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Solids with Rhombic Channels: Syntheses and Crystal Structures of $[Cu_3(NTA)_2(4,4'\text{-bpy})_2(H_2O)_2]\cdot 9H_2O$ and $[\{Cu(4,4'\text{-bpy})(H_2O)_4\}\{Cu_2(NTA)_2(4,4'\text{-bpy})\}]\cdot 7H_2O$ (NTA = Nitrilotriacetate, 4,4′-bpy = 4,4′-Bipyridine)

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Introduction

Recently, much attention has been paid to solids with one- to three-dimensional (1D−3D) extended structure, due to their relevance to topology, supramolecular chemistry, and other applications.[1] A convenient path to obtain polymeric structures is to use a bifunctional ligand, 4,4′-bipyridine (4,4′-bpy), to link metal ions to form an infinite configuration. A number of extended structures with diverse topologies have been synthesized, such as 1D linear chain,[2] zigzag chain,[3] 2D square network,[4] interwoven honeycomb,[5] 3D square grid,[6] interpenetrated square grid,[7] railroad-like network,[8] and other architecture.[9] In a previous paper,[10] we reported a neutral 2D square network containing bridging ligands 4,4′-bpy and $C_3H_2O_4^{2-}$. Herein, the syntheses and crystal structures of two extended solids, $[Cu_3(NTA)_2(4,4'\text{-bpy})_2(H_2O)_2]\cdot 9H_2O$ (**1**) and $[\{Cu(4,4'\text{-bpy})(H_2O)_4\}\{Cu_2(NTA)_2(4,4'\text{-bpy})\}]\cdot 7H_2O$ (**2**), are described. Compound **1** contains cross-linking rhombic channels, and **2** has channels formed through covalent bonds and hydrogen bonds.

Experimental Section

$Cu(Ac)_2\cdot 2H_2O$ and 4,4′-bpy were used as purchased. Infrared spectra were recorded on a Magna 750 using KBr pellets. Elemental analyses were performed in the Elemental Analysis Laboratory of our institute.

Preparation of $Cu_3(NTA)_2\cdot 2H_2O$. CuO and nitrilotriacetate acid at molar ratio 3:2 were dissolved in boiling water with strong stirring, and 5 h later, the blue solution was filtered. The blue filtrate was condensed and dried to a light blue powder by a sand bath. Anal. Calcd (found): C, 23.91 (23.67); H, 2.67 (2.51); N, 4.65 (4.87); Cu, 31.62 (31.50).

Synthesis of $[Cu_3(NTA)_2(4,4'\text{-bpy})_2(H_2O)_2]\cdot 9H_2O$ (1). Ten milliliters of an aqueous solution containing 0.2 g of $Cu_3(NTA)_2\cdot 2H_2O$ and 0.08 g of 4,4′-bpy was heated to boiling, and the resultant solution was filtered. After the blue filtrate was allowed to stand in the air for several days, 0.14 g of blue prismatic crystals of compound **1** was obtained. Yield: 36.8% (on a copper basis). Anal. Calcd (found): C, 35.67 (35.42); H, 4.68 (4.61); N, 7.80 (7.92). IR (KBr pellet, cm^{-1}): 3411.5 vs, 1610.3 vs, 1537.0 m, 1492.7 m, 1394.3 vs, 1220.7 m, 1078.0 m, 916.0 s, 815.8 s, 734.8 m, 646.0 m, 538.0 w, 501.4 w.

