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A Novel 3D Cu^{I} Metal–Organic Framework with Middle-Size Channels Despite the Sixfold ThSi$_2$ Interpenetrating Topological Structure

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A new univalent copper coordination polymer with an unusual asymmetric ThSi$_2$ topological structural network was synthesized and 1D middle-size channels were found despite the sixfold ThSi$_2$ interpenetrating topological structure.

Recently, the assembly of metal–organic open frameworks (MOFs) has attracted great attention; MOFs with various network topologies have been prepared by using metal ions and organic building blocks. MOFs with flexible or rigid microporous channels have potential applications in selective molecular recognition and separation, physical gas storage, chemical absorption, ion-exchange and heterogeneous catalysis. Structural interpenetration has been widely used to design intriguing topologies in inorganic chemistry and may enhance the stability of porous materials.[1] Despite the simple and common formula, the rigid ligand 4,4′-bpy has been used extensively to ligate metal ions into an open framework of diamond-like networks[2] or networks with rectangular channels.[3]

In previous literature the hydrothermal method has been shown to be a promising technique for preparing highly stable, infinite metal–ligand frameworks.[4] It has been found that many interesting phenomena such as ligand oxidative coupling, hydrolysis, substitution and redox reaction, can occur under the in-situ hydrothermal conditions.[5] These reactions represent new routes for constructing novel coordination polymers. Encouraged by several recent reports showing that Cu^{II} could be reduced to Cu^{I} under basic hydrothermal conditions,[6] we synthesized a new 3D MOF copper(I) coordination polymer [Cu$_2$(4,4′-bpy)$_2$-Cl](ClO$_4$) (**1**). A simple one-step synthesis procedure has been schematically illustrated in Figure 1.

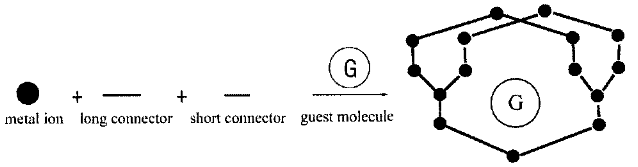

Figure 1. A schematic representation of the assembly of metal ions (dark spheres) and organic ligand connectors (dark rods: long connector; gray rods: short connector) to yield open frameworks with polygonal channels. The assembly is accompanied by the inclusion of a guest molecule G which occupies the void.

The hydrothermal reaction of Cu(ClO$_4$)$_2$ with 4,4′-bpy, pyrazine-2,3-dicarboxylic acid (or pyridine-2,6-dicarboxylic acid), and minor CuCl$_2$ led to the formation of a crystalline complex. The presence of the Cu^{I} ion in the product indicates that the Cu^{II} ion may act as an oxidant in a similar manner as shown in previous research in hydrothermal reactions.[6] Although the heterocycle carboxylic acids did not appear in the final complex **1**, they may change the pH value of the solution and therefore play a key role in the formation of the interpenetrating network. So it is quite different from the reported 2D structure of complex [Cu$_2$Cl$_2$(bpy)].[5e] We synthesized the complex [Cu$_2$Cl$_2$(bpy)] using a similar preparation procedure to complex **1** except that heterocycle multi-carboxylic acid is not involved in the starting material, and proved its structure by single-crystal X-ray diffraction.

X-ray single crystal analysis revealed that the actual crystal structure of complex **1** is a sixfold interpenetrating coordination network with a 3-connected ThSi$_2$ topological structure. This is in accordance with the fact that trigonal metal templates have a high tendency to form interpenetrated or self-inclusion compounds, if the cavities generated in this way are more than 50% of the crystal by volume.[7] In complex **1**, each Cu^{I} ion in the 3D structure is

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coordinated to two nitrogen atoms from two 4,4′-bpy ligands giving rise to a zigzag Cu–bpy chain. The chains are further connected to adjacent vertical chains via μ_2-chlorine coordination bonds and extend into a 3D net as represented in Figure 2. The pyridyl rings and Cu atoms in the same chains are coplanar. The adjacent Cu–bpy–Cu chains are cross-linked in an almost perpendicular fashion (Cu1C···Cu1···Cu1A···Cu1D = 74.6°, as shown in Figure 3). The Cu–N and Cu–Cl distances [Cu1–N1 = 1.935(3) Å, Cu1–Cl1 = 2.3791(11) Å] are comparable with those found in [CuCl(bpy)],[8a] $[(CuCl)_2(C_{10}H_7N_3)]$,[8b] and $[Cu_2Cl_2(bpy)]$.[5e] The distances between the Cu^I ions bridged by a Cl anion or by a 4,4′-bpy ligand are 4.758 and 10.968 Å, respectively. The shortest vector relating to adjacent nets equates to axis *a* (Cu···Cu inter-net distance of ca. 5.586 Å).

