Inorg. Chem. **2006**, *45*, 5799–5803

Inorganic Chemistry

Article

Synthesis and Characterization of a 3D Coordination Polymer Based on Trinuclear Triangular Cu^{II} as Secondary Building Units

Bin Ding, Long Yi, Peng Cheng,* Dai-Zheng Liao, and Shi-Ping Yan

Department of Chemistry, Nankai University, Tianjin 300071, People's Republic of China

Received January 6, 2006

The hydrothermal reaction of Cu^{II} salts with 1,2,4-triazole (Htrz) in aqueous ammonia yielded a novel metal–organic framework $\{[Cu_3(\mu_3\text{-}O)(\mu_3\text{-}trz)_3(OH)(H_2O)_6]\}_n$ (**1**), which was characterized by single-crystal X-ray diffraction, X-ray powder diffraction, thermogravimetric analysis, IR, and variable-temperature magnetic susceptibility. It crystallizes in cubic, space group $Fd\bar{3}c$ with $a = 24.644(3)$ Å, $V = 14967(3)$ Å^3, and $Z = 96$. Its framework is the first 3D structure using coordinative interactions constructed via trinuclear triangular Cu^{II} secondary building units, in which both Cu^{II} ions and trz ligands act as three-connected nodes to form a 6.8^2 net. An overall antiferromagnetic behavior was found in the compound.

Introduction

Metal–organic framework (MOF) coordination polymers have attracted tremendous attention because of their intriguing molecular topologies, their potential uses such as in ion exchange and adsorption, and their catalytic, fluorescence, and magnetic properties.[1,2] One of the most effective approaches to synthesizing MOFs is hydrothermal assembly by incorporating appropriate metal ions (connectors) with multifunctional bridging ligands (linkers).[3] The considerable amount of interest in Cu atoms was mainly due to the fact that Cu is an essential bioelement responsible for numerous catalytic processes in living organisms, where it is often present in polynuclear assemblies,[4] and to exploration of magnetostructural correlations resulting from the mutual interaction among Cu^{II} centers.[5] Recently, it had been shown that Cu ions and N1,N2-bridged ligands [pyrazole, 1,2,4-triazole (Htrz), and their derivatives] form a trinuclear triangular Cu_3X core ($X = \mu_3$-O, μ_3-OH, μ_3-Cl, μ_3-Br), which exhibited catalytic activity[6a] and interesting magnetic properties.[6b−f] Though the MOFs based on trimeric secondary building units (SBUs) were reported recently with Zn^{II},[7a] Cr^{III},[7b] Fe^{III},[7c] and Cd^{II},[7d] the arrangement of trinuclear triangular Cu^{II} clusters as SBUs into multidimensional MOFs is an interesting work, and up to now, only two papers have been written concerning the use of coordination interactions to form 1D[6f,8] and 2D networks.[8] Therefore, it remains a great

---

* To whom correspondence should be addressed. E-mail: pcheng@nankai.edu.cn.

(1) (a) Yaghi, O. M.; O'Keeffe, M.; Ockwig, N. W.; Chae, H. K.; Eddaoudi, M.; Kim, J. *Nature* **2003**, *423*, 705. (b) Evans, O. R.; Lin, W. B. *Acc. Chem. Res.* **2002**, *35*, 511. (c) Kil, S. M.; Myunghyun, P. S. *J. Am. Chem. Soc.* **2000**, *122*, 6834. (d) Zhao, B.; Cheng, P.; Chen, X.; Cheng, C.; Shi, W.; Liao, D. Z.; Yan, S. P.; Jiang, Z. H. *J. Am. Chem. Soc.* **2004**, *126*, 3012.

(2) (a) Blake, A. J.; Champness, N. R.; Hubberstey, P.; Li, W.-S.; Withersby, M. A.; Schroder, M. *Coord. Chem. Rev.* **1999**, *183*, 117. (b) Cingolani, A.; Galli, S.; Masciocchi, N.; Pandolfo, L.; Pettinari, C.; Sironi, A. *J. Am. Chem. Soc.* **2005**, *127*, 6144. (c) Dincã, M.; Long, J. R. *J. Am. Chem. Soc.* **2005**, *127*, 9376. (d) Rosi, N. L.; Kim, J.; Eddaoudi, M.; Chen, B.; O'Keeffe, M.; Yaghi, O. M. *J. Am. Chem. Soc.* **2005**, *127*, 1504. (e) Férey, G.; Mellot-Draznieks, C.; Millange, F.; Dutour, J.; Margiolaki, I. *Science* **2005**, *309*, 2040. (f) Férey, G.; Serre, C.; Mellot-Draznieks, C.; Millange, F.; Surblé, S.; Dutour, J.; Margiolaki, I. *Angew. Chem., Int. Ed.* **2004**, *43*, 6296.

