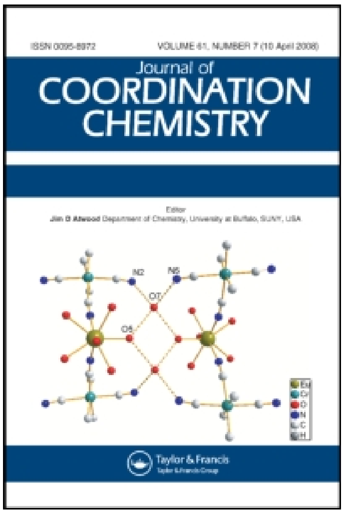

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Synthesis and characterization of two temperature-dependent copper(II) complexes based on 2,6-dimethylpyridine-3,5-dicarboxylate

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Synthesis and characterization of two temperature-dependent copper(II) complexes based on 2,6-dimethylpyridine-3,5-dicarboxylate

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Two temperature-dependent Cu(II) compounds, $[Cu(mpdaH)_2(H_2O)_4]\cdot 4H_2O$ (**1**) and $[Cu(mpdaH)_2]_n$ (**2**) ($H_2mpda = $ 2,6-dimethylpyridine-3,5-dicarboxylic acid), have been synthesized under hydrothermal conditions and characterized by X-ray single crystal diffraction, elemental analysis, thermogravimetric analyses, and IR spectra. The structure at room temperature confirms that **1** is mononuclear with the octahedral coordination geometry. However, on warming to 120°C the same reaction gives **2**, in which copper(II) has square planar coordination and is further bridged by $mpdaH^-$ ligands to form extended 2-D layers with parallelogram-like (4,4) topology. Furthermore, in both complexes, through π–π stacking and hydrogen bonding interactions, 3-D supramolecular networks are assembled.

Keywords: Temperature dependence; Crystal structures; Cu(II) complexes; 2,6-Dimethylpyridine-3,5-dicarboxylic acid

1. Introduction

Recent years have witnessed an explosion in the synthesis of metal-organic hybrid frameworks (MOFs) with different topologies, exploiting the bridging potential of different organic linkers and geometry of the metal ions [1, 2]. Hybrid solids with different topology and dimensionality constructed from the same building units provide versatile functionality [3, 4]. For the desired framework and functionality in a hybrid solid, it is important to control and understand the external factors such as temperature, pH, and solvent that govern the crystallization process and the stability of the overall crystals [3–7]. Forster *et al.* reported temperature controlled dimensionality and topology in a cobalt succinate system [6]. Later, Stock *et al.* [9], Pan *et al.* [8], and others showed that high reaction temperature and pH increase the dimensionality and

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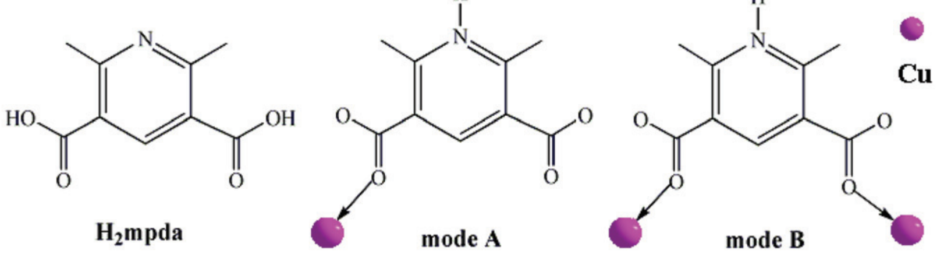
formation of M–O–M linkages [5, 7]. Multidentate N- or O-donor pyridine dicarboxylic acids, such as pyridine-2,3(5,6)-dicarboxylic acids, have been shown to be good building blocks for metal-organic materials with desired topologies, because they have two pH-dependent abstractable protons and five donor sites which can be exploited for synthesis of a variety of metal-organic frameworks through a number of binding modes. They can adopt terminal monodentate, chelating to one metal center, bridging bidentate in a *syn–syn*, *syn–anti*, and *anti–anti* configuration to two metal centers, and supramolecular hydrogen bonding and $\pi\cdots\pi$ interactions [10]. MOFs such as 1-D chains and ladders [11], 2-D grids [12], 3-D microporous networks [13], interpenetrated modes [14], and helical staircase networks [15] have been documented. In contrast, 2,6-dimethylpyrazine-3,5-dicarboxylic acid (scheme 1), a member of pyridine dicarboxylic acid family containing N- and O-donors, is rarely used [16]. In this article, we report hydrothermal syntheses and crystal structures of two temperature-dependent 2-D polymeric complexes $[Cu(mpdaH)_2(H_2O)_4]\cdot4H_2O$ (**1**) and $[Cu(mpdaH)_2]_n$ (**2**) (H_2mpda = 2,6-dimethylpyridine-3,5-dicarboxylic acid).

