1266 *Inorg. Chem.* **2010**, *49*, 1266–1270
DOI: 10.1021/ic902404b

Inorganic Chemistry
Article

A Two-Dimensional Metal-Organic Framework Based on a Ferromagnetic Pentanuclear Copper(II)

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Received December 4, 2009

The hydrothermal reaction of $CuSO_4$, 1,2-benzenedicarboxylate (phth), and 1,2-bis(imidazol-1-yl)ethane (bime) yields the two-dimensional metal-organic framework $\{[Cu_5(bime)(\mu_3\text{-}OH)_2(phth)_4](H_2O)_2\}_n$ (**1**), which is based on the pentanuclear copper(II) cluster $[Cu_5(\mu_3\text{-}OH)_2(phth)_4]$ and shows dominant ferromagnetic interactions within the pentanuclear cluster.

Introduction

Open metal-organic frameworks (MOFs) have received a great deal of attention because of their various architectures and topologies as well as their potential application in the fields of magnetism, electric conductivity, molecular adsorption, molecular recognition, and catalysis.[1] The design of effective ligands and the proper choice of metal centers is a key in the design and construction of novel metal-organic frameworks. Polynuclear copper(II) complexes, especially trinuclear copper(II) complexes with trigonal symmetry, are of considerable interest as models for the active sites of multicopper oxidases and magnetic materials.[2−8] Many

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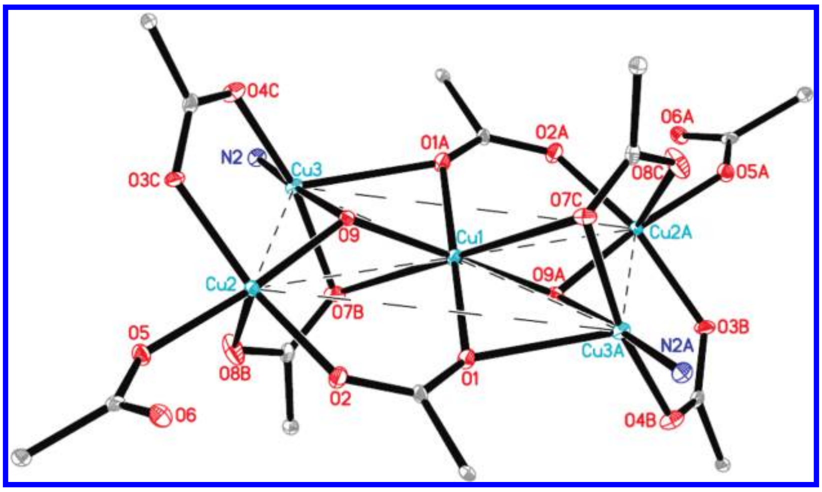

Figure 1. Coordination environment of the Cu(II) ions of compound **1**. Selected bond lengths (Å) and angles (deg): Cu1−Cu2, 3.4879(5); Cu1−Cu3, 2.9044(4); Cu2−Cu3, 3.0109(6); Cu2−Cu3A, 5.6689(8); Cu1−O9, 1.9309(19); Cu1−O1, 1.9477(18); Cu1−O7B, 2.5987(19); Cu2−O2, 1.9621(19); Cu2−O5, 1.9299(19); Cu2−O9, 1.9454(19); Cu2−O3C, 1.9951(19); Cu2−O8B, 2.256(2); Cu3−N2, 1.936(2); Cu3−O7B, 2.0145(18); Cu3−O9, 1.946(2); Cu3−O4C, 1.9520(19); Cu3−O1A, 2.4311(19); Cu1−O9−Cu2, 128.26(11); Cu1−O9−Cu3, 97.02(9); Cu2−O9−Cu3, 101.37(9); O1−Cu1−O9, 93.80(8); O1−Cu1−O7B, 105.12(7); O9−Cu1−O7B, 72.93(8); O2−Cu2−O5, 95.80(8); O2−Cu2−O9, 92.88(8); O2−Cu2−O3C, 155.16(9); O5−Cu2−O9, 169.96(8); O5−Cu2−O3C, 86.16(8); O9−Cu2−O3C, 88.09(8); O2−Cu2−O8B, 99.17(9); O5−Cu2−O8B, 83.89(8); O9−Cu2−O8B, 89.76(8); O3C−Cu2−O8B, 105.66(9); N2−Cu3−O7B, 90.23(9); N2−Cu3−O9, 174.57(9); N2−Cu3−O4C, 93.25(9); O7B−Cu3−O9, 87.72(8); O7B−Cu3−O4C, 167.51(8); O(9)−Cu3−O4C, 89.81(8); N2−Cu3−O1A, 101.07(8); O7B−Cu3−O1A, 77.85(7); O9−Cu3−O1A, 73.58(7); O4C−Cu3−O1A, 113.14(8).