Synthesis of $[\{Cu(4,4'\text{-bpy})(H_2O)_4\}\{Cu_2(NTA)_2(4,4'\text{-bpy})\}]\cdot 7H_2O$ (2). To 10 mL of an aqueous solution of 0.2 g of $Cu_3(NTA)_2\cdot 2H_2O$ and 0.06 g of $Cu(Ac)_2\cdot 2H_2O$ was added 0.08 g of 4,4′-bpy, and the resulting solution was heated to boiling and then filtered. Blue needle crystals (0.15 g) were precipitated after the blue filtrate evaporated for several days. Yield: 39.4% (on a copper basis). Anal. Calcd (found): C, 35.67 (35.50); H, 4.68 (4.59); N, 7.80 (7.95). IR (KBr pellet, cm^{-1}): 3396.1 vs, 1610.3 vs, 1535.1 m, 1492.7 m, 1398.2 vs, 1220.7 m, 1074.2 m, 914.1 s, 819.6 s, 729.0 m, 646.0 m, 572.8 w, 532.3 w, 505.3 w.

X-ray Studies. The intensity data of **1** were collected at room temperature on a Rigaku AFC5R diffractometer. The structure was solved using the MolEN program.[11] Except for the disordered O atoms of water solvates, all non-hydrogen atoms were refined anisotropically. No attempt was made to locate the hydrogen atoms of water; the other hydrogen atoms were added in fixed positions and not refined. Final full-matrix least-squares refinement converged with $R = \sum||F_o| - |F_c||/\sum|F_o| = 0.065$, $R_w = [\sum w(F_o - F_c)^2/\sum wF_o^2]^{1/2} = 0.094$. The weighting scheme was $w = 1/[\sigma^2(F_o^2) + (0.030F_o)^2 + 1.000]$.

The data collection of **2** was performed on a Siemens SMART CCD diffractometer. The structure was solved and refined by the full-matrix least-squares technique with anisotropic thermal parameters for all non-hydrogen atoms using SHELXS-86[12] and SHELXT-93.[13] No attempt was made to locate the hydrogen atoms of water; the other hydrogen atoms were added in the Riding model and not refined. Final $R = \sum||F_o|$

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(1) (a) Halasyamani, P. S.; Drewitt, M. J.; O'Hare, D. O. *J. Chem. Soc., Chem. Commun.* **1997**, 867. (b) Yaghi, O. M.; Li, G.-M. *Angew. Chem., Int. Ed. Engl.* **1995**, *34*, 207. (c) Hagrman, D.; Zubieta, C.; Rose, D. J.; Zubieta, J.; Haushalter, R. C. *Angew. Chem., Int. Ed. Engl.* **1997**, *36*, 873. (d) Kondo, M.; Yoshitomi, T.; Seki, K.; Matsuzaka, H.; Kitagawa, S. *Angew. Chem., Int. Ed. Engl.* **1997**, *36*, 1275. (e) Withersby, M. A.; Blake, A. J.; Champness, N. R.; Hubberstey, P.; Li, W.-S.; Schröder, M. *Angew. Chem., Int. Ed. Engl.* **1997**, *36*, 2327. (f) Julve, M.; Verdaguer, M.; Facus, J.; Tinti, F.; Mortal, J.; Monge, A.; Gutierrez-Puebla, E. *Inorg. Chem.* **1987**, *26*, 3520. (g) Real, J. A.; Munno, G. D.; Munoz, M. C.; Julve, M. *Inorg. Chem.* **1991**, *30*, 2701. (h) Byrn, M. P.; Curtis, C. J.; Hsiou, Y.; Khan, S. I.; Sawin, P. A.; Terzis, A.; Strouse, C. E. In *Solid-State Supramolecular Chemistry: Crystal Engineering*; MacNicol, D. D., Toda, F., Bishop, R., Eds.; Comprehensive Supramolecular Chemistry; Elsevier: Oxford, U.K., 1996; Vol. 6, p 715.

(2) (a)Yu, K. B.; Gou, S. H.; You, X. Z. *Acta Crystallogr.* **1991**, *C47*, 2653. (b) Gou, S. H.; You, X. Z.; Xu, Z.; Zhou, Z. Y.; Yu, K. B.; Yu, Y. P.; Zhu, D. L. *Acta Crystallogr.* **1991**, *C47*, 1303.