2. Experimental

All materials were of reagent grade, obtained from commercial sources and used without purification. Elemental analyses were performed on a Perkin–Elmer 240C analytical instrument. The metal analysis was performed on an ICP AES Liberty Series II Varian apparatus. IR spectra from 4000–400 cm^{-1} were measured with a Thermo Nicolet 320 FT-IR spectrometer using KBr discs. Thermal analyses (under nitrogen, heating rate 5°C min^{-1}) were carried out in a Labsys NETZSCH TG 209 Setaram apparatus.

A mixture of H_2mpda (0.098 g, 0.5 mmol), $Cu(ClO_4)_2\cdot6H_2O$ (0.185 g, 0.50 mmol) and H_2O (15 mL) was placed in a 25 mL Teflon-lined stainless steel vessel and heated to 80°C for 3 days. Slowly cooling to room temperature at a rate of 0.5°C min^{-1} gave pale blue block crystals suitable for single crystal X-ray diffraction analyses with a yield of 51% (based on Cu). Found: C, 38.46; H, 5.45; N, 4.83; Cu, 10.62. $C_{18}H_{32}N_2O_{16}Cu$ Calcd: C, 38.60; H, 5.37; N, 4.70; Cu, 10.74%. Selected IR data (KBr, cm^{-1}): 3439(br), 1645(s), 1595(s), 1412(m), 1385(s), 1345(s), 1196(m), 1124(w), 1060(w), 1029(w), 932(w), 794(w), 746(m).

The same reaction as for **1** was heated to 140°C for 3 days and then slowly cooled to room temperature at a rate of 0.5°C min^{-1}. Blue block crystals suitable for single crystal



Scheme 1. Diagram of ligand 2,6-dimethylpyridine-3,5-dicarboxylic acid (**H_2mpda**) and its two coordination modes in **1** and **2**.

X-ray diffraction analyses were obtained with a yield of 45% (based on Cu). Found: C, 42.81; H, 2.60; N, 12.24. $C_{16}H_{12}CuN_4O_8$ Calcd: C, 42.49; H, 2.66; N, 12.39%. Selected IR data (KBr, cm^{-1}): 1667(s), 1636(s), 1439(m), 1386(s), 1361(s), 1119(s), 1032(vw), 876(w), 840(w), 534(vw), 453(vw).

Complexes **1** and **2** were determined by single crystal X-ray diffraction. Suitable single crystals were mounted on a glass fiber and intensity data were collected on a Bruker APEX II diffractometer at 298 K using graphite monochromated Mo-Kα radiation ($\lambda = 0.71073$ Å). Absorption corrections were performed using SADABS [17]. The structures were solved by direct methods and refined by full-matrix least-squares against F^2 using SHELXTL software [18]. Anisotropic thermal parameters were applied to all non-hydrogen atoms. The organic hydrogens were generated geometrically and aqua hydrogens were located from difference maps and refined with isotropic temperature factors. Parameters for data collection and refinements for both the complexes are given in table 1. Selected bond lengths and angles for **1** and **2** are listed in table 2. Hydrogen-bonding data of **1** and **2** are listed in table 3.

Table 1. Crystal data and structure refinement for **1** and **2**.

