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3D Coordination Polymers with Nitrilotriacetic and 4,4′-Bipyridyl Mixed Ligands: Structural Variation Based on Dinuclear or Tetranuclear Subunits Assisted by Na–O and/or O–H···O Interactions

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The reactions of Cu(II) with the mixed nitrilotriacetic acid (H_3NTA) and 4,4′-bipyridyl (4,4′-bpy) ligands in different metal-to-ligand ratios in the presence of NaOH and $NaClO_4$ afforded two complexes, $Na_3[Cu_2(NTA)_2(4,4'\text{-bpy})]ClO_4\cdot 5H_2O$ (**1**) and $[Cu_2(NTA)(4,4'\text{-bpy})_2]ClO_4\cdot 4H_2O$ (**2**). The two complexes have been characterized by elemental analysis, IR, XRD, and single-crystal X-ray diffraction. **1** contains a basic doubly negatively charged $[Cu_2(NTA)_2(4,4'\text{-bpy})]^{2-}$ dinuclear unit which was further assembled via multiple Na–O and O–H···O interactions into a three-dimensional (3D) pillared-layer structure. **2** features a two-dimensional (2D) undulated brick-wall architecture containing a basic doubly positively charged $[Cu_4(NTA)_2(4,4'\text{-bpy})_2]^{2+}$ tetranuclear unit. The 2D network possesses large cavities hosting guest molecules and was further assembled via O–H···O hydrogen bonds into a 3D structure with several channels running in different directions.

Introduction

Pronounced interest has recently been focused on the synthesis and characterization of coordination polymers with polydentate ligands due to their relevance to coordination supramolecular chemistry, functional solid material, structural topology, and their potential applications.[1] The network topologies of diversified coordination polymers based on the molecular building blocks are usually dictated by the coordination geometry of the central metal ion and the choice of the organic ligands. However, a number of subtle factors, such as solvent, template, concentration, temperature, counteranion, etc., also play important roles to affect the structural topology of the final product. As a simple but principal synthetic strategy, controlling the topology of coordination complexes through varying the stoichiometry of metal to ligand is still challenging,[2] not only due to the possible variation of building blocks, but also due to the influence of weak supramolecular interactions, such as hydrogen bonding and electrostatic interactions.

Among the numerous ligands employed in this area, by far the most prevalent is the rigid linear connector 4,4′-bipyridyl (4,4′-bpy) or analogues, owing to their ditopic bridging[3] or monodentate coordination mode,[4] which participate in constructing various metal–bipyridyl-type subunits for self-assembly of 1D linear[5] or zigzag-like[6] chain, 2D square grid[7] or interwoven honeycomb,[8] or 3D diamondoid[9] frameworks. On the other hand, 4,4′-bpy is one of the common ligands used to form mixed-ligand complexes[10] with specific configurations. Recently, either rigid[11] or flexible[12] polycarboxylate ligands have been used in combination with

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4,4′-bpy to obtain various extended frameworks of coordination polymers, many of which show potential for functional materials. We have been interested in constructing different building blocks with tripodal ligands[13] or bipyridyl-type linear ligands[14] for the purpose of assembling structurally defined supramolecular ensembles from discrete zero dimension to polymeric multiple dimensions. In this paper, we are trying to use the simple system of nitrilotriacetic acid (H_3NTA) and copper(II) ion, by varying the amount of the auxiliary ligand (4,4′-bpy), to explore the formation of the multidimensional frameworks of coordinating polymers assisted by supramolecular interactions. Two compounds, $Na_3[Cu_2(NTA)_2(4,4'\text{-bpy})]ClO_4\cdot 5H_2O$ (**1**) and $[Cu_2(NTA)(4,4'\text{-bpy})_2]ClO_4\cdot 4H_2O$ (**2**), were obtained by controlling the stoichiometry of metal to ligand, which results in the change of the building block from a dinuclear to a tetranuclear unit, and leads to the 3D topologically structural variation assisted by Na−O and/or O−H···O interactions.

Experimental Section

All chemicals were commercial products of reagent grade and used without further purification. Infrared spectra were recorded on a Bruker EQUINOX55 FT-IR spectrophotometer in the range of 4000−400 cm^{-1} using KBr pellets. Elemental analyses were performed on a Perkin-Elmer 240C elemental analyzer. The XRD pattern was recorded on a D/Max-IIIA diffractometer with Cu Kα radiation ($\lambda = 1.540\,56$ Å) at a scanning rate of 1° min^{-1} with 2θ ranging from 5° to 60°.