compounds containing a $[Cu_3(\mu_3\text{-}OH)L_x]^{n+}$ core have been synthesized and magnetically characterized.[4,5] However, pentanuclear copper(II) complexes have been less exploited.[6−8]

We have previously synthesized several novel coordination polymers using the flexible imidazole ligand 1,2-bis(imidazol-1-yl)ethane (bime).[9] We are interested in OH-bridging polynuclear copper(II) complexes and their magnetic properties. Herein, we report on the pentanuclear copper(II) complex $\{[Cu_5(\text{bime})(\mu_3\text{-}OH)_2(\text{phth})_4](H_2O)_2\}_n$ (**1**; phth = 1,2-benzenedicarboxylate). Compound **1** has a two-dimensional framework based on the pentanuclear copper(II) cluster $[Cu_5(\mu_3\text{-}OH)_2(\text{phth})_4]$ and shows dominant ferromagnetic interactions within the pentanuclear cluster.

Results and Discussion

Crystal Structure. A single-crystal analysis[10] revealed that compound **1** consists of a two-dimensional coordination network. Figure 1 shows the coordination environment of the Cu(II) ions of compound **1** together with the pertinent bond lengths and angles. The pentanuclear copper(II) cluster $[Cu_5(\text{bime})(\mu_3\text{-}OH)_2(\text{phth})_4]$ is composed of a rectangular arrangement of four Cu(II) ions (Cu2, Cu3, Cu2A, Cu3A) with the inner angles 77.38 and 102.62° and a centered fifth ion (Cu1). The central Cu1 lies on a crystallographic inversion center, and therefore, the five copper(II) ions are coplanar. The distances from the central Cu1 ion to the peripheral Cu2 and Cu3 ions are 3.4879(5) and 2.9044(4) Å, respectively. The short edge Cu2···Cu3 of the rectangle is 3.0109(6) Å, and the long edge Cu2−Cu3A is 5.6689(8) Å. The Cu(II) ions at each short edge of the rectangle are bridged by the hydroxy oxygen ion O9. The central μ_3-oxygen atom O9 is displaced by 0.641(2) Å over the trigonal plane of the three copper(II) ions, and the Cu−O−Cu angles are 128.26(11), 97.02(9), and 101.37(9)°, respectively. The tetragonally elongated octahedral (4 + 2) coordination geometry of the central copper(II) ion Cu1 contains a CuO_6 chromophore. However, the edge copper(II) ions, Cu2 and Cu3, have a square-pyramidal geometry with an apical site occupied by O8B, O1A, and a CuO_5 chromophore. The Cu2 ion lies 0.156(2) Å over the plane defined by the basal donor atoms (O2/O5/O9/O3C). The basal plane (N2/O9/O4C/O7B) is poorly planar with a mean deviation of 0.145(2) Å, and the Cu3 ion lies 0.064(2) Å over the basal plane.