Complex	**1**	**2**
Empirical formula	$C_{18}H_{32}N_2O_{16}Cu$	$C_{18}H_{16}N_2O_8Cu$
Formula weight	596.00	451.87
Temperature (K)	298(2)	298(2)
Wavelength (Å)	0.71073	0.71073
Crystal system	Triclinic	Orthorhombic
Space group	$P\bar{1}$	*Pbcn*
Unit cell dimensions (Å, °)		
a	7.5313(4)	8.2051(5)
b	8.7553(4)	16.2579(8)
c	10.8281(5)	13.7181(6)
α	69.774(2)	90
β	69.669(2)	90
γ	83.595(2)	90
V (Å^3)	628.20(5)	1829.96(16)
Z	1	4
ρ (Calcd) (mg m^{-3})	1.575	1.64
μ (m^{-1})	0.95	1.245
$F(000)$	311	924
Crystal size (mm^3)	0.22 × 0.20 × 0.15	0.26 × 0.22 × 0.17
θ range for data collection (°)	2.68 to 25.50	2.51 to 25.50
$h/k/l$ (max, min)	−9, 9/−10, 10/−12, 13	−8, 9/−19, 17/−16, 16
Reflections collected	3772	8703
Unique	2290 [R(int) = 0.0207]	1708 [R(int) = 0.0240]
Completeness to $\theta = 27.13$ (%)	98.10	100.00
Absorption correction	Empirical	Empirical
Max. and min. transmission	Full-matrix least-squares on F^2	Full-matrix least-squares on F^2
Data/restraints/parameters	2290/12/196	1708/0/134
Goodness-of-fit on F^2	1.098	1.075
Final R_1,[a] wR_2[b] indices [$I > 2\sigma(I)$]	0.0267, 0.0705	0.0280, 0.0800
R_1, wR_2 indices (all data)	0.0269, 0.0708	0.0328, 0.0829
Largest difference peak and hole (e Å^{-3})	0.353 and −0.307	0.314 and −0.304

[a] $R = \Sigma||F_o| - |F_c|/S|F_o|$. [b] $wR = [\Sigma w(|F_o|^2 - |F_c|^2)^2/\Sigma w(F_o^2)^2]^{1/2}$. $w = 1/[\sigma^2(F_o^2) + (0.0361P)^2 + 0.2151P]$ for **1**, $w = 1/[\sigma^2(F_o^2) + (0.0460P)^2 + 1.0424P]$ for **2**, $P = (F_o^2 + 2F_c^2)/3$.

Table 2. Selected atomic distances (Å) and angles (°) for **1** and **2**.[a]

1			
Cu(1)–O(3)	2.046(1)	O(6)–Cu(1)–O(6)#1	180.0
Cu(1)–O(3)#1	2.046(1)	O(3)–Cu(1)–O(5)	88.47(5)
Cu(1)–O(6)	2.049(1)	O(3)–Cu(1)–O(5)#1	91.53(5)
Cu(1)–O(6)#1	2.049(1)	O(6)–Cu(1)–O(5)#1	91.75(6)
Cu(1)–O(5)	2.210(1)	O(6)–Cu(1)–O(5)	88.25(6)
Cu(1)–O(5)#1	2.210(1)	O(5)#1–Cu(1)–O(5)	180.0
O(3)#1–Cu(1)–O(3)	180.0	O(3)–Cu(1)–O(6)	90.08(5)
O(3)–Cu(1)–O(6)#1	89.92(5)		
2			
Cu(1)–O(1)	1.9348(15)	O(1)–Cu(1)–O(1)#2	89.07(10)
Cu(1)–O(1)#2	1.9348(15)	O(1)–Cu(1)–O(3)#3	91.27(7)
Cu(1)–O(3)#3	1.9459(15)	O(1)#1–Cu(1)–O(3)#3	165.61(7)
Cu(1)–O(3)#4	1.9459(15)	O(1)–Cu(1)–O(3)#4	165.61(7)
O(3)#2–Cu(1)–O(3)#4	91.96(10)	O(1)#1–Cu(1)–O(3)#4	91.27(7)

[a] Symmetry transformations used to generate equivalent atoms: #1: $-x$, $-y$, $-z+2$; #2: $-x$, y, $-z+1/2$; #3: $-x+1/2$, $y+1/2$, z; #4: $x-1/2$, $y+1/2$, $-z+1/2$.