Synthesis of $Na_3[Cu_2(NTA)_2(4,4'\text{-bpy})]ClO_4\cdot 5H_2O$ (1). A mixture of H_3NTA (0.192 g, 1.0 mmol) and NaOH (0.12 g, 3.0 mmol) dissolved in 2 mL of distilled water was added to an aqueous solution (5 mL) of $CuSO_4\cdot 5H_2O$ (0.25 g, 1.0 mmol) with stirring for 20 min at room temperature. Then 4,4′-bpy (0.096 g, 0.5 mmol) dissolved in 2 mL of methanol was added. The solution was refluxed for 3 h. At the end of the reaction, $NaClO_4$ (0.14 g) dissolved in 2 mL of distilled water was added, and the resulting mixture was stirred for 10 min and filtered. Slow evaporation of the clear filtrate at room temperature yielded dark blue block crystals in three weeks. Yield: 35.7% (on a copper basis). Anal. Calcd for $C_{22}H_{30}ClCu_2Na_3N_4O_{21}$: C, 28.80; H, 3.27; N, 6.10%; Found: C, 29.10; H, 3.44; N, 6.21%. IR (KBr pellet, cm^{-1}): 3443b, 1610vs, 1492w, 1449w, 1403s, 1323w, 1221w, 1116s, 920m, 823w, 738m, 651w, 627m, 538w, 502w.

Synthesis of $[Cu_2(NTA)(4,4'\text{-bpy})_2]ClO_4\cdot 4H_2O$ (2). The reaction was carried out in the same way as for **1** except that twice the amount of 4,4′-bpy (0.192 g, 1.0 mmol) was used. Dark blue column crystals of **2** were obtained in four weeks. Yield: 46.1% (on a copper basis). Anal. Calcd for $C_{26}H_{30}ClCu_2N_5O_{14}$: C, 39.0; H, 3.75; N, 8.76%; Found: C, 38.63; H, 3.64; N, 8.77%. IR (KBr pellet, cm^{-1}): 3344b, 1613vs, 1492w, 1420s, 1386m, 1223w, 1080s, 912w, 819m, 733w, 644w, 623m, 575w, 515w.

***CAUTION*!** Perchlorate salts of metal complexes are potentially explosive and should be handled with great care.

X-ray Crystallography. Single crystals of **1** and **2** with suitable dimensions were mounted onto thin glass fibers. All the intensity data were collected at 293 K on a Bruker SMART 1K CCD diffractometer (Mo Kα radiation, $\lambda = 0.710\,73$ Å) in φ and ω scan modes. Structures were solved by the direct method followed by difference Fourier syntheses, and then refined by full-matrix least squares refinement on F^2 using SHELXTL.[15] All the non-hydrogen atoms were refined with anisotropic parameters while H atoms were placed in calculated positions and refined using a riding model. Crystallographic data and refinements parameters are presented in Table S1 (Supporting Information). The selected atomic distances and bond angles of **1** and **2** are listed in Tables 1 and 2, respectively. The CCDC reference numbers are 258219 for **1** and 258220 for **2**.

Results and Discussion

Synthesis and Characterization. Complexes **1** and **2** were synthesized by similar procedures. When the molar ratio of metal to ligands (Cu:NTA:4,4′-bpy) was kept at 2:2:1, the dinuclear $[Cu_2(NTA)_2(4,4'\text{-bpy})]^{2-}$ subunit of **1** was formed. When the amount of 4,4′-bpy was increased (Cu:NTA:4,4′-bpy = 2:2:2), NTA became a bridging ligand which linked two different copper(II) ions and led to formation of a tetranuclear $[Cu_4(NTA)_2(4,4'\text{-bpy})_4]^{2+}$ subunit of **2**. It is obvious that the stronger coordinating auxiliary ligand 4,4′-bpy facilitates the structural change by altering the coordination mode of NTA ligand although NTA is in excess in the

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Table 1. Selected Atomic Distances(Å) and Bond Angle-(deg) for **1**[a]

Cu(1)−O(1)	2.130(2)	Cu(2)−O(4)	2.144(2)		
Cu(1)−O(2)	1.968(2)	Cu(2)−O(5)	2.002(2)		
Cu(1)−O(3)	1.981(2)	Cu(2)−O(6)	1.986(2)		
Cu(1)−N(1)	1.977(2)	Cu(2)−N(2)	1.969(3)		
Cu(1)−N(3)	2.022(2)	Cu(2)−N(4)	2.001(2)		
Na(1)−O(2w)	2.355(4)	Na(2)−O(1w)	2.389(3)	Na(3)−O(8)	2.545(3)
Na(1)−O(3w)	2.298(3)	Na(2)−O(4w)	2.395(3)	Na(3)−O(9)	2.475(3)
Na(1)−O(6)	2.669(3)	Na(2)−O(4w)#1	2.416(3)	Na(3)−O(10)	2.370(3)
Na(1)−O(11)	2.352(3)	Na(2)−O(9)	2.357(2)	Na(3)−O(11)	2.304(3)
Na(1)−O(12)	2.509(3)	Na(2)−O(10)	2.534(3)	Na(3)−O(12)	2.333(3)
Na(1)−O(16)	2.607(4)	Na(2)−O(13)	2.511(5)		

N(1)−Cu(1)−O(1)	100.02(10)	N(2)−Cu(2)−O(4)	94.81(10)
N(1)−Cu(1)−O(2)	95.94(10)	N(2)−Cu(2)−O(5)	96.81(10)
N(1)−Cu(1)−O(3)	95.53(9)	N(2)−Cu(2)−O(6)	97.40(10)
N(1)−Cu(1)−N(3)	177.87(10)	N(2)−Cu(1)−N(4)	175.47(11)

[a] Symmetry transformations used to generate equivalent atoms: #1 = $x + {}^{1}/_{2}$, $y + {}^{1}/_{2}$, z.