There are two kinds of phth ligands in compound **1**. One carboxylate group (O1O2) of a phth ligand has a tridentate coordination mode bridging three Cu(II) ions (Cu1, Cu3A, and Cu2) of the pentanuclear Cu(II) cluster. The other carboxylate (O3O4) shows a bidentate coordination mode bridging two Cu(II) ions (Cu2B and Cu3B) of the other pentanuclear Cu(II) cluster (Figure 2). One carboxylate group (O5O6) of the other phth ligand has a monodentate coordination mode bonding to a Cu(II) ion (Cu2) of one pentanuclear Cu(II) cluster, while the other carboxylate (O7O8) has a tridentate coordination mode bridging three Cu(II) ions (Cu1D, Cu3D, and Cu2D) of the other pentanuclear Cu(II) cluster (Figure 3). Each phth ligand connects two pentanuclear Cu(II) clusters.

Each pentanuclear copper(II) cluster is coordinated to eight carboxylate groups from eight phth ligands and two imidazole nitrogen atoms from two bime ligands. Two adjacent pentanuclear copper(II) clusters are bridged by four phth ligands and extend to form a one-dimensional chain along the *a* direction (Figure 4). The one-dimensional chain shows a “quadrangle-star” shape when viewed along the *a* direction (Figure 5). The bime ligands further link the

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(10) Crystal data for compound **1**: $C_{40}H_{32}Cu_5N_4O_{20}$, M_r = 1206.40, triclinic, space group $P\bar{1}$, a = 7.7903(10) Å, b = 10.9783(11) Å, c = 13.1952(15) Å, α = 70.556(7)°, β = 83.187(9)°, γ = 73.963(7)°, V = 1022.3(2) Å^3, Z = 1, D_c = 1.960 g cm^{-3}, $F(000)$ = 605, μ = 2.652 mm^{-1}, 10 034 reflections measured, 3716 (R_{int} = 0.0272) unique reflections, 3403 data with $I > 2\sigma(I)$, 326 parameters, R1 = 0.0286, wR2 = 0.0701, S = 1.030. CCDC No. 720895.

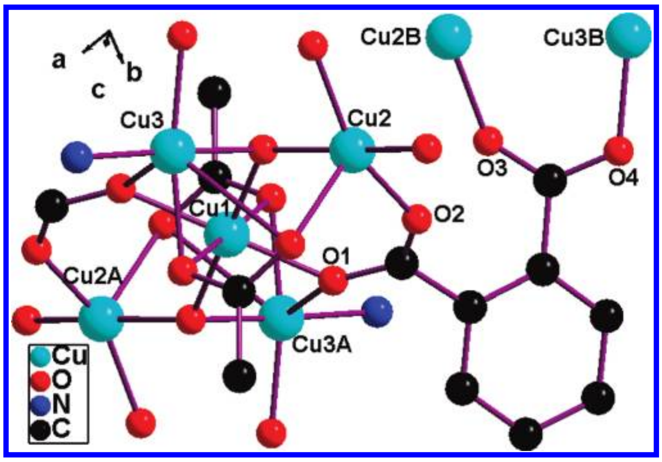


Figure 2. Coordination mode of one phth ligand (O1O2, O3O4) in compound **1**.

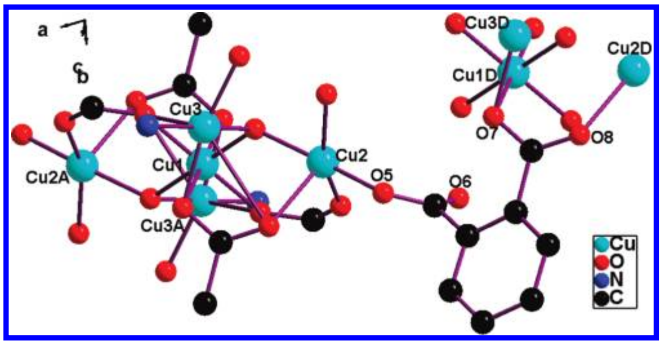


Figure 3. Coordination mode of the other phth (O5O6, O7O8) ligand in compound **1**.