(3) (a) Lu, J.; Crisci, G., Niu, T.; Jacobson, J. *Inorg. Chem.* **1997**, *36*, 5140. (b) Chen, C.; Xu, D.; Xu, Y.; Cheng, C. *Acta Crystallogr.* **1992**, *C48*, 1231.

(4) (a) Fuijita, M.; Kwon, Y. J.; Washizu, S.; Ogura, K. *J. Am. Chem. Soc.* **1994**, *116*, 1151. (b) Lu, J.; Paliwala, T.; Lim, S. C.; Yu, C.; Niu, T.-Y.; Jacobson, A. J. *Inorg. Chem.* **1997**, *36*, 923.

(5) MacGillivray, L. R.; Subramanian, S.; Zaworotko, J. *J. Chem. Soc., Chem. Commun.* **1994**, 1325.

(6) (a) Subramaian, S.; Zaworotko, M. J. *Angew. Chem., Int. Ed. Engl.* **1995**, *34*, 2127. (b) Carlucci, L.; Ciani, G.; Proserpio, D. M.; Sironi, A. *Angew. Chem., Int. Ed. Engl.* **1995**, *34*, 1895.

(7) Gable, R. W.; Hoskins, B. F.; Robson, R. *J. Chem. Soc., Chem. Commun.* **1990**, 1677.

(8) Yaghi, O. M.; Li, H.; Groy, T. L. *Inorg. Chem.* **1997**, *36*, 4292.

(9) (a)Yaghi, O. M.; Li, H. L. *J. Am. Chem. Soc.* **1996**, *118*, 295. (b) Robinson, F.; Zaworotko, M. M. *J. Chem. Soc., Chem. Commun.* **1995**, 2413. (c) Carlucci, L.; Ciani, G.; Proserpio, D. M.; Sironi, A. *J. Chem. Soc., Chem. Commun.* **1994**, 2755.

(10) Li, J. M.; Zeng, H. Q.; Chen, J. H.; Wang, Q. M.; Wu, X. T. *J. Chem. Soc., Chem. Commun.* **1997**, 1213.

(11) *MolEN, An Interactive Structure Solution Procedure*; Enraf-Nonius: Delft, The Netherlands, 1990.

(12) Sheldrick, G. M. *SHELXS-86 User Guide*; University of Göttingen: Göttingen, Germany, 1990.

(13) Sheldrick, G. M. *SHELXL-93: Program for crystal structure refinement*; Göttingen, Germany, 1993.

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Table 1. Crystallographic Data for **1** and **2**

	1	**2**
empirical formula	$C_{32}H_{50}Cu_3N_6O_{23}$	$C_{32}H_{50}Cu_3N_6O_{23}$
fw	1077.40	1077.40
a, Å	12.564(3)	16.8055(3)
b, Å	11.628(4)	23.7656(1)
c, Å	15.235(7)	11.1653(2)
β (deg)	93.64(3)	102.227(1)
V,Å^3	2221(1)	4358.2(1)
Z	2	4
space group	$P2_1/n$ (No.14)	$P2_1/c$ (No. 14)
T, °C	25	23
λ(Mo Kα) Å	0.710 69	0.710 73
ρ_{calcd}, g cm^{-3}	1.61	1.642
μ, cm^{-1}	15.1	15.42
R^a	0.065	0.068
R_w	0.094^b	0.167^c

[a] $R = \sum||F_o| - |F_c||/\sum|F_o|$. [b] $R_w = [\sum w(F_o - F_c)^2/\sum wF_o^2]^{1/2}$, $w = 1/[\sigma^2(F_o^2) + (0.030F_o)^2 + 1.000]$. [c] $R_w = [\sum w(F_o^2 - F_c^2)^2/\sum w(F_o^2)^2]^{1/2}$, $w = 1/[\sigma^2(F_o^2) + (0.0897P)^2 + 27.1492P]$ [where $P = (F_o^2 + 2F_c^2)/3$].