(3) (a) Moulton, B.; Zaworotko, M. J. *Chem. Rev.* **2001**, *101*, 1629. (b) Lu, J. Y. *Coord. Chem. Rev.* **2003**, *246*, 327.

(4) Ferguson-Miller, S.; Babcock, G. T. *Chem. Rev.* **1996**, *96*, 2889.

(5) Lo, S. M.-F.; Chui, S. S.-Y.; Shek, L.-Y.; Lin, Z.; Zhang, X.; Wen, G.; Williams, I. D. *J. Am. Chem. Soc.* **2000**, *122*, 6293.

(6) (a) Casarin, M.; Corvaja, C.; Nicola, C.; Falcomer, D.; Franco, L.; Monari, M.; Pandolfo, L.; Pettinari, C.; Piccinelli, F.; Tagliatesta, P. *Inorg. Chem.* **2004**, *43*, 5865. (b) Boèa, R.; Dlháò, Å.; Mezei, G.; Ortiz-Pérez, T.; Raptis, R. G.; Telser, J. *Inorg. Chem.* **2003**, *42*, 5801. (c) Angaridis, P. A.; Baran, P.; Boèa, R.; Cervantes-Lee, F.; Haase, W.; Mezei, G.; Raptis, R. G.; Werner, R. *Inorg. Chem.* **2002**, *41*, 2219. (d) Liu, J.; Guo, G.; Huang, J.; You, X. *Inorg. Chem.* **2003**, *42*, 235. (e) Ferrer, S.; Haasnoot, J. G.; Reedijk, J.; Mu1ller, E.; Cingi, M. B.; Lanfranchi, M.; Lanfredi, A. M. M.; Ribas, J. *Inorg. Chem.* **2000**, *39*, 1859. (f) Ferrer, S.; Lloret, F.; Bertomeu, I.; Alzuet, G.; Borrás, J.; Garcåa-Granda, S.; Liu-González, M.; Haasnoot, J. G. *Inorg. Chem.* **2002**, *41*, 5821.

(7) (a) Seo, J. S.; Whang, D.; Lee, H.; Jun, S. I.; Oh, J.; Jeon, Y. J.; Kim, K. *Nature* **2000**, *404*, 982. (b) Mellot-Draznieks, C.; Dutour, J.; Férey, G. *Angew. Chem., Int. Ed.* **2004**, *43*, 6290. (c) Férey, G.; Mellot-Draznieks, C.; Serre, C.; Millange, F.; Dutour, J.; Surble, S.; Margiolaki, I. *Science* **2005**, *309*, 2040. (d) Fang, Q.; Zhu, G.; Xue, M.; Sun, J.; Wei, Y.; Qiu, S.; Xu, R. *Angew. Chem., Int. Ed.* **2005**, *44*, 3845.

(8) Casarin, M.; Corvaja, C.; Nicola, C.; Falcomer, D.; Franco, L.; Monari, M.; Pandolfo, L.; Pettinari, C.; Piccinelli, F. *Inorg. Chem.* **2005**, *44*, 6265.

10.1021/ic060030o CCC: $33.50 © 2006 American Chemical Society

Published on Web 06/20/2006

challenge to prepare new trinuclear triangular Cu^{II}-based solid materials with high-dimensional structures.[9]

On the other hand, Htrz has gained great attention as a ligand to transition metals by the fact that it unites the coordination geometry of both pyrazoles and imidazoles and, in addition, exhibits a strong and typical property of acting as a bridging ligand between two metal centers.[10a] Using substituted Htrz's as linkers, we explored a series of triazolecadmium(II) coordination polymers at room temperature.[10b−d] Herein we report the hydrothermal synthesis and characterization of a novel 3D coordination polymer $\{[Cu_3(\mu_3\text{-}O)(\mu_3\text{-}trz)_3(OH)(H_2O)_6]\}_n$ (**1**), whose framework is constructed by trinuclear triangular Cu^{II} secondary building units.