Table 3. Distances (Å) and angles (°) of hydrogen bonds for **1** and **2**.[a]

D–H···A	*d* (D–H)	*d* (H···A)	*d* (D···A)	<(D–H···A)
1				
O(5)–H(5A)...O(7)#2	0.854(9)	1.907(10)	2.7601(19)	177(2)
O(5)–H(5B)...O(4)#1	0.857(9)	1.922(10)	2.7455(19)	161(2)
O(6)–H(6D)...O(2)#3	0.837(9)	1.945(12)	2.7645(18)	166(2)
O(6)–H(6E)...O(2)#4	0.844(9)	1.908(11)	2.7420(18)	170(2)
O(7)–H(7A)...O(1)#5	0.855(9)	2.068(13)	2.8853(18)	160(2)
O(7)–H(7B)...O(1)	0.853(9)	2.022(13)	2.8400(19)	160(2)
O(8)–H(8A)...O(5)#6	0.846(9)	2.009(12)	2.8391(19)	167(2)
O(8)–H(8B)...O(2)#5	0.842(9)	2.114(12)	2.9442(19)	169(2)
N(1)–H(1)...O(8)#4	0.861(9)	1.901(11)	2.7549(19)	175(2)
2				
N(1)–H(1)...O(4)#7	0.860(3)	1.840(3)	2.702(2)	176.5(5)

[a] Symmetry transformation used to generate equivalent atoms: #1:$-x$, $-y$, $-z+2$; #2: x, $y-1$, z; #3: x, $y-1$, $z+1$; #4: $-x+1$, $-y+1$, $-z+1$; #5: $-x+1$, $-y+2$, $-z+1$; #6: $x+1$, $y+1$, z; #7 x, $-y$, $z-1/2$.

3. Results and discussion

As revealed by single-crystal X-ray analysis, **1** is mononuclear with space group $P\bar{1}$; the molecular ORTEP plot is shown in figure 1. Each mpba^{2-} in coordination mode **A** gives one oxygen (η^1-O3/O3a) to Cu(II) (scheme 1), and the octahedral coordination of Cu(II) is completed further by four water molecules (O5, O6, O5a and O6a); O3 and O3a are *trans*. The average Cu–O distance is 2.102(1) Å. The angles of O(3)–Cu(1)–O(3)#1, O(3)–Cu(1)–O(6), and O(3)–Cu(1)–O(5) are 180°, 90.08(5)°, and 91.53(5)°, respectively (table 2).

Intermolecular interactions play a significant role in formation and stability of **1**. Discrete Cu1 units (as SBUs) are packed through the $\pi\cdots\pi$ stacking interactions between pyridine rings of adjacent Cu1 units with centroid-to-centroid distance of 3.685 Å or 3.951 Å (figure 2), resulting in a 2-D layer-like supramolecular structure with lattice water molecules in the interlayers (figure 3). The nitrogen in the central pyridinyl ring is protonated and not coordinated under the reaction conditions employed from

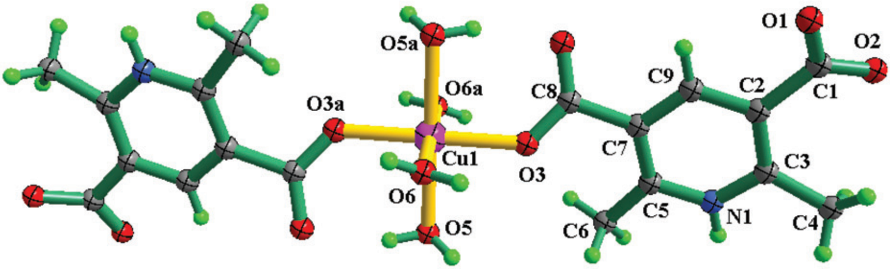


Figure 1. ORTEP drawing of **1** showing the local coordination environment of Cu^{II} with thermal ellipsoids at 50%. Uncoordinated water molecules are omitted for clarity. Symmetry code a: $-x$, $-y$, $2-z$.

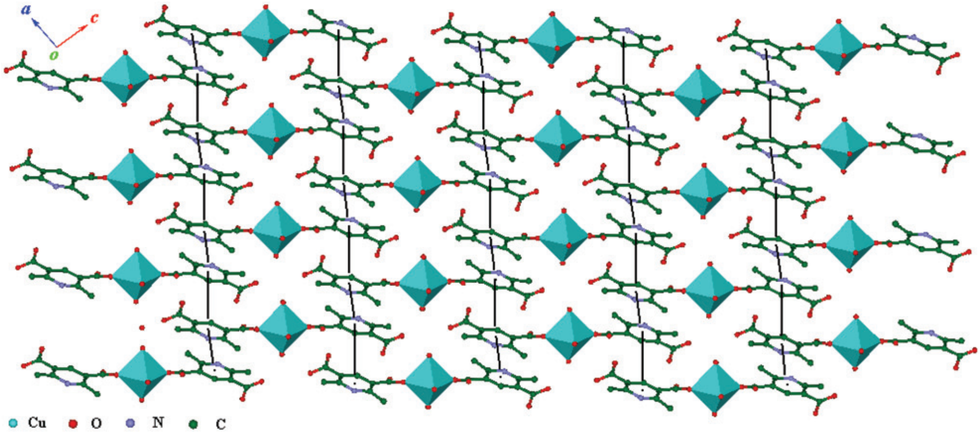


Figure 2. 2-D supramolecular layer of **1** constructed through $\pi\cdots\pi$ packing interactions viewed along the *b*-axis.

