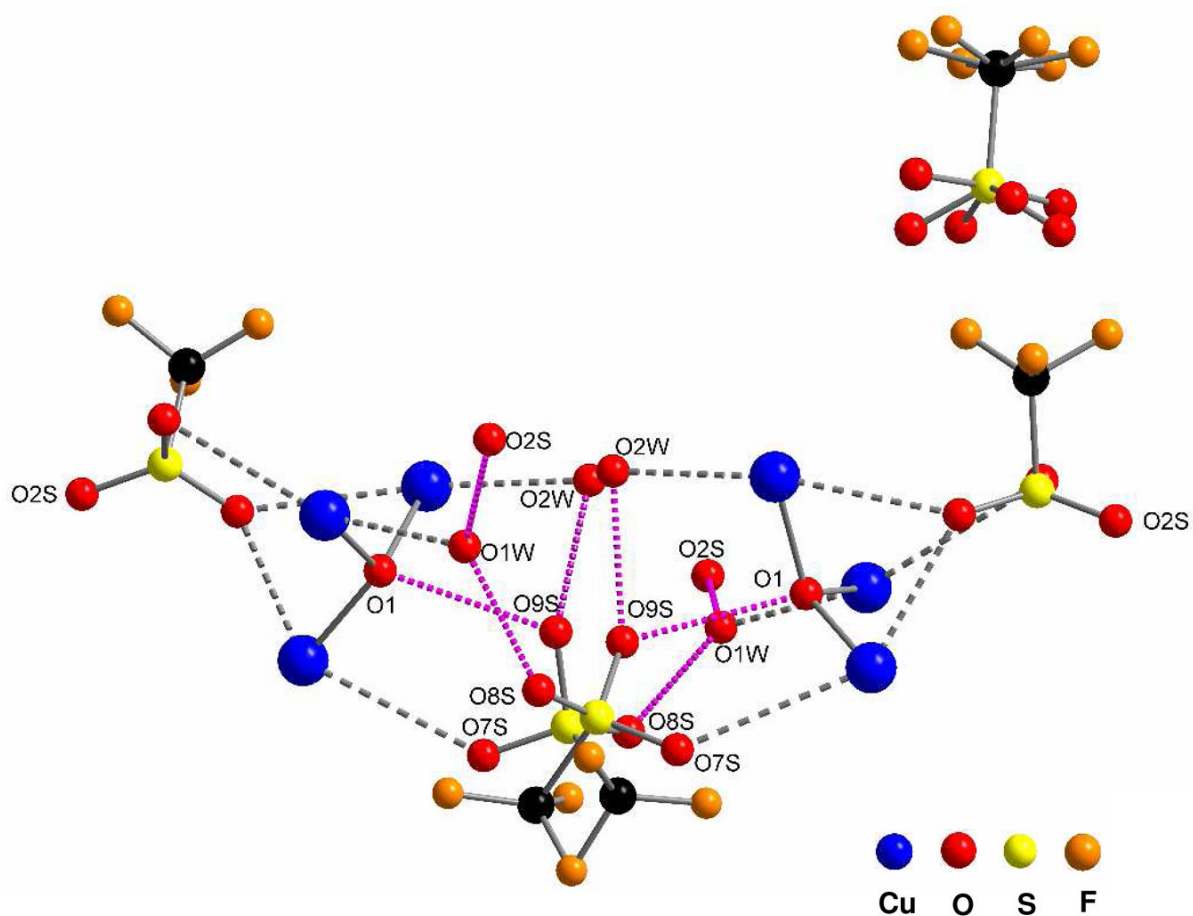


Figure 5. View of the disordered fragments, hydrogen bonding (pink dashed lines), and Cu...O interactions (gray dashed lines) in $[\text{Cu}_3(\mu_3\text{-OH})(\mu\text{-pz})_3(\mu\text{-4,4'-bpy})_{1.5}](\text{CF}_3\text{SO}_3)_2 \cdot 1.5\text{H}_2\text{O}$ (**4**). Hydrogen atoms, pyrazolates and bipyridines are omitted for clarity.

