Inorg. Chem. **2007**, *46*, 497–500

Inorganic Chemistry

Article

$\{[Cu(mtz)]_3(CuI)\}_n$: An Unprecedented Non-interpenetrated $(12^3)(12^2{\cdot}14)_3$ Network with Triple-Stranded Helices

Xi-He Huang, Tian-Lu Sheng, Sheng-Chang Xiang, Rui-Biao Fu, Sheng-Min Hu, Ya-Min Li, and Xin-Tao Wu*

State Key Laboratory of Structural Chemistry, Fujian Institute of Research on the Structure of Matter, Chinese Academy of Sciences, Fuzhou, Fujian 350002, China

Received September 13, 2006

A complex with triple-stranded helices, $\{[Cu(mtz)]_3(CuI)\}_n$, was obtained under hydrothermal conditions. The complex possesses an unprecedented non-interpenetrated $(12^3)(12^2{\cdot}14)_3$ network, which represents the first example of the largest gon value of the smallest ring for the Archimedean net reported so far.

Introduction

Metal−organic framework (MOF) coordination polymers are of growing interest owing to not only their intriguing architectures[1] but also their potential for providing the design of new materials with a widespread range of potentially useful properties including porosity, magnetism, nonlinear optical activity and catalysis, and so on,[2] of which the multiple-stranded helical coordination polymers are receiving much attention because of their many novel structures analogous to the helical arrays in pharmacology or in biological DNA chains.[3] Although remarkable efforts have been made in the new field of chemistry and materials science,[4] the control of helicity at the molecular level is still a challenge for chemists. To date, only rare examples of multiple-stranded helical 3D framework coordination polymers have appeared in the literature.[5]

The topological approach has been considered as a powerful tool for the design and interrogation of crystal structures.[6] Wells and O'Keeffe et al. have analyzed and classified a great number of nets.[7,8] Today, many network topologies in coordination polymers have been identified,[8,9] including those theoretically predicted but never observed in the world of inorganic compounds and minerals, for instance, the (12, 3) net discussed by Wells[5d,7,10] and the

---

* To whom correspondence should be addressed. E-mail: wxt@ms.fjirsm.ac.cn.

(1) (a) Bradshaw, D.; Claridge, J. B.; Cussen, E. J.; Prior, T. J.; Rosseinsky, M. J. *Acc. Chem. Res*. **2005**, *38*, 273. (b) Eddaoudi, M.; Moler, D. B.; Li, H. L.; Chen, B. L.; Reineke, T. M.; O'Keeffe, M.; Yaghi, O. M. *Acc. Chem. Res*. **2001**, *34*, 319. (c) Moulton, B.; Zaworotko, M. J. *Chem. Rev*. **2001**, *101*, 1629. (d) Yaghi, O. M.; O'Keeffe, M.; Ockwig, N. W.; Chae, H. K.; Eddaoudi, M.; Kim, J. *Nature* **2003**, *423*, 705. (e) Dai, J.-C.; Wu, X.-T.; Fu, Z.-Y.; Cui, C.-P.; Hu, S.-M.; Du, W.-X.; Wu, L.-M.; Zhang, H.-H.; Sun, R.-Q. *Inorg. Chem*. **2002**, *41*, 1391. (f) Dai, J.-C.; Wu, X.-T.; Fu, Z.-Y.; Hu, S.-M.; Du, W.-X.; Cui, C.-P.; Wu, L.-M.; Zhang, H.-H.; Sun, R.-Q. *Chem. Commun*. **2002**, 12.

(2) (a) Chui, S. S.-Y.; Lo, S. M.-F.; Charmant, J. P. H.; Orpen, A. G.; Williams, I. D. *Science* **1999**, *283*, 1148. (b) Rosi, N. L.; Eckert, J.; Eddaoudi, M.; Vodak, D. T.; Kim, J.; O'Keeffe, M.; Yaghi, O. M. *Science* **2003**, *300*, 1127. (c) Xiang, S.-C.; Wu, X.-T.; Zhang, J.-J.; Fu, R.-B.; Hu, S.-M.; Zhang, X.-D. *J. Am. Chem. Soc*. **2005**, *127*, 16352−16353. (d) Evans, O. R.; Lin, W. *Acc. Chem. Res*. **2002**, *35*, 511−522. (e) Wu, C.-D.; Hu, A.; Zhang, L.; Lin, W. *J. Am. Chem. Soc*. **2005**, *127*, 8940.