Table 2. Selected Bond Lengths (Å) and Angles (deg) for **1**

Cu(1)−O(1)	2.035(5)	Cu(2)−O(4)	1.965(6)
Cu(1)−O(7)	2.485(7)	Cu(2)−O(6)	1.973(6)
Cu(1)−N(1)	2.029(7)	Cu(2)−N(2b)^a	1.971(7)
Cu(2)−O(2)	2.118(6)	Cu(2)−N(3)	2.022(7)
O(1)−Cu(1)−O(1a)	180.000	O(2)−Cu(2)−O(6)	111.2(3)
O(1)−Cu(1)−O(7)	84.3(2)	O(2)−Cu(2)−N(2b)	90.5(3)
O(1)−Cu(1)−O(7a)	95.7(2)	O(2)−Cu(2)−N(3)	81.4(3)
O(1)−Cu(1)−N(1)	89.4(2)	O(4)−Cu(2)−O(6)	138.0(3)
O(1)−Cu(1)−N(1a)	90.6(2)	O(4)−Cu(2)−N(2b)	97.0(3)
O(7)−Cu(1)−O(7a)	180.000	O(4)−Cu(2)−N(3)	85.9(3)
O(7)−Cu(1)−N(1)	86.5(2)	O(6)−Cu(2)−N(2b)	98.6(3)
O(7)−Cu(1)−N(1a)	93.5(2)	O(6)−Cu(2)−N(3)	84.0(3)
N(1)−Cu(1)−N(1a)	180.000	N(2b)−Cu(2)−N(3)	171.9(3)
O(2)−Cu(2)−O(4)	107.3(3)		

[a] a: $-x, -y, -z$. b: $^1/_2 - x, -^1/_2 + y, -^1/_2 - z$.

$- |F_c||/\sum|F_o| = 0.068$, $R_w = [\sum w(F_o^2 - F_c^2)^2/\sum w(F_o^2)^2]^{1/2} = 0.167$, with $w = 1/[\sigma^2(F_o^2) + (0.0892P)^2 + 27.1492P]$ [where $P = (F_o^2 + 2F_c^2)/3$].

The crystallographic data are summarized in Table 1, and the selected bond lengths and angles of **1** and **2** are listed in Tables 2 and 3, respectively.

Results and Discussion

The syntheses are carried out in aqueous solution as follows:

$$Cu_3(NTA)_2{\cdot}2H_2O + 4,4'\text{-bpy} \xrightarrow{H_2O} [Cu_3(NTA)_2(4,4'\text{-bpy})_2(H_2O)]{\cdot}9H_2O \quad (1)$$

$$Cu_3(NTA)_2{\cdot}2H_2O + Cu(Ac){\cdot}2H_2O + 4,4'\text{-bpy} \xrightarrow{H_2O} [\{Cu(4,4'\text{-bpy})(H_2O)_4\}\{Cu_2(NTA)_2(4,4'\text{-bpy})\}]{\cdot}7H_2O \quad (2)$$

In eq 1, Cu^{2+} is a dication and NTA is a trianion, due to the requirement of charge balance and the lod-linking function of 4,4′-bpy, and the neutral product compound **1** has a 2D network made up of Cu^{2+} coordinated by 4,4′-bpy and NTA. But when $Cu(Ac)_2{\cdot}2H_2O$ is included, the assembly path is different in eq 2 and gives a 1D linear chain and dimer configuration. Although the empirical formulas of **1** and **2** are the same, the structures are different. It is assumed that the existence of free copper dications [of $Cu(Ac)_2$] should lead to the formation of cations in a one-dimensional array, and the reassembly of $Cu_3(NTA)_2$ and 4,4′-bpy results in the formation of a dimer anion.