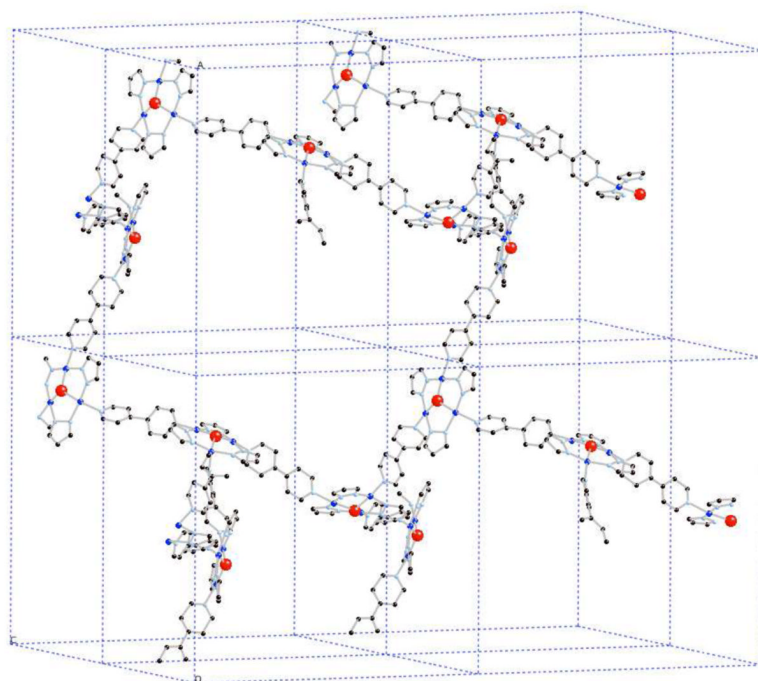


Figure 6.
Part of one of the eight interpenetrating nets of **4** shown with respect to an 8-unit cell box.

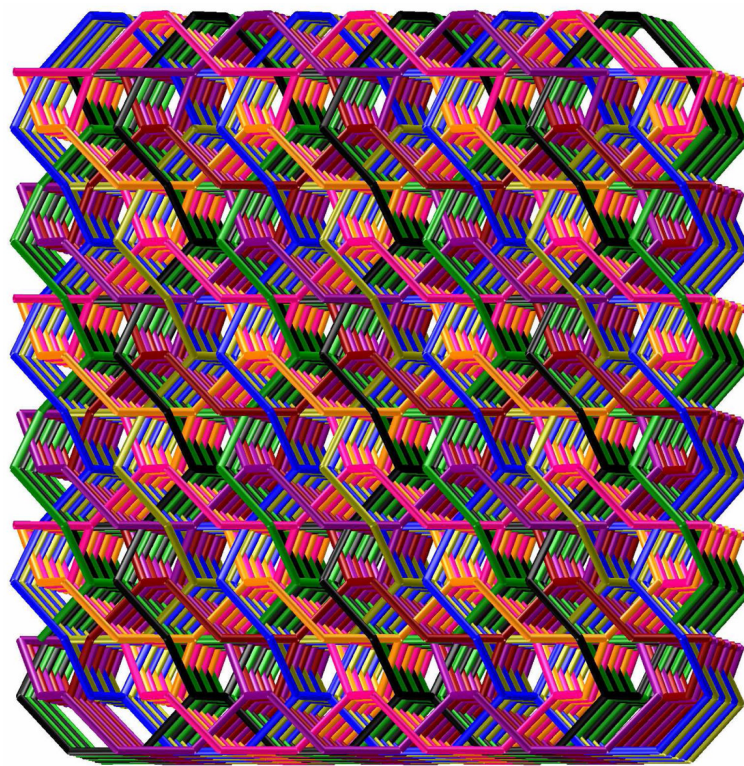


Figure 7.
Schematic representation of $\{[\text{Cu}_3(\mu_3\text{-OH})(\mu\text{-pz})_3(\text{py})(\mu\text{-4,4'-bpy})](\text{CF}_3\text{SO}_3)_2 \cdot 0.5\text{H}_2\text{O}\}_n$ (**4**)
showing the 8-interpenetrating nets in different colors.