Table 2. Selected Atomic Distances (Å) and Bond Angles (deg) for **2**[a]

Cu(1)−O(1)	1.944(2)	Cu(2)−O(6)	2.012(2)
Cu(1)−O(3)	1.943(2)	Cu(2)−O(7)	2.333(3)
Cu(1)−O(5)	2.236(2)	Cu(2)−N(2)#1	2.028(2)
Cu(1)−N(1)	1.981(2)	Cu(2)−N(3)	2.014(2)
Cu(1)−N(5)	2.034(2)	Cu(2)−N(4)#2	2.036(2)
		Cu(2)−O(5)	2.534(2)

N(1)−Cu(1)−O(1)	97.71(9)	N(3)−Cu(2)−O(6)	89.19(8)
N(1)−Cu(1)−O(3)	94.88(9)	N(3)−Cu(2)−O(7)	92.66(9)
N(1)−Cu(1)−O(5)	88.38(9)	N(3)−Cu(2)−N(2)#1	90.46(10)
N(1)−Cu(1)−N(5)	171.53(10)	N(3)−Cu(1)−N(4)#2	175.82(10)

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

reaction system. The yield of **1** is relatively lower than that of **2** probably due to its better solubility in water. The IR spectra of complex **1** and **2** show the characteristic absorptions for the NTA anion. The strong bands at 1610, 1403 cm^{-1} for **1** and 1613, 1420 cm^{-1} for **2** are assigned to the ν_{as} vibration and the ν_s vibration of CO_2^-, respectively. The presence of water in the two complexes can be confirmed by the appearance of a broad band around 3400 cm^{-1} (ν_{O-H}). The strong stretching vibrations at 1080, 623 cm^{-1} for **1** and 1116, 627 cm^{-1} for **2**, respectively, are characteristic of ClO_4^- anion.

Crystal Structure. In complex **1**, the asymmetric unit is composed of three Na^+ ions, two Cu^{2+} cations, two NTA^{3-} anions, one 4,4′-bpy, one ClO_4^- anion, and five water molecules. The two NTA molecules display the same tripodal coordination mode providing an O_3N environment to seize the copper(II) atoms, resulting in a slightly distorted trigonal bipyramid coordination geometry for both of the copper(II) atoms which are bridged by the 4,4′-bpy spacer as shown in Figure 1. Each trigonal bipyramid is completed by three O atoms (O(1), O(2), and O(3) for Cu(1) or O(4), O(5), and O(6) for Cu(2)) from NTA as the trigonal plane, and two N atoms (N(3) or N(4) from NTA and N(1) or N(2) from 4,4′-bpy) as the apexes. The spacer 4,4′-bpy which links Cu(1) and Cu(2) atoms with a Cu···Cu separation of 10.982 Å exhibits some flexibility with the two pyridyl rings twisted by 14.7°. The dinuclear anion $[Cu_2(NTA)_2(4,4'\text{-bpy})]^{2-}$ has been previously observed in a polymeric complex, $\{[Cu(4,4'\text{-bipy})(H_2O)_4][Cu_2(NTA)_2(4,4'\text{-bipy})]\}\cdot 7H_2O$.[12c] In the present case, the negative charges of the dinuclear anion are balanced by Na^+ ions other than a 1D cationic polymer in the above complex;[12c] therefore, a completely different 3D architecture is generated. All five water molecules in **1** are involved in formation of multiple intra- or intermolecular O···H−O hydrogen bonds which are summarized in Table 3. If the Na^+ ions are ignored, the coordination dinuclear unit can be regarded to be connected by these O−H···O hydrogen bonds into a 2D layered structure. As shown in Figure 2, a 1D hydrogen bonded ribbon structure is formed along the *b* axis in which four water molecules and the ClO_4^- anion are involved. Such ribbons are further linked via the fifth water molecule to give 2D layers which stack up to constitute the crystal lattice. However, this is not the full story of **1** since Na^+ ions also play an important role in crystal packing.