Table 3. Selected Bond Lengths (Å) and Angles (deg) for **2**

Cu(1)−O(15)	1.940(5)	Cu(2)−N(2)	2.012(7)
Cu(1)−O(11)	1.967(6)	Cu(2)−O(21)	2.154(6)
Cu(1)−N(3)	1.977(6)	Cu(3)−O(3)	2.024(6)
Cu(1)−N(1)	2.027(6)	Cu(3)−O(1)	2.026(6)
Cu(1)−O(13)	2.189(6)	Cu(3)−N(6a)^a	2.033(6)
Cu(2)−O(23)	1.961(6)	Cu(3)−N(5)	2.039(6)
Cu(2)−N(4)	1.971(7)	Cu(3)−O(4)	2.275(6)
Cu(2)−O(25)	1.985(7)	Cu(3)−O(2)	2.387(7)
O(15)−Cu(1)−O(11)	159.4(2)	O(25)−Cu(2)−O(21)	114.5(3)
O(15)−Cu(1)−N(3)	93.0(2)	N(2)−Cu(2)−O(21)	81.1(3)
O(11)−Cu(1)−N(3)	94.8(2)	O(3)−Cu(3)−O(1)	178.7(3)
O(15)−Cu(1)−N(1)	84.9(2)	O(3)−Cu(3)−N(6a)	91.8(2)
O(11)−Cu(1)−N(1)	85.1(2)	O(1)−Cu(3)−N(6a)	88.8(2)
N(3)−Cu(1)−N(1)	173.3(3)	O(3)−Cu(3)−N(5)	88.2(2)
O(15)−Cu(1)−O(13)	104.2(2)	O(1)−Cu(3)−N(5)	91.2(2)
O(11)−Cu(1)−O(13)	92.5(2)	N(6a)−Cu(3)−N(5)	179.4(3)
N(3)−Cu(1)−O(13)	103.2(2)	O(3)−Cu(3)−O(4)	93.2(3)
N(1)−Cu(1)−O(13)	83.5(2)	O(1)−Cu(3)−O(4)	85.6(2)
O(23)−Cu(2)−N(4)	94.0(3)	N(6a)−Cu(3)−O(4)	92.6(2)
O(23)−Cu(2)−O(25)	135.5(3)	N(5)−Cu(3)−O(4)	88.1(3)
N(4)−Cu(2)−O(25)	98.5(3)	O(3)−Cu(3)−O(2)	92.6(3)
O(23)−Cu(2)−N(2)	85.6(3)	O(1)−Cu(3)−O(2)	88.6(2)
N(4)−Cu(2)−N(2)	177.4(3)	N(6a)−Cu(3)−O(2)	89.8(2)
O(25)−Cu(2)−N(2)	83.6(3)	N(5)−Cu(3)−O(2)	89.5(2)
O(23)−Cu(2)−O(21)	106.0(3)	O(4)−Cu(3)−O(2)	173.7(2)
N(4)−Cu(2)−O(21)	96.6(3)		
O(2)···O(14b)	2.651	O(2)···O(22c)	2.771
O(3)···O(13b)	2.700	O(1)···O(21c)	2.666

[a] a: $x, y, z - 1$. b: $x, ^1/_2 - y, -^1/_2 + z$; c: $1 - x, ^1/_2 + y, -^1/_2 - z$.

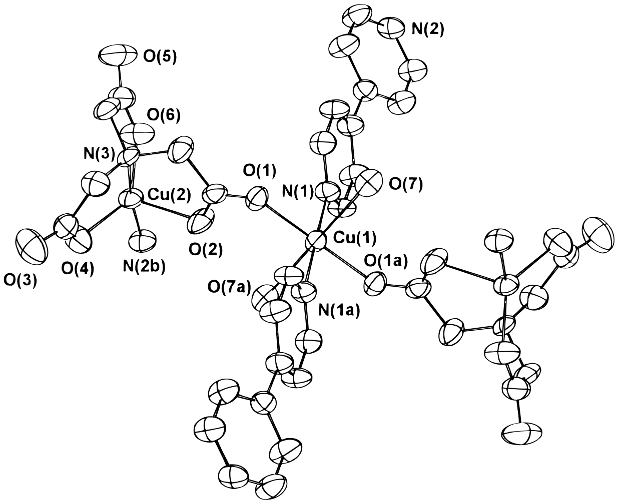

Figure 1. The local coordination of Cu(1) and Cu(2) in **1** (50% probability level). a: $-x, -y, -z$. b: $^1/_2 - x, -^1/_2 + y, -^1/_2 - z$.