(3) Watson, J. D.; Crick, F. H. C. *Nature* **1953**, *171*, 737.

(4) (a) Ezuhara, T.; Endo, K.; Aoyama, Y. *J. Am. Chem. Soc*. **1999**, *121*, 3579−3283. (b) Maggard, P. A.; Stern, C. L.; Poeppelmeier, K. R. *J. Am. Chem. Soc*. **2001**, *123*, 7742−7743. (c) Cui, Y.; Ngo, H. L.; Lin, W. *Chem. Commun*. **2003**, 1388. (d) Cui, Y.; Lee, S. J.; Lin, W. *J. Am. Chem. Soc*. **2003**, *125*, 6014.

(5) (a) Imai, H.; Inoue, K.; Kikuchi, K.; Yoshida, Y.; Ito, M.; Sunahara, T.; Onaka, S. *Angew. Chem., Int. Ed*. **2004**, *43*, 5618. (b) Grosshans, P.; Jouaiti, A.; Bulach, V.; Planeix, J.-M.; Hosseini, M. W.; Nicoud, J.-F. *Chem. Commun*. **2003**, 1336. (c) Tong, M.-L.; Chen, X.-M.; Batten, S. R. *J. Am. Chem. Soc*. **2003**, *125*, 16170. (d) Schareina, T.; Schick, C.; Abrahams, B. F.; Kempe, R. *Z. Anorg. Allg. Chem*. **2001**, *627*, 1711. (e) Ma, J.-F.; Yang, J.; Zheng, G.-L.; Li, L.; Liu, J.-F. *Inorg. Chem*. **2003**, *42*, 7531. (f) Qin, S.-B.; Lu, S.-M.; Ke, Y.-X.; Li, J.-M.; Wu, X.-T.; Du, W.-X. *Solid State Sci*. **2004**, *6*, 753.

(6) Wang, X.-L.; Qin, C.; Wang, E.-B.; Li, Y.-G.; Su, Z.-M. *Chem. Commun*. **2005**, 5450.

(7) (a) Wells, A. F. *Three-dimensional Nets and Polyhedra*; Wiley: New York, 1977. (b) Wells, A. F. *Further Studies of Three-dimensional Nets*; ACA Monograph 8; American Crystallographic Association: Buffalo, NY, 1979.

(8) (a) O'Keeffe, M.; Hyde, S. T. *Zeolites* **1997**, *19*, 370. (b) O'Keeffe, M. *Nature* **1999**, *400*, 617. (c) Ockwig, N. W.; Friedrichs, O. D.; O'Keeffe, M.; Yaghi, O. M. *Acc. Chem. Res*. **2005**, *38*, 176. (d) O'Keeffe, M. *Z. Kristallogr*. **1991**, *196*, 21.

(9) (a) Batten, S. R.; Robson, R. *Angew. Chem., Int. Ed*. **1998**, *37*, 1460. (b) Roboson, R. *J. Chem. Soc., Dalton. Trans.* **2000**, 3735. (c) Moulton, B.; Zaworoko, M. J. *Chem. Rev*. **2001**, *101*, 1629. (d) Carlucci, L.; Ciani, G.; Proserpio, D. M. *Coord. Chem. Rev*. **2003**, *246*, 247. (e) Blatov, V. A.; Carlucci, L.; Cianib, G.; Proserpio, D. M. *CrystEngComm* **2004**, *6*, 377.

(10) (a) Abrahams, B. F.; Batten, S. R.; Grannas, M. J.; Hamit, H.; Hoskins, B. F.; Robson, R. *Angew. Chem., Int. Ed*. **1999**, *38*, 1475.