Figure 3 shows the first-order sphere around Na^+ ions which are closely surrounded by O atoms from NTA^{3-}, solvated water, and ClO_4^- anions. Six Na atoms are connected with twenty-four O atoms leading to an apparent $[Na_6O_{24}]$ cluster, which possesses an inversion center with only half of the atoms being crystallographically independent. The Na−O distances are listed in Table 1, indicating the strong Na−O electrostatic interactions which sometimes were also considered as coordination bonds in the literature.[16] The Na1 ion lies in the distorted octahedral geometry consisting of three O atoms (O6, O11, and O12) from NTA, one O atom (O16) from ClO_4^- anion, and two O atoms (O2w and O3w) from water solvates. The same distorted octahedral geometry of Na2 is formed by two O atoms (O9 and O10) from another NTA, one O atom (O13) from another ClO_4^-, and three water O atoms (O1w, O4w, and O4w′). The Na3 ion coordinates to five O atoms (O8, O9, O10, O11, and O12) from two NTA anions, displaying the distorted trigonal bipyramidal geometry. Six inversion center symmetry related Na polyhedra share edges to form the $[Na_6O_{24}]$ cluster as depicted in Figure 3. Such $[Na_6O_{24}]$ clusters are bridged by four ClO_4^- anions to the neighboring $[Na_6O_{24}]$ clusters, giving the 2D extended layer as shown in Figure S1 (Supporting Information). Therefore, **1** is actually a pillared-

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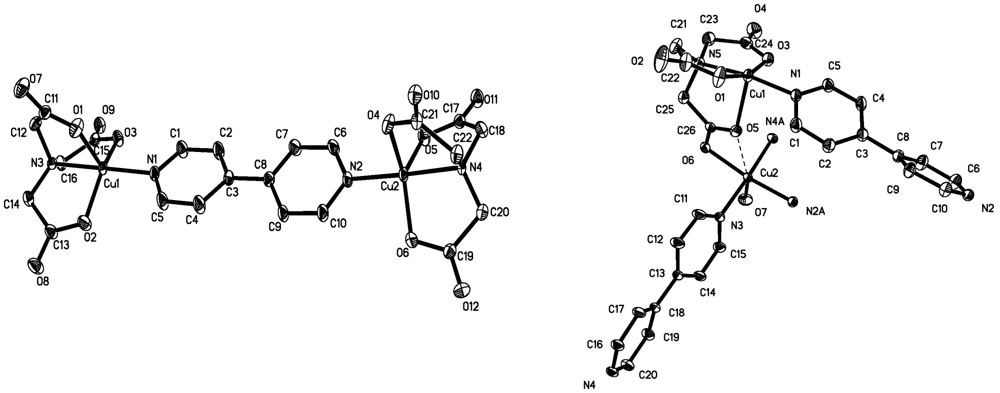

Figure 1. View of the asymmetric unit in **1** (left) and **2** (right) showing the coordination environment of copper atoms.

Table 3. Geometry Parameters for Hydrogen Bonds in **1**[a]

D−H···A	d(D−H)	d(H···A)	∠DHA	d(D···A)
O2W−H2D···O5W	0.86	1.98	152	2.76
O3W−H3D···O7[b]	0.87	1.91	178	2.77
O3W−H3C···O7[c]	0.86	2.00	157	2.81
O1W−H1D···O10[b]	0.84	2.05	172	2.89
O1W−H1C···O15[b]	0.84	2.09	156	2.88
O2W−H2C···O1[c]	0.85	2.02	150	2.79
O4W−H4C···O4[d]	0.85	1.97	170	2.81
O4W−H4D···O8[e]	0.85	1.91	172	2.75
O5W−H5D···O3[f]	0.87	1.98	174	2.84
O5W−H5C···O8[g]	0.88	1.91	174	2.79

[a] Distances in angstroms and angles in degrees. [b−g] Symmetry transformations used to generate equivalent atoms: $b = -x + 2, -y - 1, -z + 1$; $c = x, -y - 1, z + {}^1/_2$; $d = x + {}^1/_2, y + {}^1/_2, z$; $e = -x + {}^5/_2, -y - {}^3/_2, -z + 1$; $f = -x + 2, y, -z + {}^3/_2$; $g = -x + 2, y + 1, -z + {}^3/_2$.

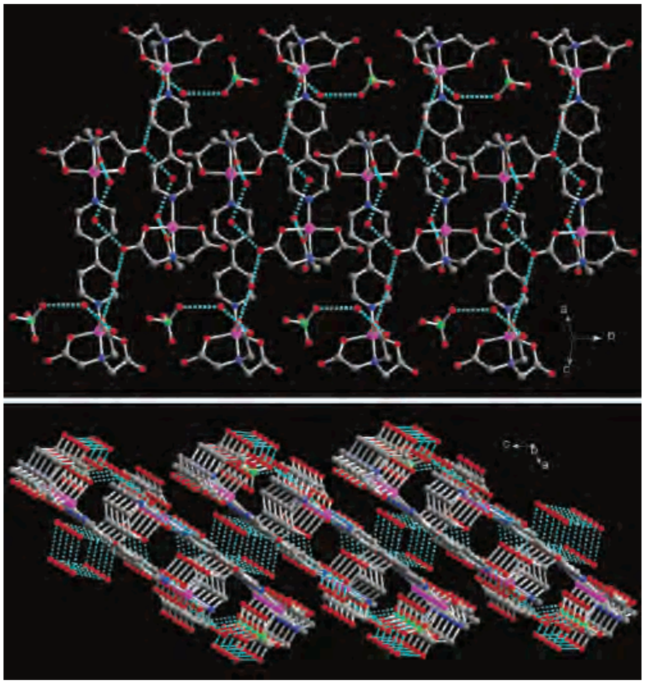

Figure 2. View ofthe O−H···O hydrogen bonds in **1**: 1D hydrogen bonded ribbon structure in the *b* direction (top) and 2D layered structure in the (010) plane (bottom). H atoms are omitted for clarity, and the hydrogen bonds are represented by broken lines.

layer structure,[17] as shown in Figure 4, composed of inorganic layers of coordination Cu and Na atoms and organic pillars of 4,4′-bpy spacers. The separation between the layers is about 17 Å, and the whole crystal packing is stabilized by strong Na−O interactions and multiple O−H···O hydrogen bonds.