Experiment Section

Preparation. $\{[Cu_3(\mu_3\text{-}O)(\mu_3\text{-}trz)_3(OH)(H_2O)_6]\}_n$ (1). A mixture of Htrz (5 mmol, 0.32 g), $CuSO_4 \cdot 5H_2O$ (5 mmol, 1.25 g), and aqueous ammonia (25%, 10.0 mL) was refluxed for 1 h and then was put in a 15-mL acid digestion bomb and heated at 180 °C for 3 days. A clear blue solution was obtained, and the crystal products were collected after allowing the solution to reach room temperature over several weeks, yielding 81% (based on Cu^{II} salts). Elem anal. Calcd for **1**: C, 13.44; H, 3.58; N, 23.51. Found: C, 13.11; H, 3.62; N, 23.78. ICP: Cu 34.88% (calcd 36.03%). IR (KBr): ν 3423s, 1637m, 1511m, 1400m, 1294w, 1172m, 1101m, 1001w, 668m cm^{-1}.

Characterization. Elemental analyses (C, H, and N) were performed on a Perkin-Elmer 240 CHN elemental analyzer. The metal content of the complex was carried out using an inductively coupled plasma (ICP) atomic emission spectroscopy (AES) spectrometer. IR spectra were recorded in the range 400−4000 cm^{-1} on a Bruker TENOR 27 spectrophotometer using a KBr pellet. Thermogravimetric analysis (TGA) experiments were performed on a NETZSCH TG 209 instrument with a heating rate of 10 °C min^{-1}. Powder X-ray diffraction (PXRD) measurements were recorded on a D/Max-2500 X-ray diffractometer using Cu Kα radiation. Variable-temperature magnetic susceptibilities were measured on a Quantum Design MPMS-7 SQUID magnetometer. Diamagnetic corrections were made with Pascal's constants for all of the constituent atoms (-79.8×10^{-6} emu mol^{-1}).

Crystal Structure Determination. Diffraction intensities for **1** were collected on a computer-controlled Bruker SMART 1000 CCD diffractometer equipped with graphite-monochromated Mo Kα radiation with a radiation wavelength of 0.71071 Å by using the ω-scan technique. Lorentz polarization and absorption corrections were applied. The structures were solved by direct methods and refined with a full-matrix least-squares technique using the *SHELXS-97* and *SHELXL-97* programs.[11] Anisotropic thermal parameters were assigned to all non-H atoms. The organic H atoms were generated geometrically; the H atoms of the water molecules were located from difference maps and refined with isotropic temperature factors. Analytical expressions of neutral-atom scattering factors were employed, and anomalous dispersion corrections were incorporated. The crystallographic data and bond lengths and angles for **1** are listed in Tables 1 and 2, respectively. The CCDC reference number is 282738. The data can be obtained free of charge upon application to CCDC, 12 Union Road, Cambridge CB21EZ, U.K. [fax (+44) 1223-336-033; e-mail deposit@ccdc.cm.ac.uk].

Table 1. Crystal Data and Structure Refinement Information for **1**

compound	1
formula	$C_2H_{5.34}CuN_3O_{2.67}$
fw	177.64
temp (K)	293(2)
cryst size (mm^3)	$0.46 \times 0.34 \times 0.28$
cryst syst	cubic
space group	$Fd\bar{3}c$
a (Å)	24.644(3)
b (Å)	24.644(3)
c (Å)	24.644(3)
α (deg)	90
β (deg)	90
γ (deg)	90
V ($Å^3$)	14967(3)
Z	96
limiting indices	$-32 \le h \le 25$ $-32 \le k \le 30$ $-32 \le l \le 28$
$F(000)$	8513
ρ (Mg/m^3)	1.892
abs coeff (mm^{-1})	3.433
data/restraints/param	757/0/53
GOF	1.170
R1[a] [$I = 2\sigma(I)$]	0.0388
wR2[a] (all data)	0.1144

[a] $R1 = \sum||F_o| - |F_c||/|F_o|$; $wR2 = [\sum w(F_o^2 - F_c^2)^2/\sum w(F_o^2)^2]^{1/2}$.