10.1021/ic0617341 CCC: $37.00

"dense" $7^5 \cdot 9$ net suggested by O'Keeffe et al.[8d,11] Although many topological networks, especially the three-connected networks, with single-stranded helices have been reported,[7] much less effort has been focused on the study of the non-interpenetrated networks with multiple-stranded helices. Only a few such nets, for example, the (12, 3) net mentioned above and the (8, 4)[5c] net, have appeared in the literature. For the (12, 3) net, 12 is the largest gon value of the smallest ring considered by Wells.[7] In this Article, we report a novel framework, $\{[Cu(mtz)]_3(CuI)\}_n$ (**1**; Hmtz = 3,5-dimethyl-1,2,4-triazole), which is constructed by triple-stranded helices of $\{[Cu(mtz)]_3\}_n$ and $Cu^{I}I$ secondary building units. The structure of **1** can be classified as an unprecedented chiral, non-interpenetrated $(12^3)(12^2 \cdot 14)_3$ net with triple-stranded helices. This three-connected topology represents the largest gon value of the smallest ring for the Archimedean net reported so far.[12]

Experimental Section

Materials and Instrumentation. All reagents were obtained from commercial sources and used without further purification. Elemental analyses were performed on a Vario EL III elemental analyzer. The Fourier transform IR spectrum was obtained on a Perkin-Elmer Spectrum-one instrument using KBr pellets in the range of 4000−×ff400 cm^{-1}. Powder X-ray diffraction patterns were recorded on a PANalytical X'pert pro X-ray diffractometer with graphite-monochromatized Cu Kα radiation ($\lambda = 1.542$ Å). Photoluminescence analysis was performed on an Edinburgh FLS920 fluorescence spectrometer. Thermogravimetric analyses (TGA) and differential scanning calorimetry (DSC) were carried out on a Netzsch STA449C system at a heating rate of 10 °C min^{-1} under a N_2 atmosphere.

Preparation of 1. A mixture of $Cu_2CO_3(OH)_2 \cdot H_2O$ (0.239 g, 1.0 mmol), KI (0.249 g, 1.5 mmol), aqueous ammonia (25%, 1 mL), and acetonitrile (8 mL) was heated in a 15-mL capacity Teflon-lined reaction vessel at 140 °C for 3 days and then cooled to room temperature over a period of 24 h. The pale-yellow hexagonal prism crystals of complex **1** were filtered, washed with water, and dried in air in 20% yield (0.065 g). Elem anal. Calcd for $C_{12}H_{18}Cu_4IN_9$ (**1**): H, 2.71; C, 21.53; N, 18.83. Found: H, 2.58; C, 21.64; N, 18.92. IR spectrum (KBr pellets, cm^{-1}): 3311(w), 3244(m), 2997(w), 2911(w), 1595(s), 1520(vs), 1499(vs), 1466(m), 1416(vs), 1371(s), 1343(s), 1272(m), 1181(m), 1095(m), 1041(m), 1018(m), 988(m), 841(w), 767(s), 691(s), 629(m), 495(m), 431(s).

X-ray Crystallographic Studies. A single crystal of **1** with dimensions 0.06 × 0.04 × 0.04 mm^3 was used for structural determinations on a Rigaku R-AXIS IP diffractometer using graphite-monochromatized Mo Kα radiation ($\lambda = 0.710\,73$ Å) at room temperature using the ω-scan technique. Lorentz polarization and absorption corrections were applied. The structure was solved by direct methods and refined with full-matrix least-squares techniques using the *SHELXS-97* and *SHELXL-97* programs.[13] All non-H atoms were located by difference Fourier maps and subjected to anisotropic refinement. H atoms were added according to the theoretical models. Crystallographic data and selected bond lengths and angles are listed in Tables 1 and 2, respectively.

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

complex	**1**
formula	$C_{12}H_{18}Cu_4IN_9$
fw	669.41
cryst syst	hexagonal
space group	*P*63
a (Å)	11.784(4)
c (Å)	8.527(4)
V (Å^3)	1025.5(7)
Z	2
D_c (g cm^{-3})	2.168
μ (mm^{-1})	5.612
reflns collected/unique (R_{int})	10074/1566 (0.0365)
R1^a [$I > 2\sigma(I)$]	0.0215
wR2^b (all data)	0.0548
GOF on F^2	1.050
Flack parameter	0.0010 (0.0215)