For complex **2**, the asymmetric unit is composed of two Cu^{2+} cations, one NTA^{3-} anion, two 4,4′-bpy, ClO_4^- anion, and four water molecules. Figure 1 demonstrates the coordinate environments of two crystallographically independent Cu atoms which show significantly different coordination geometry. Cu(1) is five coordinated similar to that in **1**, but the coordination geometry has been changed from trigonal bipyramidal to square pyramidal which is completed by three O atoms [O(1), O(3), O(5)] of NTA, one N atom [N(5)] of NTA, and one N atom [N(1)] of 4,4′-bpy. The O(1), O(3), N(1), and N(5) atoms comprise the basal plane while the O(5) atom occupies the apical position. By contrast, Cu(2) is six bonded to three N atoms from three different 4,4′-bpy spacers, two O atoms from one NTA, and one water molecule. Three N atoms and O(6) comprise the equatorial plane while O(5) and O(7) atoms lie in the axial positions with elongated bond distances (2.534(2) and 2.333(3) Å) due to the Jahn−Teller effect. Compared with complex **1**, Cu(1) in **2** is not only linked to Cu(2) through 4,4′-bpy with a Cu(1)···Cu(2) separation of 11.128 Å but also bridged to another crystallographically equivalent Cu(2) via one carboxylate arm of NTA with a Cu(1)···Cu(2) separation of 4.607 Å. Therefore, the NTA displays a tripodal coordination mode toward Cu(1) while it displays a chelating coordination mode toward Cu(2) and bridges two Cu atoms via one carboxylate group, acting as a hexadentate ligand. Thus, a dicationic tetranuclear subunit, $[Cu_4(NTA)_2(4,4'\text{-bpy})_2]^{2+}$, has been generated as shown in Figure 5.

The cyclic tetranuclear units are connected with each other via the second type of 4,4′-bpy to give a 2D undulated network. For simplicity, we can consider that the propagation of the second type of 4,4′-bpy spacers from the basic tetranuclear unit in opposite directions leads to a 1D ladder structure[5a,18] as depicted in Figure 6. The cyclic tetranuclear units act as the rungs of the ladders, resulting in a cavity of 12 × 22 Å dimensions (Cu···Cu separation). Several water

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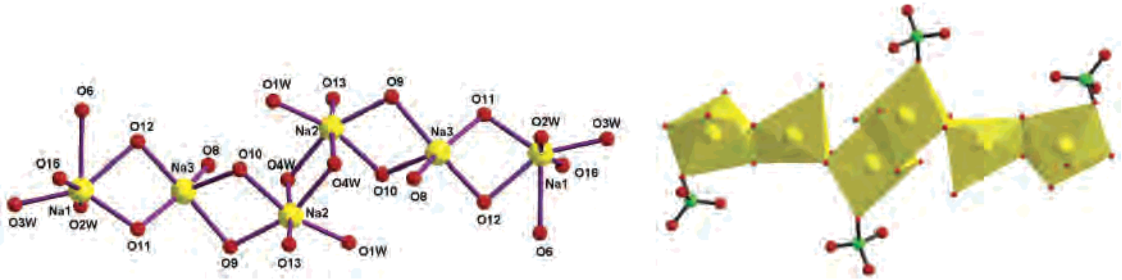

Figure 3. [Na_6O_{24}] cluster formed in **1**: Na−O connectivity (left) and coordination sphere of Na^+ ions shown in the polyhedral mode (right).

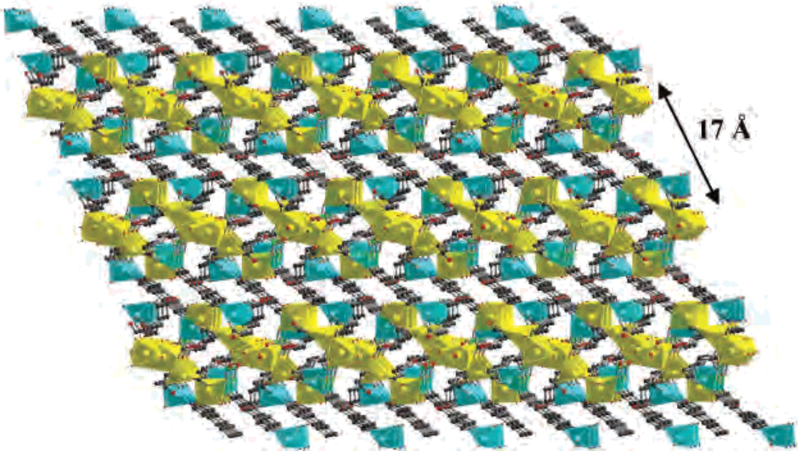

Figure 4. 3D pillared-layer structure of **1**. H atoms are omitted for clarity, and metal ions are represented by polyhedra (Cu in cyan and Na in yellow).