The X-ray analysis reveals that there are two types of copper(II) coordination environments, 6- and 5-coordinate, in compound **1**. Figure 1 shows the local coordination of Cu(1) and Cu(2). Cu(1) (inversion center) has a Jahn−Teller elongated tetragonally distorted octahedral symmetry, completed by three pairs of symmetry-related atoms, equatorially by two O atoms of the carboxylate of NTA [Cu(1)−O(1), 2.035(5) Å] and two N atoms of 4,4′-bpy [Cu(1)−N(1), 2.029(7) Å] and axially by two water oxygen atoms [Cu(1)−O(7), 2.485(7) Å]. The coordination geometry around each Cu(2) is a distorted trigonal bipyramid, with three O of NTA as the trigon [Cu(2)−O(4), 1.965(6) Å; Cu(2)−O(6), 1.973(6) Å; Cu(2)−O(2), 2.118(6) Å] and one N of NTA [Cu(2)−N(2), 1.971(7) Å] and one N of 4,4′-bpy [Cu(2)−N(3), 2.022(7) Å] as the apexes. Cu(1) is linked to Cu(2) through 4,4′-bpy and bound to Cu(2)′ by NTA, with a Cu(1)−Cu(2) separation of 11.04 Å and Cu(1)−Cu(2)′ 5.34 Å,

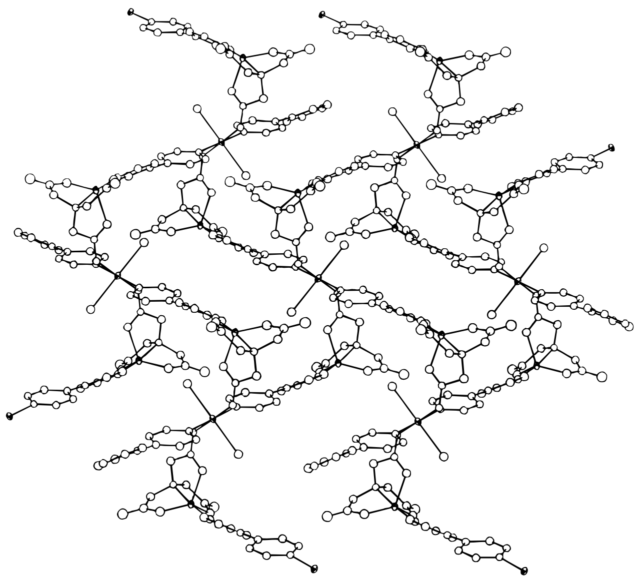

Figure 2. The two-dimensional network of **1**.

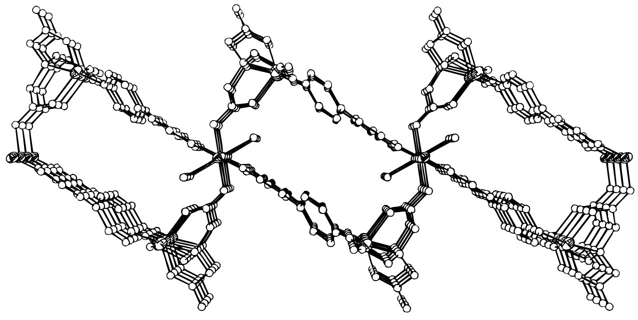

Figure 3. The cross-linking channels in **1** viewed down the *b* direction.

respectively, which extends to a 2D network as shown in Figure 2. The 4,4′-bpy displays flexibility; the N(1) and N(2) pyridine rings of 4,4′-bpy twist by 30.1°. This distortion is due to the fact that each 4,4′-bpy acts as a bismonodentate ligand linking two Cu(II) atoms in different coordination modes.