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

Table 2. Selected Bond Lengths (Å) and Angles (deg) for **1**^{a}

Cu1−I1	2.7478(14)	Cu2−I1	2.9691(10)
Cu1−N1	2.019(3)	Cu2−N2	1.885(3)
Cu2−N3$^{\#1}$	1.896(2)		
N1$^{\#2}$−Cu1−N1	115.68(5)	N1−Cu1−I1	102.17(8)
N2−Cu2−N3$^{\#1}$	158.19(12)	N2−Cu2−I1	100.20(8)
N3$^{\#1}$−Cu2−I1	101.33(8)	Cu2$^{\#2}$−I1−Cu2	111.161(13)
Cu1−I1−Cu2	72.276(14)		

^{a} Symmetry transformations used to generate equivalent atoms: #1, *y*, $-x + y$, $z - {}^1/_2$; #2, $-x + y$, $-x + 1$, *z*.

Results and Discussion

Crystal Structure and Network Topology. Single-crystal X-ray structural analysis revealed that **1** crystallizes in the chiral space group $P6_3$. The asymmetric unit of complex **1** contains two crystallographically unique Cu^{I} centers, one I atom, and one mtz ligand synthesized in situ.[14] The Cu1 and I1 atoms lie on the 3-fold axis, while the Cu2 atom and the mtz ligand locate on the general sites. As shown in Figure 1a, the Cu1 atom has a distorted tetrahedral coordination with one I atom and three N atoms from three mtz ligands, while the Cu2 atom is three-coordinated to one I atom and two N atoms from two mtz ligands in a distorted T shape . The I1 atom adopts a peculiar "anchor fluke-shape" coordination with one Cu1 atom and three Cu2 atoms. The Cu2 atoms are bridged alternatively by the mtz ligands in the "imidazolate mode", forming a right-hand-helical chain[15] along the 6_3 axis with a long helical distance of 25.581(12) Å (3 times the *c*-axis length). Every three helical chains further intertwine to generate a triple-stranded helix (Figure

---

(11) (a) Carlucci, L.; Ciani, G.; Macchi, P.; Proserpio, D. M. *Chem. Commun.* **1998**, 1837. (b) Zhang, J.; Kang, Y.; Zhang, R.-B.; Li, Z.-J.; Cheng, J.-K.; Yao, Y.-G. *CrystEngComm* **2005**, *7*, 177.

(12) More than a 1000 nets have been collected and described in detail at the Web site of the O'Keeffe group at Arizona State University; see http://okeeffe-ws1.la.asu.edu/RCSR/home.htm. For the Archimedean net, 8 is the largest gon value of the smallest ring in this Web site.

(13) Sheldrick, G. M. *SHELXL97 and SHELXS97, Program for X-ray Crystal Structure Solution and Refinement*; University of Göttingen: Göttingen, Germany, 1997.

(14) (a) Zhang, J.-P.; Chen, X.-M. *Chem. Commun.* **2006**, 1689. (b) Zhang, J.-P.; Lin, Y.-Y.; Huang, X.-C.; Chen, X.-M. *Chem. Commun.* **2005**, 1258. (c) Zhang, J.-P.; Zheng, S.-L.; Huang, X.-C.; Chen, X.-M. *Angew. Chem., Int. Ed.* **2004**, *43*, 206. (d) Zhang, J.-P.; Lin, Y.-Y.; Huang, X.-C.; Chen, X.-M. *J. Am. Chem. Soc.* **2005**, *127*, 5495.

(15) The crystal selected for diffraction reflections measured displays the right-handed helicity, but the second crystal chosen at random was found to have the opposite handedness.

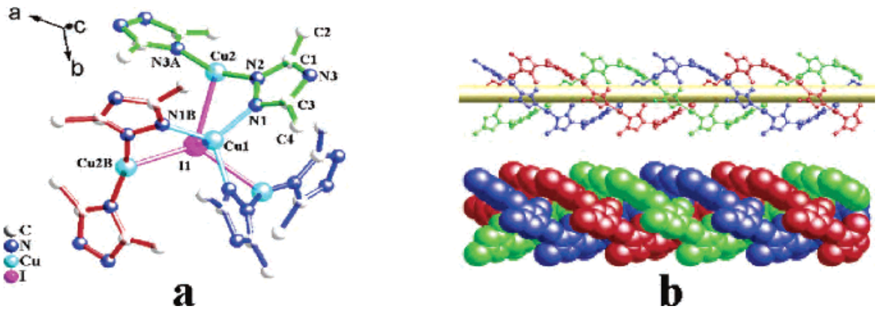

Figure 1. (a) Atom-labeling scheme showing a CuI unit connecting three helical chains (represented by different bond colors). H atoms have been omitted for clarity. Symmetry codes: (A) $y, -x + y, z - {}^1/_2$; (B) $1 - y, 1 + x - y, z$. (b) View of the triple-stranded helix of **1** (top) and a space-filling model of the triple-stranded helix (bottom).