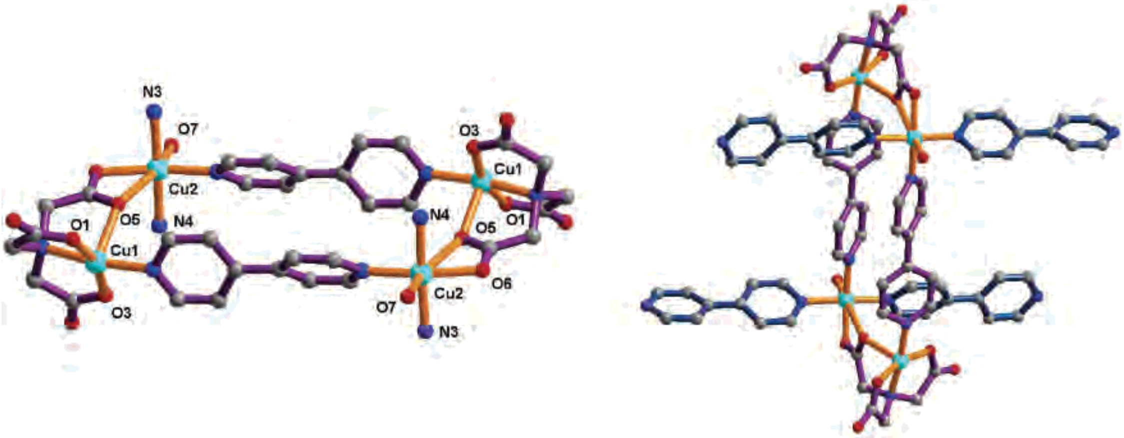

Figure 5. Representation of the tetranuclear subunit of **2**: cyclic [$Cu_4(NTA)_2(4,4'\text{-bpy})_2]^{2+}$ (left) and propagation via additional 4,4′-bpy spacers (right).

molecules and ClO_4^- anions are accommodated inside the cavity and fixed by hydrogen bonding formation. Such ladders are fused along the side rails, resulting in a 2D network with brick-wall topology as shown in Figure 7. This kind of brick-wall network containing cyclic rungs is unusual because the "T-shaped" joints consist of different spacers: two linear 4,4′-bpy and one cyclic tetranuclear unit, in good comparison to the common "T-shaped" building blocks comprising the uniform 2D brick-wall networks,[19] and those containing weak ligand-unsupported metal−metal interactions.[20,21] With the small metallacycles as one side, such a nonuniform brick-wall structure may endow the following advantages: (a) potential functionization of the network itself, (b) leaving cavities inside the network, and (c) avoiding interpenetration effectively.

It is noteworthy that various O−H···O hydrogen bonds are formed involving oxygen atoms from NTA anions, the ClO_4^-, anions and water solvates, which are summarized in Table 4. As shown in Figure S2 (Supporting Information), oxygen atoms which are hydrogen bonded form an extended

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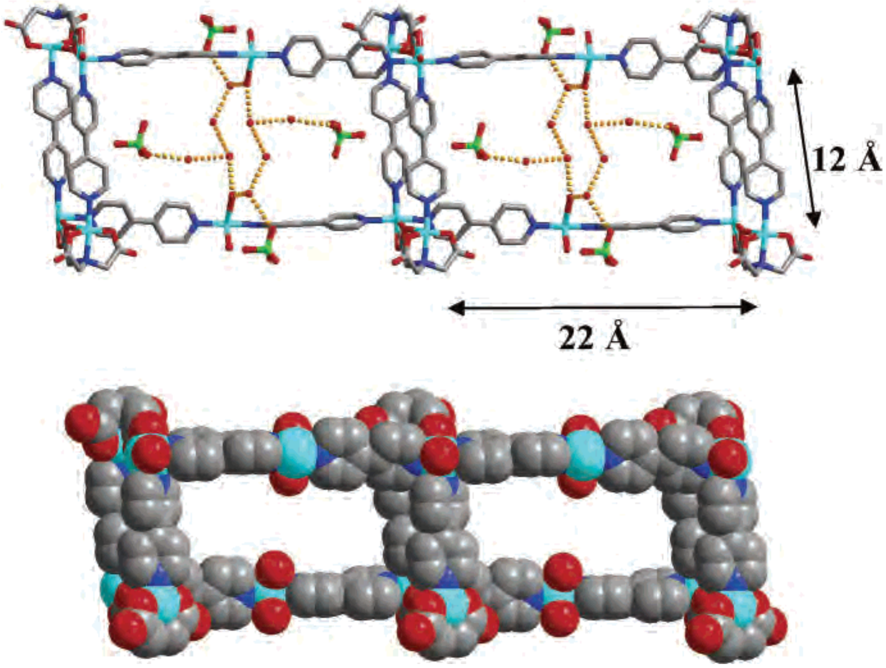

Figure 6. Representation of the ladder structure containing cyclic tetranuclear rungs in **2**: stick mode with hydrogen bonded guest molecules (left) and space-filling mode (right) showing inner cavities.