Table 2. Bond Lengths (Å) and Angles (deg) for **1**[a]

Cu(1)−O(1)	1.9564(5)	Cu(1)−N(1)	1.970(3)
Cu(1)−N(1)A	1.970(3)	Cu(1)−N(2)B	1.997(3)
O(1)−Cu(1)C	1.9563(5)	O(1)−Cu(1)D	1.9563(5)
N(1)−C(1)	1.316(4)	N(1)−N(1)E	1.364(5)
N(2)−C(1)E	1.346(4)	N(2)−C(1)	1.344(4)
N(2)−Cu(1)F	1.997(3)		
O(1)−Cu(1)−N(1)	89.00(7)	O(1)−Cu(1)−N(1)A	89.00(7)
N(1)−Cu(1)−N(1)A	178.01(15)	O(1)−Cu(1)−N(2)B	180.0
N(1)−Cu(1)−N(2)B	91.00(7)	N(1)A−Cu(1)−N(2)B	91.00(7)
Cu(1)C−O(1)−Cu(1)	120.0	Cu(1)C−O(1)−Cu(1)D	120.0
Cu(1)−O(1)−Cu(1)D	120.0	C(1)−N(1)−N(1)E	106.56(17)
C(1)−N(1)−Cu(1)	132.8(2)	N(1)E−N(1)−Cu(1)	120.45(8)
C(1)E−N(2)−C(1)	103.4(3)	C(1)E−N(2)−Cu(1)F	128.20(17)
C(1)−N(2)−Cu(1)F	128.20(17)	N(1)−C(1)−N(2)	111.7(3)

[a] Symmetry transformations used to generate equivalent atoms: A, $z + {}^3/_4$, $-y + 1$, $x - {}^3/_4$; B, $-z + 1$, $x - {}^1/_4$, $y - {}^1/_4$; C, $-z + {}^3/_4$, $-x + {}^5/_4$, $y - {}^1/_2$; D, $-y + {}^5/_4$, $z + {}^1/_2$, $-x + {}^3/_4$; E, $-x + {}^3/_2$, $-z + {}^1/_2$, $-y + {}^1/_2$; F, $y + {}^1/_4$, $z + {}^1/_4$, $-x + 1$.

Results and Discussion

It is noted that hydrothermal synthesis in aqueous ammonia was rarely performed in previous research. In this contribution, a 3D MOF with high yield was obtained by employing such conditions. The as-synthesized samples are blue cubic-shaped crystals, which are stable in air and insoluble in common solvents. The crystals exhibit large solubility in aqueous ammonia (25%) and can recrystallize from the resulting solution. The existence of the aqueous ammonia during the synthesis of the 3D MOF played an important

---

(9) (a) Seeber, G.; Kögerler, P.; Kariuki, B. M.; Cronin, L. *Chem. Commun.* **2004**, 1580. (b) Schnack, J.; Nojiri, H.; Köerler, P.; Cooper, G. J. T.; Cronin L. *Phys. Rev. B* **2004**, *70*, 174420.

(10) (a) Haasnoot, J. G. *Coord. Chem. Rev.* **2000**, *200−202*, 131. (b) Yi, L.; Ding, B.; Zhao, B.; Cheng, P.; Liao, D. Z.; Yan, S. P.; Jiang, Z. H. *Inorg. Chem.* **2004**, *43*, 33. (c) Ding, B.; Yi, L.; Wang, Y.; Cheng, P.; Liao, D. Z.; Yan, S. P.; Jiang, Z. H. *Dalton Trans.* **2006**, 665. (d) Yi, L.; Yang, X.; Cheng, P.; Lu, T. B. *Cryst. Growth Des.* **2005**, *5*, 1215.

(11) (a) Sheldrick, G. M. *SHELXS-97, Program for Crystal Structure Solution*; Göttingen University: Göttingen, Germany, 1997. (b) Sheldrick, G. M. *SHELXL-97, Program for Crystal Structure Refinement*; Göttingen University: Göttingen, Germany, 1997.

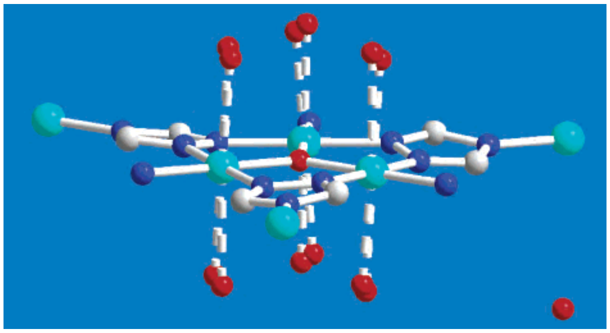

Figure 1. ORTEP drawing of the coordination unit in **1**. H atoms were omitted for clarity. Color code: red, O; cyan, Cu; gray, C; blue, N; white dotted line, a weak Cu−O coordination bond.

role as the solvent for the compound, which allows for the possibility of formation of single crystals. Considering the structure, we suppose that hydrothermal synthesis helped with the formation of trinuclear triangular Cu^{II} SBUs in solution. The 3D crystals were formed via self-assembly of these SBUs during slow evaporation of the solution.