steric hindrance of two methyl groups situated *ortho*- to nitrogen. With $mpbaH^-$ in **1** monodentate η^1 to one Cu(II) and the second carboxyl remaining free, there are many hydrogen bonds in the crystal lattice (see table 3), between lattice water and the non-coordinated carboxylate, lattice water and coordinated carboxylate, lattice water and coordinated water, coordinated water and uncoordinated carboxylate and among lattice water molecules. By these hydrogen bonding interactions, the 2-D layers are assembled into a 3-D supramolecular network (see figure 3).

Complex **2** is insoluble in common solvents such as ethanol, chloroform, acetone, acetonitrile, benzene, and water. Single-crystal analysis reveals that **2** has a two-dimensional layer structure with parallelogram-like (4,4) topology. As shown in figure 4, the Cu is four-coordinate from four oxygens from four different $mpdaH^-$ ligands to form a square-planar coordination geometry with mean deviation 0.1934 Å from plane defined by O1, O1A, O3B, O3C, and Cu1. The mean Cu–O bond distance of 1.9403(15) Å is comparable with that found in reported square-planar Cu complexes with CuO4 coordination [19].

The $mpdaH^-$ in **2** is $\mu_2(\eta^1{:}\eta^1)$–O (each oxygen O1/O3 connects one Cu^{II}, and two carboxylate groups coordinate to two Cu^{II} ions) coordination mode **B** (scheme 1). From this coordination of $mpdaH^-$, an extended 2-D layer structure was formed as depicted in figure 5(a), in which two neighboring Cu^{II} centers are bridged by one $mpdaH^-$ ligand

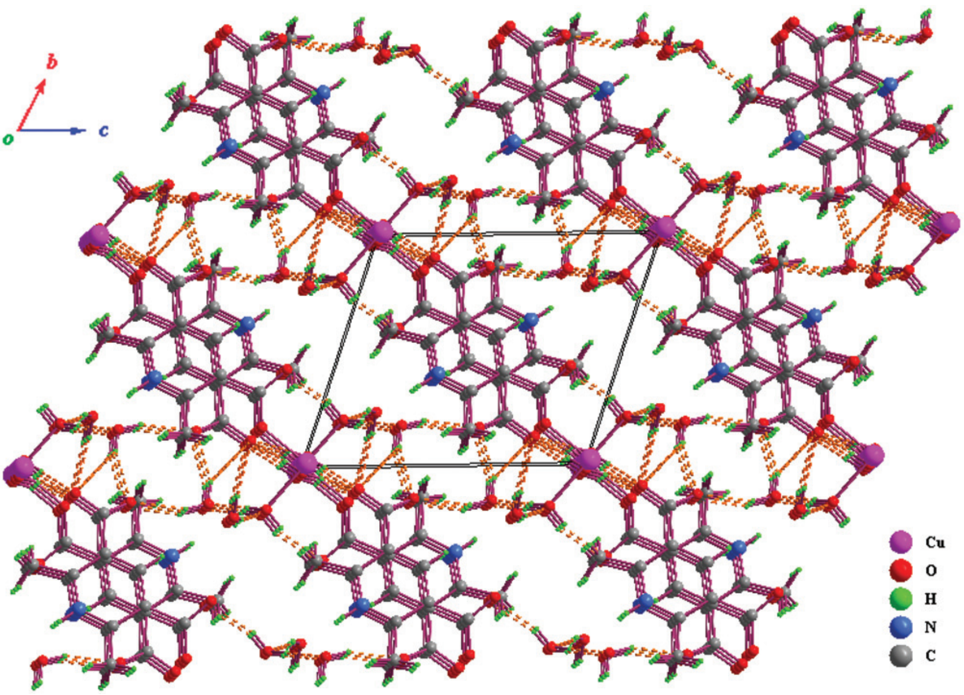


Figure 3. 3-D supramolecular network of **1** fabricated through $\pi\cdots\pi$ packing and hydrogen bonding O–H···O and N–H···O interactions viewed along the *a*-axis.