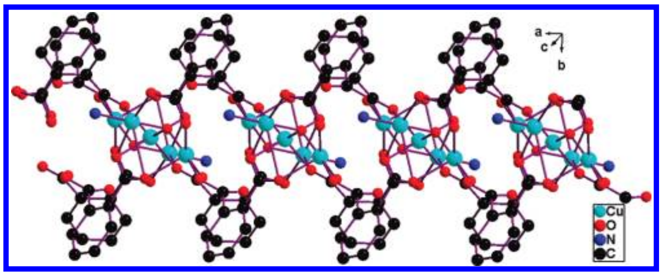


Figure 4. The $[Cu_5(\mu_3\text{-}OH)_2(phth)_4]_n$ one-dimensional chain of compound **1**.

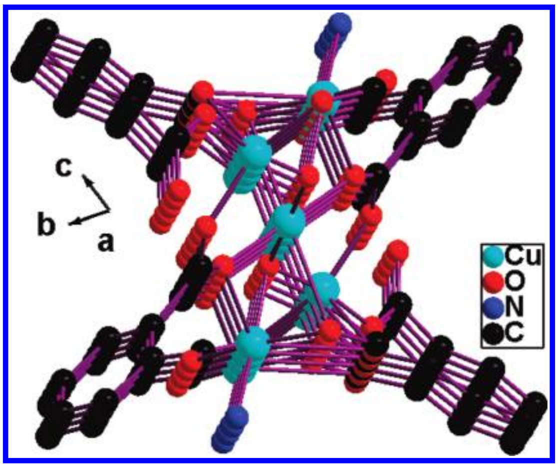


Figure 5. The "quadrangle-star" shape of $[Cu_5(\mu_3\text{-}OH)_2(phth)_4]_n$ as viewed in a one-dimensional chain along the *a* direction.

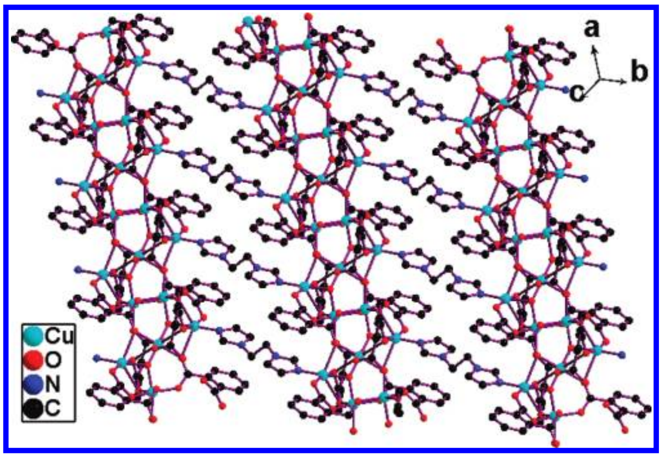


Figure 6. Two-dimensional network of compound **1**.

one-dimensional chains, resulting in a two-dimensional coordination network (Figure 6). When superimposed, the two-dimensional networks are stacked in an offset fashion so that the convex part of one network projects into the concave part of the other network (Figure S1, Supporting Information). The lattice water molecules form hydrogen bonds with the COO oxygen atoms of the phth ligands.

The pentanuclear core $[Cu_5(\mu_3\text{-}OH)_2(phth)_4]$ of compound **1** is different from that of $[Cu_5(\mu_3\text{-}OH)_2(\mu\text{-}O_2CMe)_6]^{2+}$ in three complexes reported by Chakravarty and colleagues.[8b,c] The $[Cu_5(\mu_3\text{-}OH)_2(\mu\text{-}O_2CMe)_6]^{2+}$ unit contains six COO groups and is cationic,[8b,c] while the $[Cu_5(\mu_3\text{-}OH)_2(phth)_4]$ core of compound **1** is neutral and each unit contains eight COO groups. Other copper(II) complexes containing pentanuclear cores have also been synthesized.[6−8] Most of them, however, are discrete molecules or one-dimensional chains in which the pentanuclear cores are linked via weak aqua oxygen bridges (Cu−O = 2.425(2) Å).[8b,c] The one-dimensional ladderlike coordination polymer $[Cu_5(NO_3)_{10}(dpyatriz)_2(CH_3CN)_2]\cdot 7CH_3CN$ (dpyatriz = 2,4,6-tris(dipyridin-2-ylamino)-1,3,5-triazine), containing nitrate anion bridges,[7e] has also been synthesized. Compound **1** is the first two-dimensional network based on a pentanuclear copper(II) cluster.