Single-crystal analysis reveals that **1** contains trinuclear triangular Cu^{II} SBUs, which are further linked via triazolatos to form a 3D MOF. As shown in Figure 1, the SBU of **1** consists of a planar $Cu_3(\mu_3\text{-}O)$ core supported by bridging N1,N2-triazolatos, while N4-triazolates complete the square-planar coordination of the Cu atoms. The disordered water molecules weakly coordinate to Cu^{II} ions with distances of 2.568 and 2.747 Å. The $[Cu_3(\mu_3\text{-}O)(\mu_3\text{-}trz)_3]$ unit has 3-fold symmetry. The $Cu_3(\mu_3\text{-}O)$ moiety is trigonal planar with a Cu−O distance and a Cu−O−Cu angle of 1.9561(5) Å and 120.0°, respectively, providing the Cu···Cu distance of 3.388 Å. The shortest Cu···Cu distance between neighbor trinuclear SBUs is 6.022 Å.

The arrangement of four trinuclear triangular Cu^{II} SBUs generates a molecular cage (Figure 2), which can be considered as tertiary building units (TBUs).[7b] The cage consists of four six-membered rings (made of six N1,N4-bridged triazolatos and six Cu atoms) and six four-membered rings (made of four N1,N4-bridged triazolatos and four Cu atoms). The overall 3D MOF of **1** is built up by a series of these TBUs (Figure 3). OH^- anions are far away from Cu^{II} centers, and the nearest distance between two neighbor OH^- anions is 2.952 Å. **1** is the first report of a 3D structure using coordinative interactions constructed via trinuclear triangular Cu^{II} units and the first example in which the triply bridging character of triazolato ligands leads to a 3D coordination structure.

In the coordination network of **1**, both trz and Cu^{II} act as three-connected nodes and the topology of the MOF can be represented as a unique 6.8^2 net, as shown in Figure 4. A number of topologies of special crystal networks were illustrated, which are now known (or were shown by Wells) to be displayed by real crystal structures.[12] While the trinuclear triangular Cu^{II} SBU can be considered as a node, each node is six-connected and the topology of the MOF for **1** can be represented as a (4,6) uniform net.

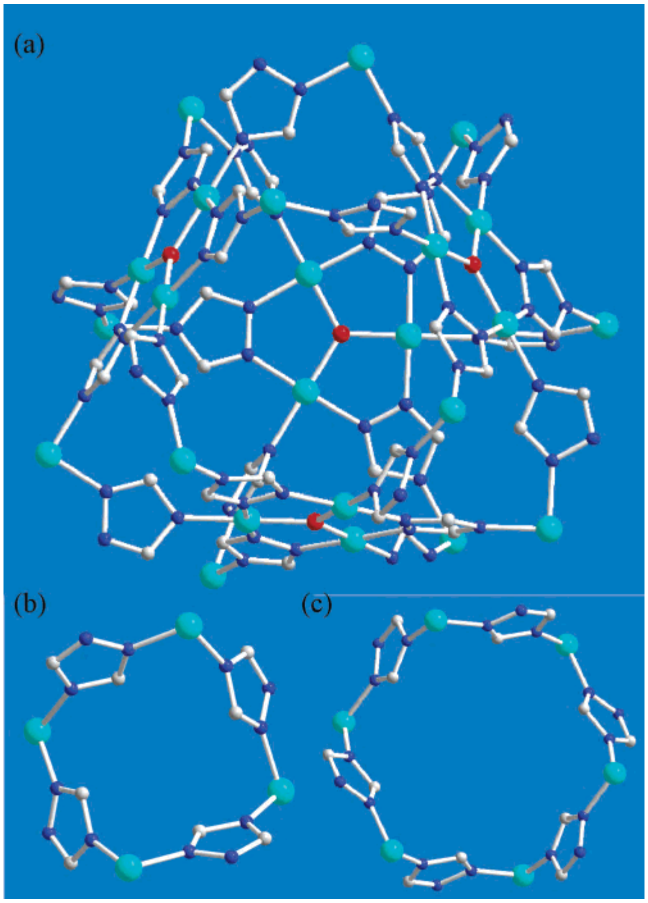

Figure 2. (a) Perspective view of the molecular cage in **1** (H atoms and guest molecules are omitted for clarity). (b) Four-membered ring. (c) Six-membered ring. Color code: cyan, Cu; blue, N; gray, C; red, O.