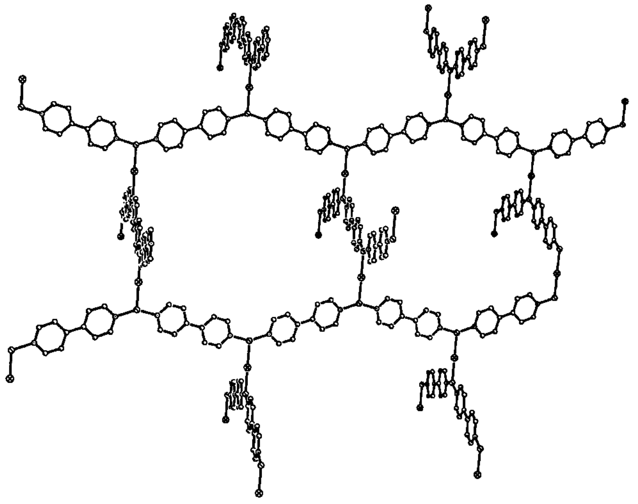

Figure 2. A view of a single framework of complex **1** with the perchlorate anion omitted.

Recent studies have shown the tendency of Cu^I to form multi-dimensional structural units with halogen atoms and 4,4′-bpy under hydrothermal conditions. In these complexes the copper ions will always be four-coordinate and the structure will usually be 2D[5e,8–10] (except for complex [CuBr(bpy)][5e] that possesses a 3D structure formed by perpendicular interlocking 2D nets). To the best of our knowledge, no structurally characterized example of three-coordinate Cu^I ions with bpy groups and hetero atoms has been documented to date. Compound **1** is a novel example of three-coordinate Cu^I with bpy and Cl^-. It has a sixfold interpenetrating $ThSi_2$ topological structure of Class Ia with the interpenetration vector equating to axis *a*. This topological structure is rare, and the only known example is MOF $[Cu_2(4,4'\text{-bpy})_3](NO_3)_2(H_2O)_{1.25}$,[4a] but this has a different Class IIIa.

The most striking feature of complex **1** is that despite the sixfold interpenetrating 3D networks, complex **1** shows an unusual open framework containing middle-size hexagonal channels running along axis *a*, as shown in Figure 4 (the side lengths of the hexagonal channels are 4.16 and 6.66 Å, respectively). Guest perchlorate anions reside in the channels as counterions. The PLATON[11] programme reveals that the voids in complex **1** occupy 24.1% of the crystal volume (after the removal of the guest molecules). To compare the structural differences (especially in interpenetration) of complex **1** with $[Cu_2(4,4'\text{-bpy})_3](NO_3)_2(H_2O)_{1.25}$,[4a] we synthesized its isomorph $[Cu_2(4,4'\text{-bpy})_3](ClO_4)_2(H_2O)_2$ (**2**). From Figure 3, we can see that the interpenetration structures of the two polymers are different, while the latter possesses less channels as generally discussed in the literature.[4a] This is because of the two opposing rotations within the building unit of complex **2**: the pyridyl rings of two independent 4,4′-bpy rotate along the C–C single bond axis with dihedral angles of 33.3 and 40.1°; and the adjacent Cu–bpy–Cu chains are cross-linked with a lower angle (Cu1a···Cu1···Cu1c···Cu1e = 63.3°) compared to complex **1**.

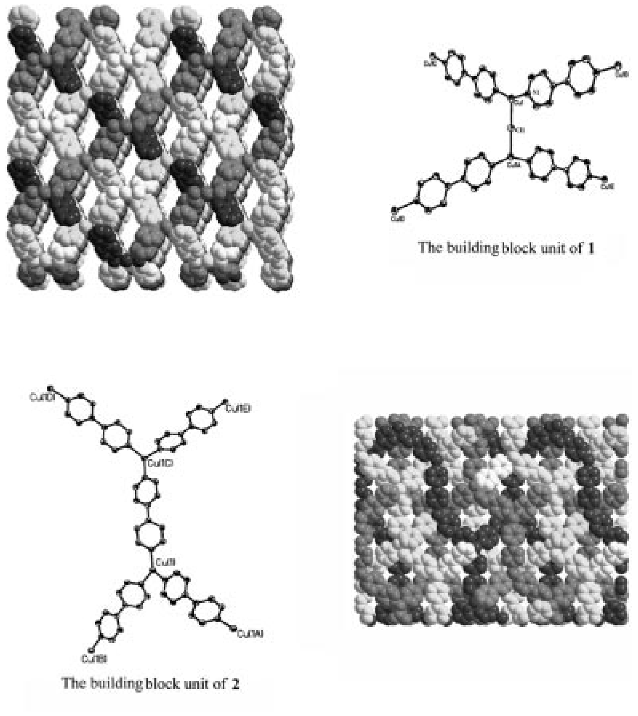

Figure 3. Schematic views of the 3D interpenetrating networks of complexes **1** (top) and **2** (bottom) along axis *a* showing the 1D channels.