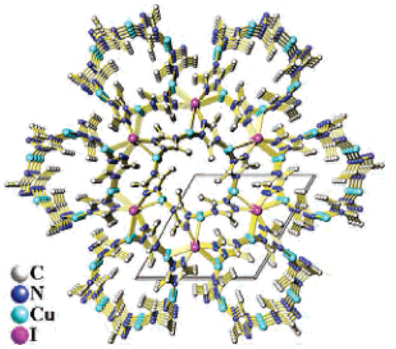

Figure 2. Perspective view of **1** along the *c* axis. H atoms are omitted for clarity.

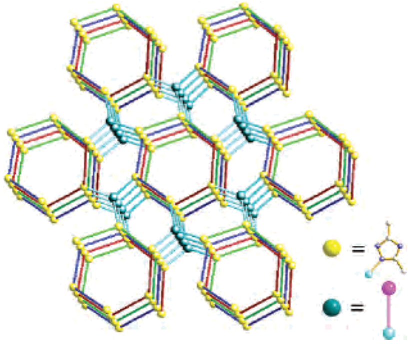

Figure 3. $(12^3)(12^2{\cdot}14)_3$ net in the structure of **1**. The helical chains of the triple-stranded helices were marked as three different colors (blue, red, and green) for clarity.

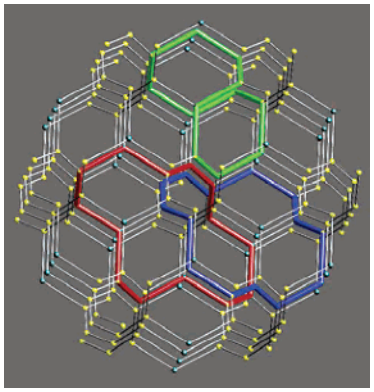

Figure 4. $(12^3)(12^2{\cdot}14)_3$ net in highest symmetry. Highlighting shows three types of shortest circuits (one 12-gon and two 14-gons). Catenation of the 14-gon shortest circuits illustrates that this net is a self-penetrating network.

1b). The triple-stranded helices with the same helicity array along the *c* axis in a hexagonal arrangement are further linked through the Cu1 and I1 atoms of the Cu^II fragment, forming a non-interpenetrating 3D chiral framework. Half of the methyl groups of the mtz ligands locate in the channel formed by the triple-stranded helix (Figure 2). It should be noted that the Cu−I [2.969(1) Å] or Cu−N [2.019(3) Å] bond between the Cu^II fragment and the $\{[Cu(mtz)]_3\}_n$ triple-stranded helix is much weaker than the Cu−I bond [2.748(2) Å] in the CuI fragment or the Cu−N bonds [1.885(3)−1.896(2) Å] in the $\{[Cu(mtz)]_3\}_n$ triple-stranded helix. Thus, the 3D framework structure of the complex can be described as consisting of neutral triple-stranded helices to which are linked the CuI fragments through a weaker interaction. By a comparison of complex **1** with another copper(I) triazoate, $[Cu(mtz)]_n$, previously reported by Chen et al.,[14c] it can be found that in both compounds there exist helical chains with the same component of $[Cu(mtz)]_n$ and a similar connection mode between the Cu atoms and the mtz ligands. In complex $[Cu(mtz)]_n$, the helical chain is composed of double-stranded helices, with the helices being right- and left-handed along the 4_2 axis, respectively. In complex **1**, however, the helical chain consists of triple-stranded helices with only the right-handed direction along the 6_3 axis. The bond angle of N−Cu−N within the helical chain in complex $[Cu(mtz)]_n$ [134.3(1)°] is greatly smaller than that in complex **1** [158.2(2)°]. On the other hand, in complex $[Cu(mtz)]_n$, each helical chain is linked to four adjacent antiparallel chains through interchain Cu−N bonds into a 3D net, resulting in a centrosymmetric 2-fold interpenetrated network. However, all of the triple-stranded helices of complex **1** have the same helicity; the 3D framework structure of the complex is formed by the connection of the neutral triple-stranded helices to the CuI fragments through a weaker interaction.