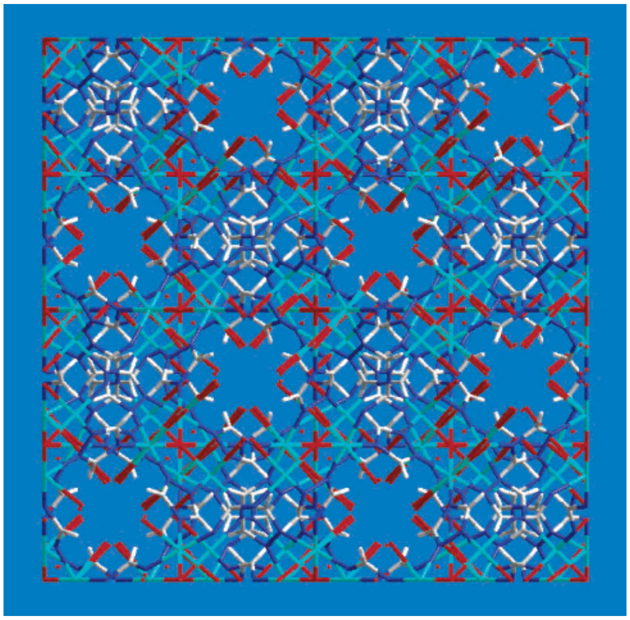

Figure 3. Perspective view of the 3D MOF of **1** along the *c* direction. Color code: cyan, Cu; blue, N; gray, C; red, O. H atoms are omitted for clarity.

---

(12) (a) Wells, A. F. *Three-dimensional Nets and Polyhedra*; Wiley-Interscience: New York, 1977. (b) Wells, A. F. *Further Studies of Three-dimensional Nets*; ACA Monograph 8; American Crystallographic Association: Buffalo, NY, 1979. (c) Hill, R. J.; Long, D.-L.; Champness, N. R.; Hubberstey, P.; Schröder, M. *Acc. Chem. Res.* **2005**, *38*, 337.

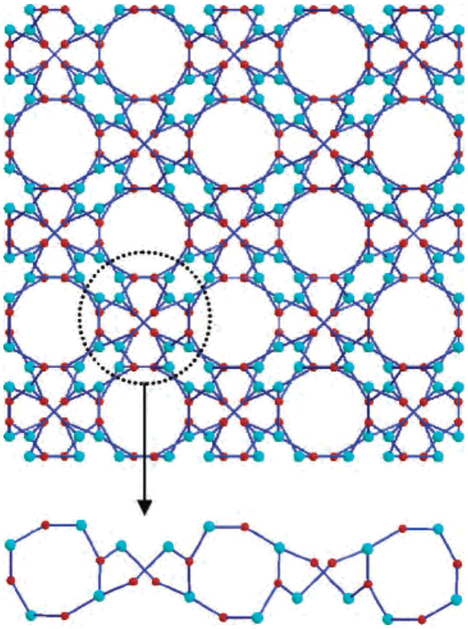

Figure 4. Perspective view of the topology of a 6.8^2 uniform net. Color code: cyan, Cu; red, trz.

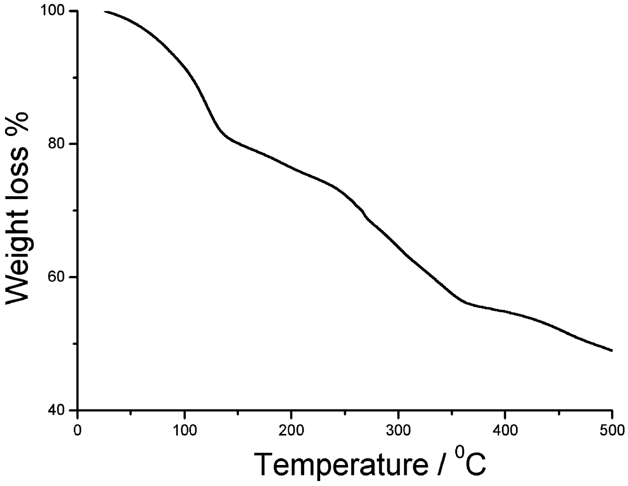

Figure 5. TGA curve of **1**.