Complex **1** is very stable in air at ambient temperature and is almost insoluble in common solvents such as water, alcohol, acetonitrile, chloroform, acetone, and toluene, being consistent with its polymeric nature. Thermal gravimetric analysis (TGA) from 80 to 500 °C indicates that complex **1** is thermally stable up to 240 °C (see Supporting Information, Figure S1). After heating a sample of complex **1** directly to 200 °C and keeping it for 1 h in an oven, the framework remains intact [monitored by X-ray powder diffraction (XRPD), see Supporting Information, Figure S2]. No signal was found in the ESR spectrum for complex **1**, which confirms that all the copper atoms in complex **1** are univalent.

In summary, a novel three-coordinate Cu^I polymer possessing a sixfold interpenetrating 3D $ThSi_2$ topological

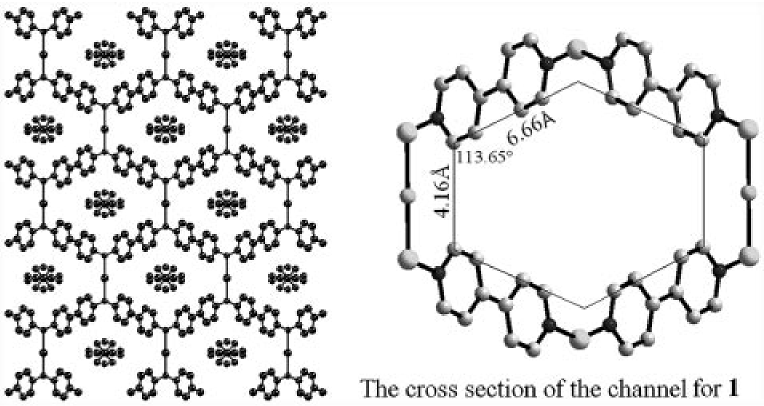

Figure 4. A ball and stick diagram of complex **1** showing the 1D channels formed by interpenetration.

structure was synthesized under hydrothermal conditions and characterized. Middle-size 1D channels were formed in the complex. To the best of our knowledge, there is no previous example of MOFs forming with mixed connectors containing the $ThSi_2$ topological structure.[12,13] The compound forms a 3-connected network with novel topology that has implications for understanding the relationship between related nets.

Experimental Section

General Remarks: All chemicals were obtained from commercial sources and used as received. The C, H, N microanalyses were carried out with a Vario EL elemental analyzer. The IR spectra were recorded with a Magna-IR 750 spectrophotometer using the KBr pellet technique. Thermal gravimetric analysis (TGA) was carried out with a Perkin–Elmer TGA 7 thermogravimetric analyzer in N_2 condition with a heating rate of 10 °C min^{-1}. The electron paramagnetic resonance (EPR) powder spectrum was recorded at X-band with a Bruker ER 200B spectrometer. Powder XRD was performed with a Bruker D8 Advance X-ray diffractometer with monochromatized Cu-K_α radiation (λ = 1.5418 Å).

Preparations

Synthesis of $[Cu_2(4,4'\text{-bpy})_2Cl](ClO_4)$ (1): A mixture of $Cu(ClO_4)_2\cdot 6H_2O$ (0.186 g, 0.5 mmol), pyrazine-2,3-dicarboxylic acid (0.084 g, 0.5 mmol), 4,4′-bpy (0.096 g, 0.5 mmol), $CuCl_2$ (0.017 g, 0.1 mmol), and water (18.0 mL) in the molar ratio of 5:5:5:1:10000 was sealed in a 25-mL stainless steel reactor with Teflon liner, and heated directly to 180 °C. After being kept at 180 °C for 72 h, it was cooled slowly to 30 °C at a rate of 2 °C/h. From a large quantity of red deposit, the resulting orange block crystals of **1** were separated, washed, and dried in air (yield ca. 10% based on Cl). Replacing pyrazine-2,3-dicarboxylic acid by equivalent pyridine-2,6-dicarboxylic acid, the same crystals were obtained (yield ca. 5% based on Cl). $C_{10}H_8ClCuN_2O_2$ (287.17): calcd. C 41.83, H 2.81, N 9.76; found C 41.65, H 2.55, N 9.52. The pH value of the residuary solution is 4. IR (KBr): $\tilde{\nu}$ = 3441, 3070, 3042, 1635, 1601, 1526, 1482, 1408, 1326, 1215, 1109, 1084, 963, 817, 799, 724, 673, 625, 475.