A unique feature is demonstrated in Figure 3: there are cross-linking rhombic channels parallel to the crystallographic *b* axis in compound **1**. The cross-sectional area of the channel is ca. 4 Å × 8 Å. Each channel can be simplified as a helical chain, and these helical chains are alternately connected on the Cu(1) atom to form the 2D structure; the thread pitch of the helical chain is exactly the *b* length 11.63 Å. Some solvent water molecules, O(12), O(13), and O(15), penetrate into the channels; the other solvent water molecules are located between the 2D layers.

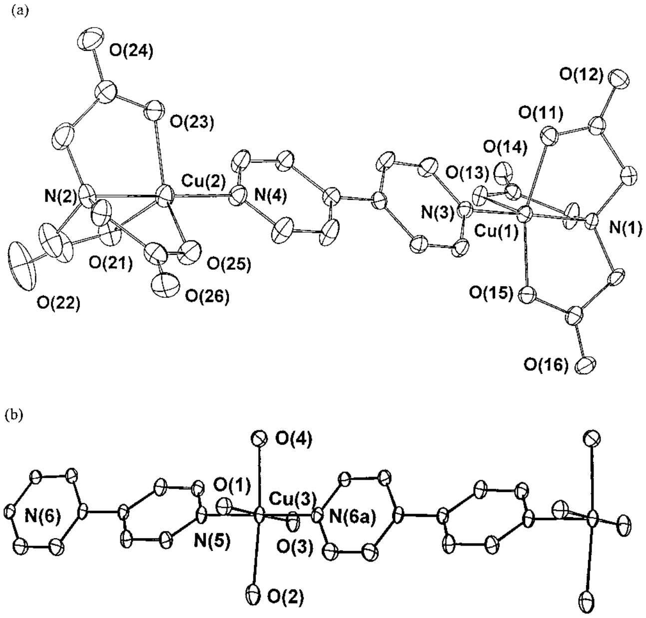

Figure 4. The dimer anion (a) and cations in a one-dimensional array (b) in **2** (20% probability level). a: $x, y, -1 + z$.

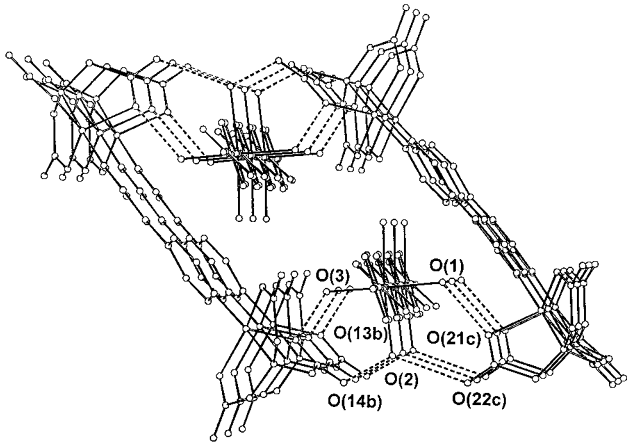

Figure 5. The rhombic channel in **2**. b: $x, {}^{1}/_{2} - y, -{}^{1}/_{2} + z$; c: $1 - x, {}^{1}/_{2} + y, -{}^{1}/_{2} - z$.