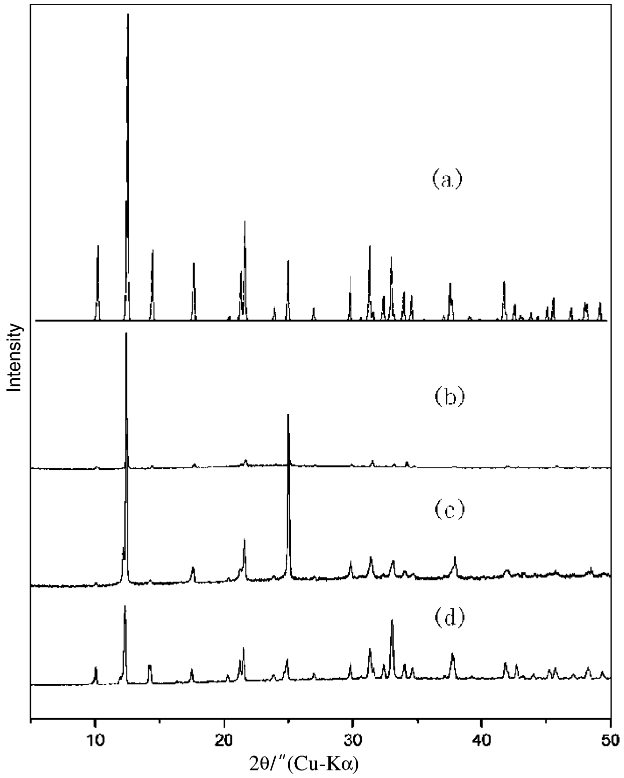

Figure 6. PXRD patterns of simulated (a), 120 °C (b), rehydrated (c), and as-synthesized (d) samples of **1**.

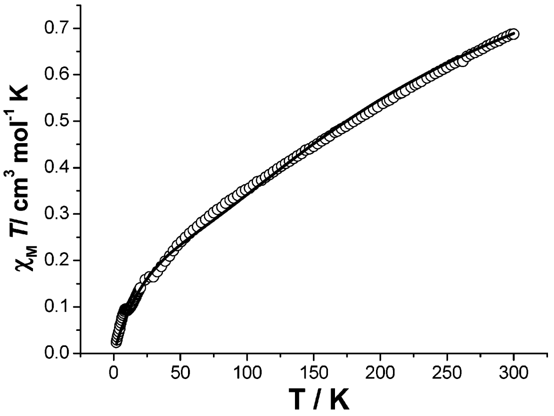

Figure 7. Thermal dependence of the $\chi_M T$ (○) curves for compound **1**. Continuous lines correspond to the best least-squares fit.

TGA (Figure 5) showed 21.1% weight loss between room temperature and 140 °C for **1**, in agreement with the corresponding calculated values of 20.2%, due to the loss of water molecules. The relatively low temperature for loss of water molecules exhibits their weak coordination. Then the continuous weight losses from 140 to 500 °C correspond to the continuous decomposition of trz ligands and anions.

The simulated and experimental PXRD patterns of **1** are shown in Figure 6. They are in good agreement with each other, which proves the phase purity of the as-synthesized product. To check the porosity, the as-synthesized crystalline solid was placed in a high-vacuum oven at 120 °C for 6 h with a 21.32% weight loss to obtain the evacuated solid. In the PXRD pattern of the evacuated solid, the main sharp diffraction peaks slightly shift to higher 2θ values and the noticeable diffraction intensity decreases compared with those of the as-synthesized solid. This fact shows that a certain structural change or distortion occurs after removal of the water molecules. The conjecture was further justified by the PXRD pattern of the evacuated solid after soaking in water for 10 h, in which the peak positions and their intensities are nearly coincident to those observed for the as-synthesized solid. The whole cycle can be repeated several times without a significant loss of crystallinity of the material.