Synthesis of $[Cu_2(4,4'\text{-bpy})_3](ClO_4)_2(H_2O)_2$ (2): A mixture of $Cu(ClO_4)_2\cdot 6H_2O$ (0.186 g, 0.5 mmol), 4,4′-bpy (0.096 g, 0.5 mmol), KI (0.083 g, 0.5 mmol), and water (18.0 mL) in the molar ratio of 1:1:1:1000 was sealed in a 25-mL stainless steel reactor with Teflon liner, and heated directly to 180 °C. After being kept at 180 °C for 72 h, it was cooled slowly to 30 °C at a rate of 2 °C/h. The resulting brown block crystals of complex **2** were washed and dried in air (yield ca. 15% based on Cu). $C_{15}H_{14}ClCuN_3O_5$ (830.56): calcd. C 43.34, H 3.37, N 10.11; found C 42.98, H 3.51, N 9.89. IR (KBr): $\tilde{\nu}$ = 3392, 3075, 3044, 1600, 1530, 1483, 1409, 1322, 1217, 1087, 818, 799, 673, 625, 473.

X-ray Crystallography

Crystal Data for Complex 1: $C_{10}H_8ClCuN_2O_2$, M = 287.17, orthorhombic, space group *Pnnn*, a = 5.5864(18) Å, b = 12.769(4) Å, c = 15.621(5) Å, V = 1114.3(6) Å^3, Z = 4, Dc = 1.712 g cm^{-3}, μ (Mo-K_α) = 2.183 cm^{-1}, F(000) = 576, 1144 reflections measured, 829 [$I \geq 2\sigma(I)$] unique reflections were used in all calculations. The final R_1 = 0.0508, wR_2 = 0.1341, S = 1.086.

Crystal Data for Complex 2: $C_{15}H_{14}ClCuN_3O_5$, M = 415.28, orthorhombic, space group *Fddd*, a = 18.747(2) Å, b = 23.355(3) Å, c = 30.404(4) Å, V = 13312(3) Å^3, Z = 16, Dc = 1.658 g cm^{-3}, μ (Mo-K_α) = 1.505 cm^{-1}, F(000) = 6752, 6258 reflections measured, 3839 [$I \geq 2\sigma(I)$] unique reflections were used in all calculations. The final R_1 = 0.0520, wR_2 = 0.1034, S = 1.054. Data collections ($2.61 \leq \theta \leq 24.83°$ for complex **1**, $2.20 \leq \theta \leq 33.54°$ for complex **2**) were performed at 293 K with a Bruker SMART 1000 CCD diffractometer (Mo-K_α, λ = 0.71073 Å). The structures were solved with direct methods (SHELXS-97) and refined by full-matrix least-squares (SHELXL-97).

CCDC-227621 (for complex **1**) and -292359 (for complex **2**) contain the supplementary crystallographic data for this paper. These data can be obtained free of charge from The Cambridge Crystallographic Data Centre via www.ccdc.cam.ac.uk/data_request/cif.

Supporting Information (for details see the footnote on the first page of this article): TGA curve and X-ray powder diffration pattern of **1**.

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[1] a) M. Eddaoudi, D. B. Moler, H. Li, B. Chen, T. M. Reineke, M. O'Keeffe, O. M. Yaghi, *Acc. Chem. Res.* **2001**, *34*, 319–330; b) S. R. Batten, R. Robson, *Angew. Chem. Int. Ed. Engl.* **1998**, *37*, 1460–1494; c) M. J. Zaworotko, *Angew. Chem. Int. Ed.* **2000**, *39*, 3052–3054; d) P. J. Hagrman, D. Hagrman, J. Zubi-

eta, *Angew. Chem. Int. Ed.* **1999**, *38*, 2638–2684; e) C. Janiak, *Angew. Chem. Int. Ed. Engl.* **1997**, *36*, 1431–1434; f) S. Kitagawa, R. Kitaura, S. Noro, *Angew. Chem. Int. Ed.* **2004**, *43*, 2334–2375.

[2] a) P. J. Stang, D. H. Cao, S. Saito, A. M. Arif, *J. Am. Chem. Soc.* **1995**, *117*, 6273–6283.; b) S. Subramanian, M. J. Zaworotko, *Angew. Chem. Int. Ed. Engl.* **1995**, *34*, 2127–2129; c) M. Fujita, Y. J. Kwon, S. Washizu, K. Ogura, *J. Am. Chem. Soc.* **1994**, *116*, 1151–1152.