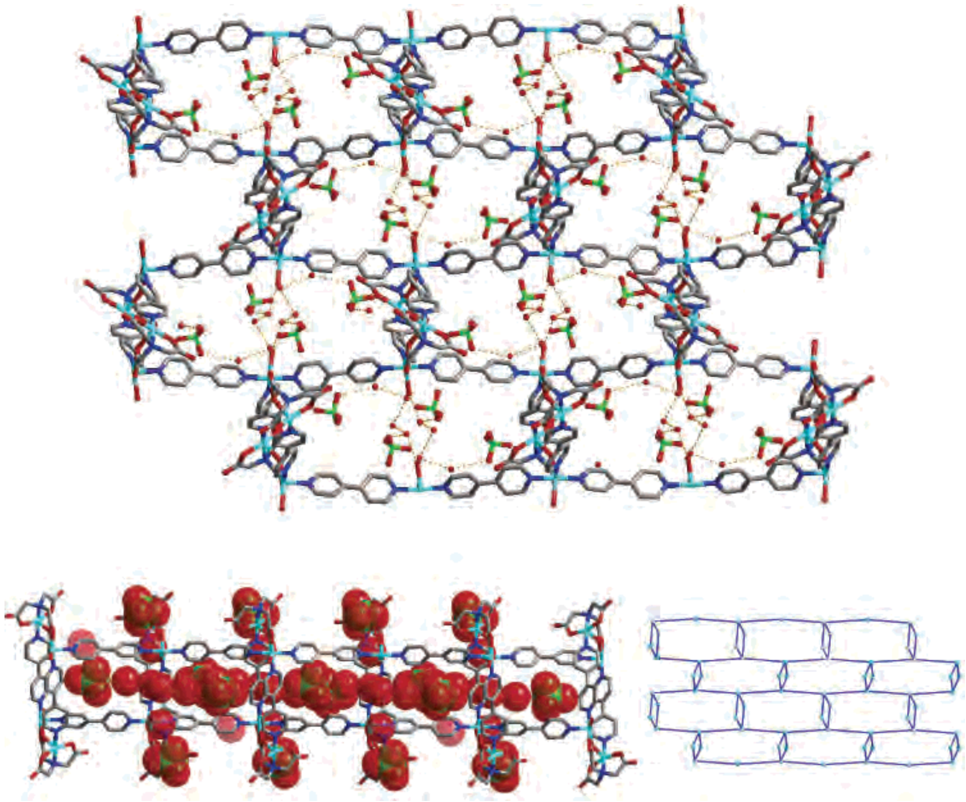

Figure 7. Perspective (top) or side (bottom left) view of the 2D brick-wall structure of **2** hosting water and counteranion molecules, and the schematic representation of the brick-wall backbone containing cyclic rungs (bottom right).

1D array containing alternating eight-membered and 12-membered rings. Such arrays run through the cavities formed within the 2D networks to generate the 3D hydrogen bonded framework. If viewed from different directions, several channels can be found, suggesting that the 3D framework is porous, but not empty. Two kinds of 4,4′-bpy in **2** exhibit different flexibility: one with the pyridine rings twisted by 40.9° and the other with the pyridine rings twisted by only 18.2°.

From the above discussion we can see that changing the amount of the auxiliary 4,4′-bpy can dramatically alter the coordination behavior between NTA and copper(II) ions, both the coordination mode of NTA and the coordination geometry of copper(II). In complex **1**, two 4,4′-bpy bridged

Table 4. Geometry Parameters for Hydrogen Bonds in **2**[a]

D−H···A	d(D−H)	d(H···A)	∠DHA	d(D···A)
O7−H7D···O12[b]	0.83	1.98	173	2.80
O13−H13C···O4	0.82	1.90	172	2.71
O7−H7C···O14	0.85	1.92	170	2.76
O14−H14C···O13[c]	0.82	1.99	161	2.78
O12−H12D···O2	0.85	2.07	137	2.75
O12−H12C···O9[d]	0.84	2.14	166	2.96
O14−H14D···O2[e]	0.82	2.05	157	2.83
O13−H13D···O11[e]	0.83	2.46	143	3.16

[a] Distances in angstroms and angles in degrees. [b−e] Symmetry transformations used to generate equivalent atoms: $b = x + {}^{1}/_{2}, -y + {}^{1}/_{2}, z + {}^{1}/_{2}$; $c = x + 1, y, z$; $d = -x - 1, -y, -z + 1$; $e = -x + {}^{1}/_{2}, y + {}^{1}/_{2}, -z + {}^{3}/_{2}$.