Magnetic Properties. A preliminary magnetic study of compound **1** has been performed. Magnetic susceptibilities were measured in the 1.8−300 K range with a SQUID magnetometer and are plotted in Figure 7. The room-temperature value for $\chi_M T$ (2.53 emu mol^{-1} K) is higher than the expected value for five uncoupled S = $^1/_2$ spins (2.1 emu mol^{-1} K for g = 2.1), indicating the presence of ferromagnetic coupling, even at 300 K. The value increases rapidly with decreasing temperature down to 6 K, where it shows a maximum (3.84 emu mol^{-1} K) at ca. 6 K. It then decreases rapidly and reaches 3.21 emu mol^{-1} K at 1.8 K.

Careful inspection of the crystal structure of compound **1** indicated that the four exchange integrals J_1, J_2, J_3, and J_4 (see Chart 1) are required to model the data properly because of the unsymmetrical μ_3-OH bridges. S_1, S_2, S_3, S_{2A}, and S_{3A} correspond to the spin operators of the Cu1, Cu2, Cu3, Cu2A, and Cu3A magnetic centers, respectively. Magnetic properties were analyzed based on the

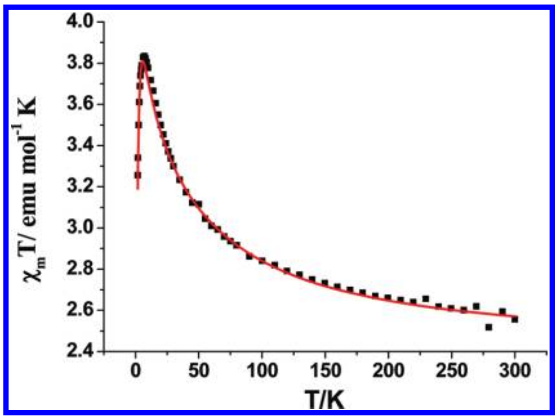
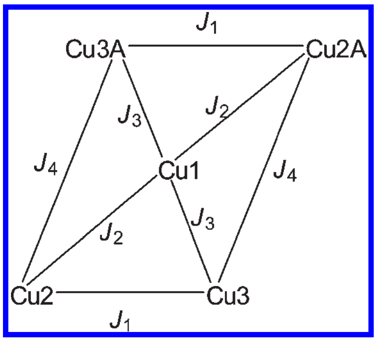


Figure 7. Plot of $\chi_M T$ vs T for compound **1** for each pentamer. The solid line represents a fit to the theoretical model; see the text for the fitting parameters.

Chart 1. Exchange Pathways in **1**



Hamiltonian and take into account the interpentamer interaction (zj').

$$\check{H} = -2J_1(\hat{S}_2\hat{S}_3 + \hat{S}_{2A}\hat{S}_{3A}) - 2J_2(\hat{S}_1\hat{S}_2 + \hat{S}_1\hat{S}_{2A}) - 2J_3(\hat{S}_1\hat{S}_3 + \hat{S}_1\hat{S}_{3A}) - 2J_4(\hat{S}_2\hat{S}_{3A} + \hat{S}_3\hat{S}_{2A}) \quad (1)$$

$$\chi_M = \chi_{Cu5}/(1 - 2zj'/Ng^2\beta^2) \quad (2)$$

The calculations were carried out using the MAGPACK package.[7c,8d,8e,11] The best fitting results gave $J_1 = 16.67$ cm^{-1}, $J_2 = -17.43$ cm^{-1}, $J_3 = 48.33$ cm^{-1}, $J_4 = 7.90$ cm^{-1}, $zj' = 0.040$ cm^{-1}, and $g = 2.16$ ($R = \sum_n[(\chi_M T)_{\text{exptl}} - (\chi_M T)_{\text{calcd}}]^2/\sum_n(\chi_M T)_{\text{exptl}}{}^2 = 3.98 \times 10^{-5}$).