[3] O. M. Yaghi, H. Li, *J. Am Chem. Soc.* **1996**, *118*, 295–296.

[4] a) O. M. Yaghi, H. Li, *J. Am. Chem. Soc.* **1995**, *117*, 10401–10402; b) S. O. H. Gutschke, M. Molinier, A. K. Powell, R. E. P. Winpenny, P. T. Wood, *Chem. Commun.* **1996**, 823–824; c) S. S. Y. Chui, S. M. F. Lo, J. P. H. Charament, A. G. Orpen, I. D. Williams, *Science* **1999**, *283*, 1148–1150; d) L. A. Gerrard, P. T. Wood, *Chem. Commun.* **2000**, 2107–2108.

[5] a) C. M. Liu, S. Gao, H. Z. Kou, *Chem. Commun.* **2001**, 1670–1671; b) S. O. H. Gutschke, D. J. Price, A. K. Powell, P. T. Wood, *Inorg. Chem.* **2000**, *39*, 3705–3707; c) W. B. Lin, Z. Y. Wang, L. Ma, *J. Am. Chem. Soc.* **1999**, *121*, 11249–11250; d) O. R. Evans, R. G. Xiong, Z. Y. Wang, G. K. Wong, W. B. Lin, *Angew. Chem. Int. Ed.* **1999**, *38*, 536–538; e) J. Y. Lu, B. R. Cabrera, R. J. Wang, J. Li, *Inorg. Chem.* **1999**, *38*, 4608–4611; f) S. M. F. Lo, S. S. Y. Chui, L. Y. Shek, Z. Lin, X. X. Zhang, G. H. Wen, I. D. Williams, *J. Am. Chem. Soc.* **2000**, *122*, 6293–6294.

[6] a) X. M. Zhang, M. L. Tong, X. M. Chen, *Angew. Chem. Int. Ed.* **2002**, *41*, 1029–1031; b) J. Tao, Y. Zhang, M. L. Tong, X. M. Chen, T. Yuen, C. L. Lin, X. Y. Huang, J. Li, *Chem. Commun.* **2002**, 1342–1343; c) X. M. Zhang, X. M. Chen, *Eur. J. Inorg. Chem.* **2003**, 413–417; d) M. L. Tong, L. J. Li, K. Mochizuki, H. C. Chang, X. M. Chen, Y. Li, S. Kitagawa, *Chem. Commun.* **2003**, 428–429; e) K. Jin, X. Y. Huang, L. Pang, J. Li, A. Appel, S. Wherland, *Chem. Commun.* **2002**, 2872–2873; f) J. P. Zhang, S. L. Zheng, X. C. Huang, X. M. Chen, *Angew. Chem. Int. Ed.* **2004**, *43*, 206–209; g) Y. Z. Zheng, M. L. Tong, X. M. Chen, *New J. Chem.* **2004**, *28*, 1412–1415.

[7] P. Losier, M. J. Zaworotko, *Angew. Chem. Int. Ed. Engl.* **1996**, *35*, 2779–2782.

[8] a) O. M. Yaghi, G. M. Li, *Angew. Chem. Int. Ed. Engl.* **1995**, *34*, 207–209; b) J. Y. Lu, B. R. Cabrera, R. J. Wang, J. Li, *Inorg. Chem.* **1998**, *37*, 4480–4481.

[9] a) D. Hagrman, R. P. Hammond, R. C. Haushalter, J. A. Zubieta, *Chem. Mater.* **1998**, *10*, 2091–2100; b) R. P. Hammond, M. Cavaluzzi, R. C. Haushalter, J. A. Zubieta, *Inorg. Chem.* **1999**, *38*, 1288–1292.

[10] B. R. Cabrera, R. J. Wang, J. Li, T Yuen, in *Solid State Chemistry of Inorganic Materials II*, Proceedings of the Symposium of the Materials Research Society, Boston, MA, November 30–December 4, **1998**; Materials Research Society, Warrendale, PA, **1999**, p. 493.

[11] A. L. Spek, *PLATON*, A Multipurpose Crystallographic Tool, Utrecht University, Utrecht, **1999**.

[12] V. A. Blatov, L. Carlucci, G. Ciani, D. M. Proserpio, *CrystEngComm* **2004**, *65*, 377–395.

[13] N. W. Ockwig, O. D. Friedrichs, M. O'Keeffe, O. M. Yaghi, *Acc. Chem. Res.* **2005**, *38*, 176–182.

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