The crystal structure of **2** contains two kinds of configurations: cations in a one-dimensional array and a dimer anion as illustrated in Figure 4. In the dimer, Cu(1) and Cu(2) have the same coordination environments, distorted trigonal bipyramid. Each bipyramid is completed by three O of NTA as the trigon [Cu(1)−O(11), 1.967(6) Å; Cu(1)−O(13), 2.189(6) Å; Cu(1)−O(15), 1.940(5) Å; Cu(2)−O(21), 2.154(6) Å; Cu(2)−O(23), 1.961(6) Å; Cu(2)−O(25), 1.985(7) Å] and one N of NTA [Cu(1)−N(1), 2.027(6) Å; Cu(2)−N(2), 2.012(7) Å] and one N of 4,4′-bpy [Cu(1)−N(3), 1.977(6) Å; Cu(2)−N(4), 1.971(7) Å] as the apexes. In the one-dimensional chain, Cu(3) has a Jahn−Teller distorted octahedral symmetry provided by two N of 4,4′-bpy [Cu(3)−N(5), 2.039(6) Å; Cu(3)−N(6), 2.033(6) Å] along the chain and four water oxygen atoms perpendicular to the chain [Cu(3)−O(1), 2.026(6) Å; Cu(3)−O(3), 2.024(6) Å; and two longer bond lengths Cu(3)−O(2), 2.387(7) Å; Cu(3)−O(4), 2.275(6) Å]. The water molecules form strong intermolecular hydrogen bonds to the oxygen atoms of the carboxylate of NTA, with the following distances: O(1)···O(21c), 2.666 Å; O(2)···O(14b), 2.651 Å; O(2)···O(22c), 2.771 Å; O(3)···O(13b), 2.700 Å. These hydrogen bonds link the one-dimensional chain to the neighboring dimers, which results in the formation of a novel rhombic channel; this is an interesting feature of compound **2**. Figure 5 demonstrates the formation of the channel; two sides of the rhombus are formed by hydrogen bonds through coordinated water molecules, and the other two sides are constructed from 4,4′-bpy ligands. As the Cu(3)(4,4′-bpy)$(H_2O)_4$ independent unit extends to a one-dimensional chain, the rhombus extends to be a rhombic channel. This channel is parallel to the crystallographic *c* axis, the channel size is ca. 11 Å × 11 Å. Noncoordinated water molecule O(04) lies in the channel, and the other water molecules occupy the space around the channel. The 4,4′-bpy in **2** also displays flexibility; the pyridine rings of 4,4′-bpy twist by 12.9° in the dimer and 28.0° in the one-dimensional chain.

These two compounds both contain two kinds of coordination modes, distorted octahedron and distorted trigonal bipyramid. The coordination environment of 5-coordinate Cu(II) in **2** is very similar to that of **1**, but the situation of octahedrally coordinated Cu(II) [Cu(1) of **1** and Cu(3) of **2**] is different. Besides two N atoms, there are two water molecules and two oxygen atoms of carboxylate coordinated to Cu(1) of **1** while there are four water molecules coordinated to Cu(3) of **2**. Water oxygen atoms are terminally coordinated to copper, so cations are afforded in a one-dimensional array in **2**, which results in the formation of a dimer anion; but in **1**, due to the bridging function of the carboxylate ligand coordinated to Cu(1), a 2D network is found. The coordination of solvent (water) molecules can influence the specific framework structure that is formed, this in accord with the results of $[Zn(4,4'\text{-bpy})_2(H_2O)_2]SiF_6$ and $[Zn(4,4'\text{-bpy})_2(SiF_6)n]\cdot DMF$.[6a,7]

Additionally, both compounds **1** and **2** have rhombic channels, but there are three different points: (a) the channels in **1** are made up of covalent bonds, and the channels in **2** are constructed from both hydrogen bonds and covalent bonds; (b) each channel in **1** is derived from a helical chain while that of **2** is formed through the shifting of the rhombus; (c) each sectional rhombus of the channel in **1** has four copper atoms, but each sectional rhombus of the channel in **2** contains six copper atoms. The channel size in **1** is ca. 4 Å × 8 Å, and the channel size in **2** is ca. 11 Å × 11 Å.

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Supporting Information Available: X-ray crystallographic files in CIF format for the structure determination of complexes $[Cu_3(NTA)_2(4,4'\text{-bpy})_2(H_2O)_2]\cdot 9H_2O$ and $[\{Cu(4,4'\text{-bpy})(H_2O)_4\}\{Cu_2(NTA)_2(4,4'\text{-bpy})\}]\cdot 7H_2O$ are available. This material is available free of charge via the Internet at http://pubs.acs.org.

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