The magnetic susceptibilities of **1** were measured in the temperature range from 2 to 300 K under an applied magnetic field of 5 kOe (Figure 7). The $\chi_M T$ value is 0.687 cm^3 K mol^{-1} at 300 K, which is much lower than the value expected for three independent Cu^{II} ions. As the T is lowered, $\chi_M T$ decreases, reaching values of 0.440 cm^3 K mol^{-1} at 147 K, which correspond to the spin-only value of 0.437 cm^3 K mol^{-1} for one unpaired electron with $g = 2.11$. This behavior indicates a quite strong antiferromagnetic interaction between the Cu^{II} ions, with an unpaired electron per Cu_3 unit in the ground state. The value of $\chi_M T$ keeps on decreasing as the temperature is lowered, reaching the value of 0.024 cm^3 K mol^{-1} at 2 K. The magnetic behavior of **1** must be dominated by the presence of two magnetic exchange pathways, one resulting from the Cu−N−N−Cu together with Cu−O−Cu bridges in the trinuclear core and the other from the triazolate bridges that link the two adjacent trinuclear cores. With respect to the superexchange magnetic coupling through these bridges, to date, the available magnetic data for complexes based on this type of bridge indicate strong anitferromagnetic coupling for the former[6] and relatively weak coupling for the latter.[13]

From a structural viewpoint, the title compound exhibits a 3D framework, but keeping in mind the capacity of the bridges to transmit magnetic interactions and the overall appearance of the $\chi_M T$ curve, we tried to fit the experimental magnetic data by using the equation for a trinuclear Cu^{II} complex. In the trinuclear SBU, the three metal ions are structurally equivalent, and so that $J_1 = J_2 = J_3 = J$, the spin Hamiltonian in eq 1 will describe the interactions of the spins.

$$H = -J(S_1 \cdot S_2 + S_2 \cdot S_3 + S_1 \cdot S_3) \qquad (1)$$

From this Hamiltonian, a solution of the magnetic susceptibility may be derived as follows:

$$(\chi_M)_{tri} = (N\beta^2 g^2/4kT)[1 + 5\exp(3J/2kT)]/[1 + \exp(3J/2kT)] + N\alpha \qquad (2)$$

where N, g, β, k, and T have their usual meanings. Because of further assembly of the SBUs into a 3D MOF, the interaction between trinuclear units in **1** was introduced as eq 3,[14] where z is 6.

$$\chi_M = (\chi_M)_{tri}/[1 - (2zj'/N\beta^2 g^2)(\chi_M)_{tri}] \qquad (3)$$

A relatively good fit could be achieved (solid lines in Figure 7) over the whole experimental curve with the parameters $J = -112.5$ cm^{-1}, $g = 2.11$, $j' = -11.6$ cm^{-1}, and $R = 0.011$ $\{R = \Sigma[(\chi_M)^{obs} - (\chi_M)^{calc}]^2/[(\chi_M)^{obs}]^2\}$. The negative coupling constant J and j' confirms the existence of a strong antiferromagnetic exchange within **1**. For further research, one needs to understand that the value of −112.5 cm^{-1} in **1** is considerably lower than the J value reported for $[PPN]_2[Cu_3(\mu_3\text{-}O)(\mu\text{-}pz)_3Cl_3]$.[6c] Even if the fit is not completely satisfactory, the calculated J and j' value is in good agreement with the structural characteristics, and it can be considered as a relatively good approximation.

Conclusion

In conclusion, hydrothermal synthesis in aqueous ammonia was performed, and the first example of a 3D MOF using coordinative interactions constructed via trinuclear triangular Cu^{II} SBUs was isolated. The MOF shows a three-connected 6.8^2 topology, while the SBUs as nodes provide a (4,6) uniform net. Complex **1** shows that 1,2,4-triazolato has a strong tendency to bridge metal ions through its three N atoms to have the capablility of providing a strong antiferromagnetic interaction between metal ions.

Acknowledgment. This work was supported by the National Natural Science Foundation of China (Grants 20425103 and 90501002) and the State Key Project of Fundamental Research of MOST (Grant 2005CCA01200), People’s Republic of China.

Supporting Information Available: Crystallographic data in CIF format and additional Figure S1. This material is available free of charge via the Internet at http://pubs.acs.org.

IC060030O

---

(13) Strotkamp, K. G.; Lippard, S. J. *Acc. Chem. Res.* **1982**, *15*, 318.

(14) Escuer, A.; Vicente, R.; Penalba, E.; Solans, X.; Font-Bardia, M. *Inorg. Chem.* **1996**, *35*, 248.