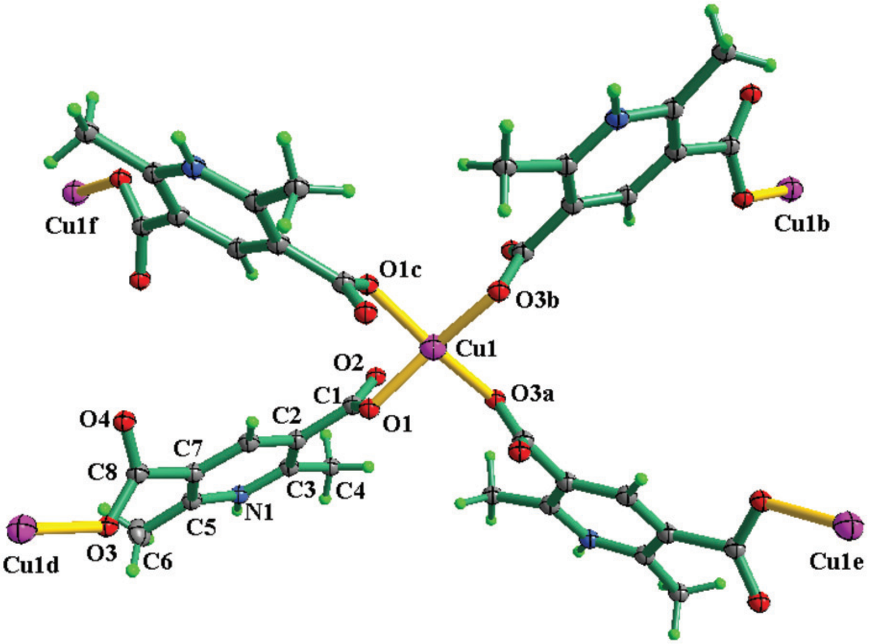


Figure 4. Coordination environment of Cu(II) in **2** with 50% probability thermal ellipsoids. Symmetry code a: 0.5−*x*, 0.5−*y*, *z*; b: −0.5 + *x*, 0.5 + *y*, 0.5−*z*; c: −*x*, *y*, 0.5−*z*; d: 0.5 + *x*, −0.5 + *y*, 0.5−*z*; e: 0.5 + *x*, 0.5 + *y*, 0.5−*z*; f: −0.5 + *x*, −0.5 + *y*, 0.5−*z*.