The observed J values can be correlated to the molecular structure by considering the available exchange pathways between the Cu(II) ions. Cu1···Cu3 and Cu2···Cu3 are connected via a μ_3-OH bridge with the bridging angles 97.02(9) and 101.37(9)°, respectively, and therefore show ferromagnetic interactions ($J_3 = 48.33$ cm^{-1}, $J_1 = 16.67$ cm^{-1}). On the other hand, Cu1···Cu2 is linked by a μ_3−OH bridge with a bridging angle of 128.26(11)°, which results in an antiferromagnetic exchange interaction ($J_2 = -17.43$ cm^{-1}).[8e,12] Cu2···Cu3A is joined by a O2−C−O1 carboxylate group and shows a weak ferromagnetic interaction ($J_4 = 7.90$ cm^{-1}). The interpentamer magnetic exchange interaction through the phth bridges shows a very weak ferromagnetic interaction ($zj' = 0.040$ cm^{-1}). Field-dependent magnetizations at 1.8 K for compound **1** are shown in Figure S2 (Supporting Information).

Some pentanuclear copper(II) complexes have been synthesized,[6−8] eight of which contain the $[Cu_5(OH)_2]^{8+}$ core.[8] Among these, the four complexes $[Cu_5(\mu_3\text{-}OH)_2(O_2CMe)_6(Him)_4(H_2O)](ClO_4)_2$, $[Cu_5(\mu_3\text{-}OH)_2(O_2CMe)_6(Him)_4(H_2O)_4](ClO_4)_2$, $[Cu_5(\mu_3\text{-}OH)_2(O_2CMe)_6(1\text{-}Meim)_4](ClO_4)_2$ (Him = imidazole, 1-Meim = 1-methylimidazole),[8b,c] and $K_{10}[Cu_5(OH)_4(H_2O)_2(A\text{-}\alpha\text{-}SiW_9O_{33})_2]\cdot 18.5H_2O$[8e] contain a μ_3-O bridge. To the best of our knowledge, all the reported pentanuclear copper(II) complexes containing the $[Cu_5(\mu_3\text{-}OH)_2]^{8+}$ core exhibit an antiferromagnetic coupling interaction (note that some reported complexes have not undergone magnetic measurements). Bounalis and colleagues reported the "S"-shaped pentanuclear Cu(II) cluster $[Cu_5(O_2CMe)_6\{pyC(O)(OH)pyC(O)(OH)py\}_2]$, which exhibits both ferro- and antiferromagnetic intramolecular interactions.[7h] However, compound **1** contains the $[Cu_5(\mu_3\text{-}OH)_2]^{8+}$ core and shows dominant ferromagnetic interactions within the pentanuclear cluster.

EPR Spectra. The X-band EPR spectrum of compound **1** was recorded on a polycrystalline powder sample at room temperature and at 110 K (Figure S3, Supporting Information). The EPR spectrum at room temperature shows a broad band centered at $g = 2.14$, which is close to the fitting result of the magnetic properties ($g = 2.16$). The EPR spectrum at 110 K shows a broad band in the low-field region because of the presence of $S = {}^5/_2$ zero-field splitting (ZFS).

Thermal Analysis. Thermogravimetric analysis (TG) was carried out to explore the thermal stability of compound **1**. In the TG curve (Figure S4, Supporting Information) of compound **1**, the first weight loss of 3.12% in the 90−190 °C region corresponds to the loss of lattice water (calculated 2.98%). The anhydrous network is then thermally stable until 230 °C. The main and rapid weight loss of 51.12% in the 230−300 °C region can tentatively be attributed to the removal of four phth groups (two O atoms remain; calculated 51.75%). The slow weight loss of 17.18% in the 300−836 °C region can tentatively be attributed to the removal of one bime (calculated: 13.43%), and the remaining mass (28.33%) may be CuO (calculated 32.93%). The final mass (25.42%) may be Cu_2O (calculated 29.63%) upon heating to 980 °C.