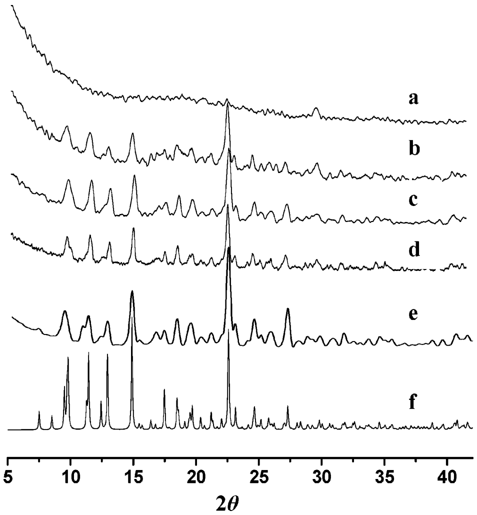

Figure 8. Powder X-ray pattern of **2** after heat treatment at 250 °C (a), 200 °C (b), 150 °C (c), 100 °C (d), and 25 °C (e) and simulation based on the single-crystal analysis (f).

Cu atoms are coordinated with two tripodal tetradentate NTA ligands. The strong electrostatic interactions of Na−O and hydrogen bonding interactions of O−H···O play important roles in dictating the 3D architecture but have no remarkable influence on the coordination mode of NTA. The dinuclear $[Cu_2(NTA)_2(4,4'\text{-bpy})]^{2-}$ remains the same as found in the polymeric complex $\{[Cu(4,4'\text{-bipy})(H_2O)_4][Cu_2(NTA)_2(4,4'\text{-bipy})]\}\cdot 7H_2O$.[12c] By contrast, with addition of one more 4,4′-bpy ligand in **2** the dinuclear unit in **1** has been changed to a tetranuclear unit. The NTA exhibits a tripodal−chelating−bridging coordination mode acting as a hexadentate ligand, showing the common versatility of the polycarboxylate ligands.[10,11] Two kinds of 4,4′-bpy ligands play different roles to generate an unusual 2D brick-wall network containing cyclic tetranuclear sides.

Thermal Stability. The X-ray single-crystal structural analysis indicates that open cavities in **2** are occupied by guest H_2O molecules and counteranions. The powder X-ray diffraction measurement of the bulk as-prepared product gives a reasonable XRD pattern (Figure 8) which closely matches the simulated one from the single-crystal data, indicating that such a brick-wall structure can be quantitatively constructed in pure phase. To investigate the robustness and thermal stability of such a porous framework, a TGA study combined with powder XRD pattern recorded at elevated temperature was carried out to elucidate framework integrity upon removal of the solvent guest molecules. The TGA curve shows a gradual weight loss (about 9%) before 200 °C, corresponding to the loss of four H_2O molecules. The framework starts to decompose after 200 °C, which is indicated by two consecutive main weight losses in the ranges 228−236 and 262−290 °C, followed by a slow weight loss between 300 and 450 °C. Figure 8 demonstrates the XRD patterns of the as-prepared product of **2** calcined at 100, 150, 200, and 250 °C for 1 h, respectively. It is clear that the diffraction profiles of the samples heated to 100 and 150 °C are almost the same as that of the as-prepared sample with slight intensity variation. The XRD pattern recorded at 200 °C shows noticeable intensity decrease, but all the salient peaks still match the simulated ones, indicating that the porous framework is maintained after guest removal. Increasing the temperature to 250 °C results in the formation of an amorphous solid as illustrated by the absence of peaks in the XRD pattern, consistent with the result of TGA that the framework collapses after 200 °C.

Conclusion

The effect of the stoichiometry of metal to ligands on the framework of coordination polymers has been investigated by changing the amount of the auxiliary ligands. The coordination flexible NTA ligand facilitates formation of different building blocks with the presence of different amount of 4,4′-bpy ligand. A pillared-layer architecture based on anionic $[Cu_2(NTA)_2(4,4'\text{-bpy})]^{2-}$ dinuclear unit has been obtained, in which the 3D framework is sustained by Na−O electrostatic interactions and O−H···O hydrogen bonding. With addition of 4,4′-bpy ligand a brick-wall network based on a cationic $[Cu_4(NTA)_2(4,4'\text{-bpy})_2]^{2+}$ tetranuclear unit has been constructed. The brick-wall network possesses large cavities hosting small guest molecules, and multiple O−H···O hydrogen bonds are formed between the 2D networks which direct the packing of the 2D networks allowing several cross-running channels in the crystal lattice. The TGA study indicated that the porous framework is stable upon heating to 200 °C.

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Supporting Information Available: Crystallographic data in CIF format, table of crystallographic data for **1** and **2**, views of the 2D layer formed by $[Na_6O_{24}]$ clusters in **1**, and 3D infinite framework sustained by O−H···O hydrogen bonds in **2**.

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