Table 1Crystallographic data and structure refinement details for **1** – **4**.

	1	2	3	4
Empirical formula	C ₂₆ H ₂₆ Cu ₃ F ₆ N ₉ O _{7.50} S ₂	C ₅₂ H ₄₈ Cu ₆ F ₁₂ N ₁₈ O ₁₄ S ₄	C ₂₆ H ₂₃ Cu ₃ F ₆ N ₉ O _{7.5} S ₂	C ₅₂ H ₅₀ Cu ₆ F ₁₂ N ₁₈ O ₁₇ S ₄
Formula weight	953.30	1886.56	950.27	1936.58
Temperature (K)	293 (2)	298(2)	298(2)	298(2)
Wavelength (Å)	0.71073	0.71073	0.71073	0.71073
Crystal system	Monoclinic	Orthorhombic	Orthorhombic	Tetragonal
Space group	C2/c (No. 15)	Pbca (No. 61)	Pca2 ₁ (No. 29)	P4 ₂ bc (No. 106)
a (Å)	34.815(3)	18.166(2)	16.583(4)	18.853(2)
b (Å)	10.6357(7)	18.211(2)	13.153(3)	18.853(2)
c (Å)	21.033(1)	21.200(3)	34.538(8)	20.639(3)
β (°)	99.485(2)	90	90	90
Volume (Å ³)	7681.5(9)	7013(2)	7533(3)	7336(2)
Z	8	4	8	4
D _{calc} (Mg m ⁻³)	1.647	1.787	1.676	1.753
μ (mm ⁻¹)	1.838	2.011	1.874	1.928
F(000)	3824	3776	3800	3880
Crystal size (mm)	0.39 × 0.34 × 0.31	0.19 × 0.19 × 0.18	0.16 × 0.15 × 0.12	0.18 × 0.13 × 0.12
θ range (°)	2.00 to 26.39	1.85 to 27.50	1.18 to 23.39	2.16 to 23.33
Reflections collected	23222	50849	38801	33568
Ind. Refl.	7810 [R _{int} = 0.0411]	7901 [R _{int} = 0.0332]	10566 [R _{int} = 0.1040]	33568 [R _{int} = 0.1259]
Ind. Refl.[I > 2σ(I)]	6 201 [R _{int} = 0.0201]	5952 [R _{int} = 0.0232]	5560 [R _{int} = 0.1021]	5257 [R _{int} = 0.1021]
Data/restraints/param.	6201 / 0 / 483	5952 / 0 / 482	5560 / 69 / 814	5257 / 34 / 398
Goodness-of-fit on F ²	1.042	1.085	0.980	1.185
R (F); Rw(F) [I > 2σ(I)]	0.0356; 0.1026	0.0356; 0.0892	0.0904; 0.2232	0.0846; 0.1925
R; Rw (all data)	0.0482; 0.1115	0.0556; 0.0988	0.1661; 0.2719	0.1522; 0.2193
Largest peak/hole (e Å ⁻³)	0.927 and -0.444	0.570 and -0.429	0.963 and -0.546	1.472 and -0.650

Table 2

Selected bond lengths (Å) and angles (°) for **1**.

Cu(1)-O(1)	1.983(2)	Cu(3)-O(3)	2.380(2)	N(4)-Cu(3)-N(9)	91.3(1)
Cu(1)-N(7)	2.029(3)	N(6)-Cu(1)-N(7)	91.6(1)	N(5)-Cu(3)-N(9)	91.5(1)
Cu(2)-O(1)	2.003(2)	N(1)-Cu(1)-N(7)	90.0(1)	O(1)-Cu(3)-N(9)	172.31(9)
Cu(2)-N(8)	2.026(2)	O(1)-Cu(1)-N(7)	177.0(1)	N(9)-Cu(3)-O(3)	90.08(9)
Cu(3)-O(1)	2.001(2)	N(3)-Cu(2)-N(8)	95.4(1)	Cu(2)-O(1)-Cu(3)	113.40(8)
Cu(3)-N(9)	2.024(2)	N(2)-Cu(2)-N(8)	89.8(1)	Cu(2)-O(1)-Cu(1)	115.45(9)
		O(1)-Cu(2)-N(8)	173.69(9)	Cu(3)-O(1)-Cu(1)	116.05(9)

Table 3

Selected bond lengths (Å) and angles (°) for **2**.