Taking the structural feature of complex **1** into account, the network can be best described as an unprecedented binodal $(12^3)(12^2{\cdot}14)_3$ net when the Cu^II unit is treated as one three-connected node and the Cu2 atom and a neighboring mtz ligand as another three-connected node. The novel $(12^3)(12^2{\cdot}14)_3$ net is shown in Figure 3. The "long" *Schläfli* symbol for this network is $(12_4{\cdot}12_4{\cdot}12_4)(12_4{\cdot}12_4{\cdot}14_9)_3$. The shortest ring involving each node in this net is 12-gon and/or 14-gon (Figure 4). Similar to the (12, 3) and (8, 4) nets mentioned above, the $(12^3)(12^2{\cdot}14)_3$ network is also a self-penetrating one, of which the two 14-gon smallest rings are passing through each other. When the $\{[Cu1I][Cu2(mtz)]_3\}$ clusters are assigned as a six-connected node, an acs net $(4^9{\cdot}$

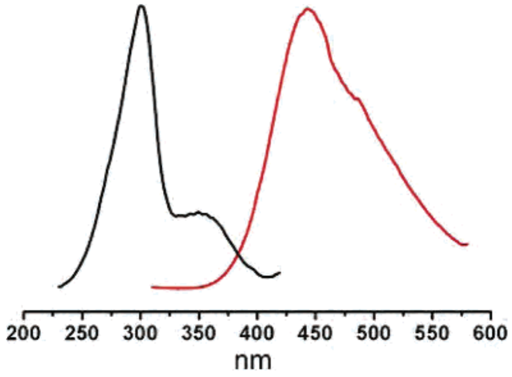

Figure 5. Solid-state excitation (left) and emission (right) spectra of **1** at room temperature.

6^6) can be derived (Figure S2 in the Supporting Information). However, it should be noted that the acs net cannot show the most interesting structural feature; i.e., the complex consists of neutral triple-stranded helices to which are linked CuI fragments through a weaker interaction.

Physical Properties. Complex **1** emits a very strong blue luminescence at room temperature. A broad emission peak with a maximum at 443 nm was observed with 300-nm excitation (Figure 5). The luminescent decay profile of **1** can be fitted with a triple-exponential decay function with $\tau_1 = 2.087\ \mu$s (62.55%), $\tau_2 = 9.211\ \mu$s (27.25%), and $\tau_3 = 83.71\ \mu$s (10.2%). The long emission lifetimes could be assigned to metal-to-ligand charge-transfer triplet excited states (^{3}[MLCT]), which are similar to other copper(I) 1,2,4-triazolates reported previously.[15c,d,16] The TGA of complex **1** shows that the complex has no weight loss below 400 °C but decomposes at a higher temperature than 400 °C.

Conclusion

In summary, we have prepared and characterized an unprecedented non-interpenetrating 3D chiral network of $(12^3)(12^2{\cdot}14)_3$ with triple-stranded helices. The gon value of the smallest ring in this $(12^3)(12^2{\cdot}14)_3$ network is the largest for the Archimedean net reported so far.

Acknowledgment. This research was supported by National Science and Technology of China (Grants 001CB1089, 20333070, 90206040, 90406024, and 20673118) and of Fujian Province (Grants 2005HZ01-1, 2004HZ01-1, 2006J0014, and Z0513022).

Supporting Information Available: X-ray crystallographic data in CIF format, simulated and experimental powder XRD patterns for **1**, the acs net in the structure of **1**, the luminescent decay profile of complex **1**, and the TGA and DTA curves of **1**.

IC0617341

---

(16) Zhang, J.-P.; Lin, Y.-Y.; Huang, X.-C.; Chen, X.-M. *Dalton Trans.* **2005**, 3681.