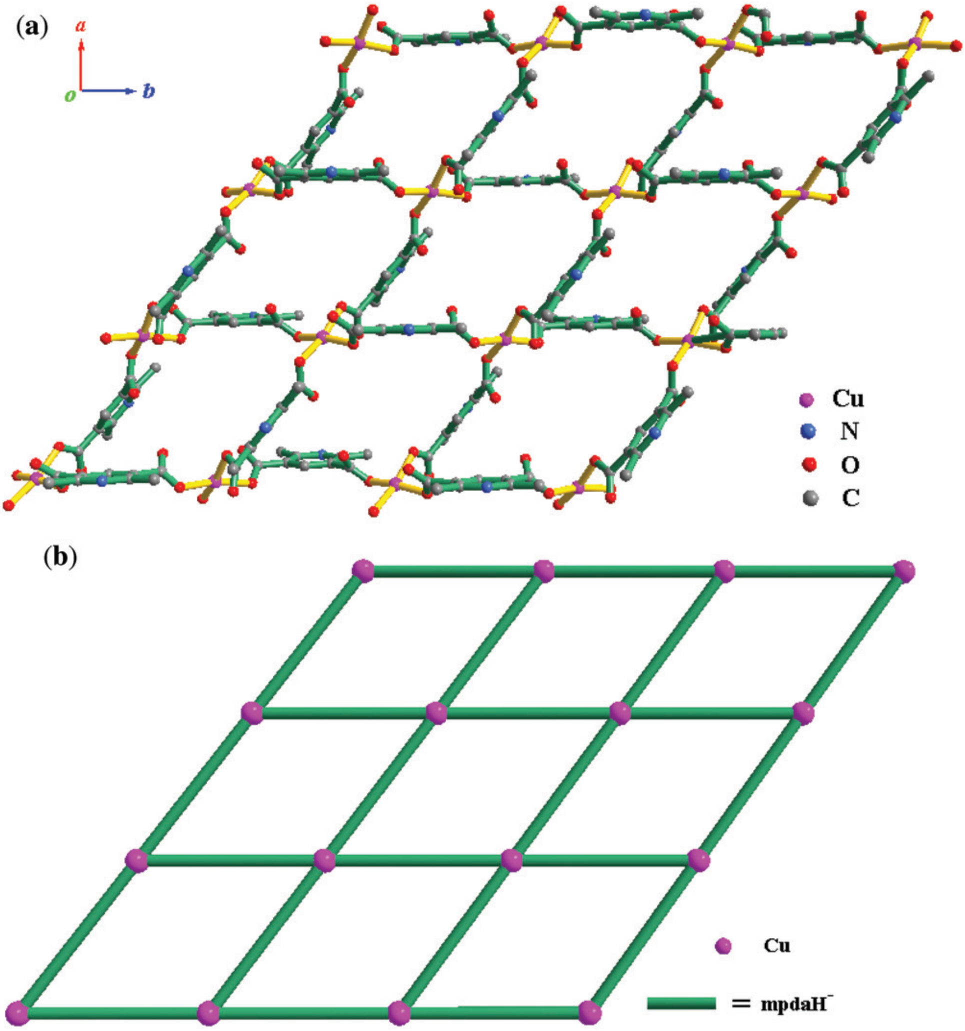


Figure 5. (a) and (b) View of the 2-D layer with (4,4) topology viewed along the *c* axis in **2**.

to form a 32-membered macrometallacyclic structure [$Cu_4(mpdc)_4$] with a Cu–Cu separation of 9.106 Å. The dihedral angle between two carboxylate groups (O1–C1–O2 and O3–C8–O4) of a $mpdaH^-$ is 64.8°. The 2-D layer can also be viewed as growth of [$Cu_4(mpdc)_4$] subunits interconnected. By treating Cu as the node and bridging ligand $mpdaH^-$ as the rod, an ideal 2-D layer with (4,4) topology is obtained as illustrated in figure 5(b).

Due to existence of N–H and uncoordinated C–O bonds of $mpdaH^-$, strong interlayer hydrogen bonds $N(1)–H(1)\cdots O(4)$ (table 3) between nitrogens and uncoordinated carboxyl oxygens (O4) together with $\pi\cdots\pi$ packing interactions from two pyridine rings of neighboring layers at 3.840 Å result in formation of a 3-D supramolecular network structure (figure 6).

Reaction temperature has significant effect on formation of these Cu(II) complexes (scheme 2). In the low temperature water environment **1** was formed. With increased