Cu(1)-O(1)	2.004(2)	N(6)-Cu(1)-N(7)	90.4(1)	O(1)-Cu(2)-N(8)	173.1(1)
Cu(1)-N(7)	2.048(2)	N(1)-Cu(1)-N(7)	93.66(9)	N(5)-Cu(3)-N(9)	89.9(1)
Cu(1)-O(2)	2.431(2)	O(1)-Cu(1)-N(7)	176.3(1)	N(4)-Cu(3)-N(9)	93.2(1)
Cu(2)-O(1)	1.980(2)	N(7)-Cu(1)-O(2)	88.88(9)	O(1)-Cu(3)-N(9)	168.7(1)
Cu(2)-N(8)	2.026(2)	N(3)-Cu(2)-N(8)	91.2(1)	Cu(2)-O(1)-Cu(3)	113.91(9)
Cu(3)-O(1)	1.997(2)	N(2)-Cu(2)-N(8)	93.3(1)	Cu(2)-O(1)-Cu(1)	114.2(1)
Cu(3)-N(9)	2.013(2)			Cu(3)-O(1)-Cu(1)	114.4(1)

Table 4Selected bond lengths (Å) and angles (°) for **3**.

Cu(4)-N(15)	1.863(18)	Cu(1)-O(1)-Cu(3)	113.8(6)
Cu(4)-N(10)	1.946(16)	Cu(1)-O(1)-Cu(2)	115.3(6)
Cu(4)-O(2)	1.995(11)	Cu(2)-O(1)-Cu(3)	109.4(6)
Cu(4)-N(18)	2.034(6)	Cu(4)-O(2)-Cu(5)	113.6(5)
Cu(5)-N(11)	1.961(17)	Cu(4)-O(2)-Cu(6)	114.3(5)
Cu(5)-N(12)	1.962(16)	Cu(5)-O(2)-Cu(6)	110.6(5)
Cu(5)-O(2)	1.986(10)		
Cu(5)-N(16)	2.016(15)		
Cu(6)-N(14)	1.954(16)		
Cu(6)-N(13)	1.960(17)		
Cu(6)-O(2)	2.013(11)		
Cu(6)-N(17)	2.067(7)		

Table 5

Selected bond lengths (Å) and angles (°) for **4**.^a

Cu(1)-N(6)	1.952(15)	N(1)-Cu(1)-N(9)	89.3(5)	N(5)-Cu(3)-N(8)#1	95(2)
Cu(1)-O(1)	1.991(9)	N(6)-Cu(1)-N(9)	93.4(5)	N(4)-Cu(3)-N(8)#1	89(2)
Cu(1)-N(9)	2.000(8)	O(1)-Cu(1)-N(9)	172.1(5)	O(1)-Cu(3)-N(8)#1	176(2)
Cu(2)-O(1)	1.988(9)	N(3)-Cu(2)-N(7)	97.3(5)	Cu(2)-O(1)-Cu(1)	112.8(4)
Cu(2)-N(7)	2.039(8)	N(2)-Cu(2)-N(7)	88.1(6)	Cu(2)-O(1)-Cu(3)	110.1(4)
Cu(3)-O(1)	1.995(9)	O(1)-Cu(2)-N(7)	171.2(4)	Cu(1)-O(1)-Cu(3)	115.5(5)
Cu(3)-N(8)#1	2.007(16)				

^aSymmetry transformations used to generate equivalent atoms: #1 $y, -x+1, z-1/2$; #2 $-y+1, x, z+1/2$