Conclusion

In summary, we hydrothermally synthesized a copper(II) complex containing a pentanuclear copper(II) cluster, $[Cu_5(\mu_3\text{-}OH)_2(phth)_4]$. We found that adjacent pentanuclear copper(II) clusters are bridged by four phth ligands and extend to form a one-dimensional chain. A two-dimensional coordination network is further formed because the chains are linked by bime ligands. Compound **1** is the first known two-dimensional network based on a pentanuclear copper(II) cluster. Compound **1** contains a $[Cu_5(\mu_3\text{-}OH)_2]^{8+}$ core

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and shows dominant ferromagnetic coupling interactions. This work provides new information regarding polynuclear copper(II) chemistry and magnetic chemistry. The design and synthesis of new polynuclear copper(II) complexes are underway in our laboratory.

Experimental Section

Materials and Physical Measurements. All reagents were of analytical grade and were used without further purification. 1,2-Bis(imidazol-1-yl)ethane (bime) was synthesized according to the literature method.[13] Elemental analyses for C, H, and N were performed on a Perkin-Elmer 240C analyzer. IR spectra were obtained using KBr pellets on a Nicolet 170SX FT-IR spectrophotometer in the 4000−400 cm^{-1} region. EPR spectra were recorded on a Bruker EMX-10/12 instrument. Variable-temperature magnetic susceptibilities were measured with a MPMS-7 SQUID magnetometer. Diamagnetic corrections were made using Pascal's constants for all constituent atoms. TG analysis was carried out on a Thermal Analyst 2100 TA Instrument and a SDT 2960 simultaneous TGA-DTA instrument with flowing nitrogen at a heating rate of 10 °C/min.

Synthesis of Compound 1. A solution of H_2phth (0.067 g, 0.40 mmol) in 10 mL of H_2O was adjusted to pH 6 with NEt_3 (0.076 g, 0.75 mmol), and $CuSO_4 \cdot 5H_2O$ (0.125 g, 0.50 mmol) was added with stirring. Then, bime (0.016 g, 0.10 mmol) dissolved in 10 mL of EtOH was added. The mixture was added to a 30 mL Teflon-lined stainless autoclave, and this was sealed and heated to 110 °C for 3 days and then cooled to room temperature. Blue block-shaped crystals were collected. Yield: 0.094 g (78% based on phth and bime). Anal. Calcd for $C_{40}H_{32}Cu_5N_4O_{20}$ (compound **1**): C, 39.82; H, 2.67; N, 4.65. Found: C, 39.75; H, 2.64; N, 4.61. IR data (cm^{-1}): 3450 m, 3126 w, 2349 w, 2321 w, 1613 m, 1544 s, 1482 w, 1443 w, 1389 vs, 1297 w, 1243 w, 1111 w, 1027 w, 958 w, 844 w, 756 w, 702 w, 656 w, 556 w, 471 w.

X-ray Crystallography. A single crystal of compound **1** suitable for X-ray crystallography was carefully selected under an optical microscope and glued to thin glass fibers. Diffraction data were collected on a Rigaku Mercury CCD diffractometer with graphite-monochromated Mo Kα radiation ($\lambda = 0.71073$ Å). Intensities were collected using the ω scan technique. The structures were solved by direct methods and refined with the full-matrix least-squares technique (SHELXTL-97).[14] The hydrogen atom positions for the bime and phth ligands were determined using a theoretical calculation and were included in the final refinement according to the riding model approximation. The hydrogen atoms of OH^- and H_2O were located using difference Fourier maps and were included in the final refinement. CCDC reference number: 720895.

Acknowledgment. This work was supported by the Natural Science Foundation of China (No. 20671066), Jiangsu Province (No. BK2006049), the Key Laboratory of Coordination Chemistry, and the Key Laboratory of Organic Synthesis of Jiangsu province.

Supporting Information Available: A CIF file giving crystallographic data for compound **1** and figures giving additional plots of the structures, the EPR spectra, and the TG curve. This material is available free of charge via the Internet at http://pubs.acs.org.

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