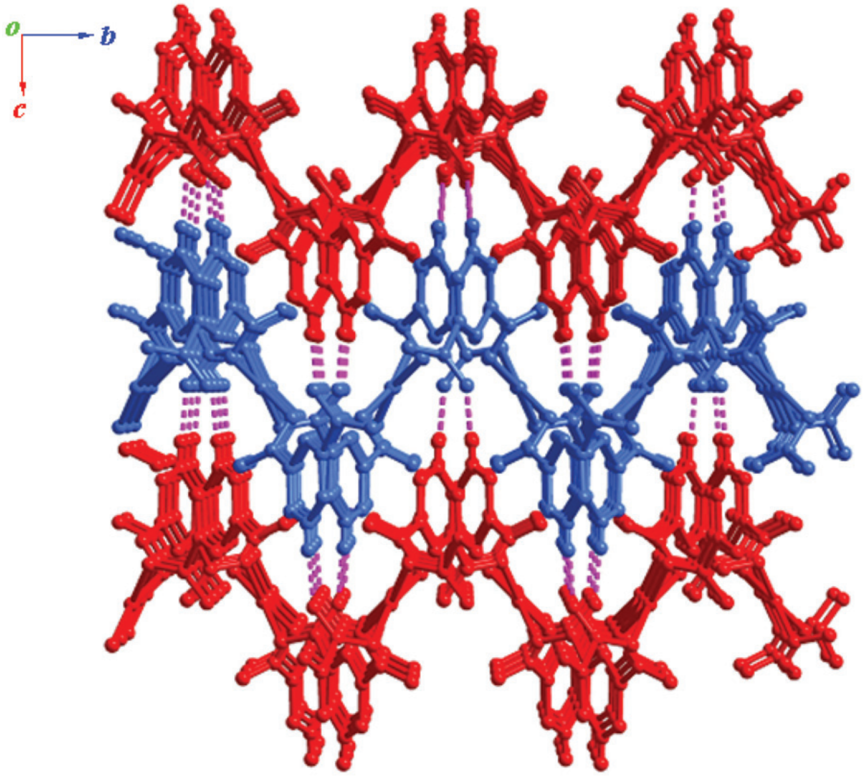
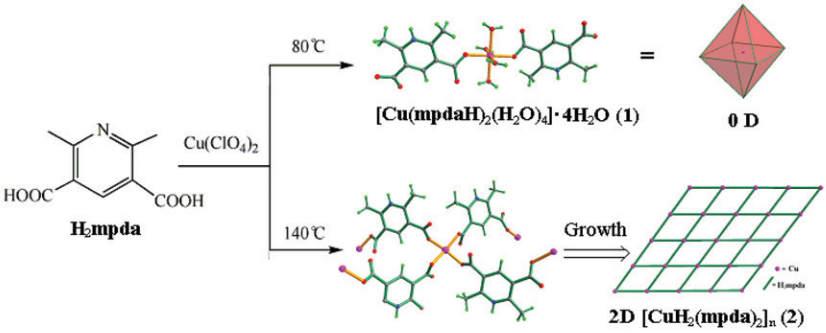


Figure 6. 3-D supramolecular network in **2** fabricated through $\pi\cdots\pi$ packing and hydrogen bonding N–H⋯O interactions viewed along the *a*-axis.



Scheme 2. Assembling strategies of **1** and **2** tuned by the reaction temperature.

temperature, the large $mpdaH^-$ easily coordinates to Cu^{II} ion and results in formation of **2** without any water, indicating that hydrothermal synthesis at high temperature creates condensed products with little or no water content [20].

The IR spectra of **1** show the ν_{H_2O} from $3600–3100\,cm^{-1}$. The ν^{-}_{sCOO} absorptions are at $1412–1345\,cm^{-1}$, while the uncoordinated carboxyl absorption is not observed, presumably from strong hydrogen-bonding. IR spectra of **2** have the asymmetric stretching vibrations $v_{as}(COO^-)$ at $1667–1636\,cm^{-1}$ and symmetric stretching vibrations $v_s(COO^-)$ at 1386–1361 cm^{-1}. The difference $\Delta(v_{as}(COO^-)–v_s(COO^-))$ around 280 cm^{-1} indicate bridging carboxylate in monodentate mode [21], as proved by the X-ray crystal structure analysis of $[CuH_2(mpdc)_2]_n$. The absence of strong bands from 1690 to 1730 cm^{-1} in **1** and **2** indicates that all ligands are deprotonated [22].

The thermogravimetric analysis (TGA) shows that **1** has three weight-loss steps. First, a 11.8% weight loss from 70 to 110°C can be attributed to loss of four non-coordinated water molecules (Calcd: 12.1%). The second weight loss (12.5%) from 150 to 205°C corresponds to loss of four coordinated water molecules (Calcd: 12.1%). The third stage from 286°C corresponds to loss of mpdaH$^-$. Preliminary thermogravimetric analysis of $[CuH_2(mpdc)_2]_n$ shows no weight loss below 351°C and coordination framework decomposition above 385°C.

We have synthesized and characterized two new copper coordination polymers with different topologies from different reaction temperatures. Compound **1** is a mononuclear neutral complex, while **2** has a 2-D network structure containing a 32-member macrometallacycle with (4,4) topology. Obviously, these results suggest a subtle change in temperature may have significant influence on the assembly process and the resulting architecture of metal-organic frameworks.

Supplementary material

CCDC Reference Nos are 705793 and 697481 for **1** and **2**, respectively. Crystallographic data for the structural analysis have been deposited with the Cambridge Crystallographic Data Center. These data can be obtained free of charge at www.ccdc.cam.ac.uk/conts/retrieving.html (or from the Cambridge Crystallographic Data Center, 12, Union Road, Cambridge CB2 1EZ, UK; Fax: +44 1223 336033; Email: deposit@ccdc.cam.ac.uk).

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