A New Porous 3-D Framework Constructed From Fivefold Parallel Interpenetration of 2-D (6,3) Nets: A Mixed-Valence Copper(I,II) Coordination Polymer $[Cu^{I}_2Cu^{II}(4,4'\text{-bpy})_2(pydc)_2]\cdot 4H_2O$

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A mixed-valence copper(I,II) coordination polymer $[Cu^{I}_2Cu^{II}(4,4'\text{-bpy})_2(pydc)_2]\cdot 4H_2O$ (4,4′-bpy = 4,4′-bipyridine and pydc = pyridine-2,4-dicarboxylate) featuring the "metal-complex ligands" $[Cu^{II}(pydc)_2]^{2-}$ was designed and synthesized hydrothermally from $Cu(MeCO_2)_2$, pyridine-2,4-dicarboxylate, 4,4′-bipyridine and NaOH. This compound was shown by single-crystal structure analysis to be the first porous 3-D framework constructed from fivefold parallel interpenetration of 2-D (6,3) nets. The one-dimensional channels occupying 17.4% of the crystal volume are occupied by guest water molecules and the porous network is stable after removal of the lattice water molecules, as indicated by TGA and PXRD measurements. The high stability of the 3-D framework may be attributed to the multiple entanglement of the 2-D nets.

Introduction

Within the currently very active research field of coordination polymers, microporous coordination frameworks are functionally related to zeolites, while intertwining networks show intriguing topologies in inorganic chemistry and may enhance the stability of the porous materials.[1−5] Both porous and intertwining frameworks are of fundamental importance in structural design and in the understanding of structure-property correlation. A two-dimensional (2-D) (6,3) net — similar to a brick-wall — is one of the most common topologies in coordination polymers; intertwining of these 2-D (6,3) nets can also ccur in parallel way.[6−8] Surprisingly, most networks consisting of parallel intertwining of (6,3) nets are overall 2-D arrays and only a single 3-D framework constructed from doubly parallel interpenetration of (6,3) nets has been reported to date.[9] Furthermore, the numbers of parallel intertwining (6,3) nets are limited to two, three and six in the known complexes.[6−8,10−13] Recently, we and others have developed routes to mixed-valence copper(I,II)[14−17] and "metal-complex ligand" (or metallo-ligand) complexes[18−20] under hydrothermal or solvothermal conditions. As a sequel, we report here a new porous mixed-valence copper(I,II) coordination polymer $[Cu^{I}_2Cu^{II}(4,4'\text{-bpy})_2(pydc)_2]\cdot 4H_2O$ (4,4′-bpy = 4,4′-bipyridine and pydc = pyridine-2,4-dicarboxylate), which contains "metal-complex ligands" and is the first 3-D framework constructed from fivefold parallel intertwining of two-dimensional (6,3) nets.

Results and Discussion

Compound **1** was synthesized under mild hydrothermal conditions (160 °C and 72 hours) and its formation is strongly influenced by the reaction conditions, especially the temperature, reaction time and pH value. The dark brown colour of **1** indicates that it is possibly a mixed-valence copper(I,II) complex. The IR spectrum of complex **1** shows characteristic bands of the dicarboxylate groups at 1634 and 1607 cm^{-1} for the antisymmetric stretching and at 1373 and 1339 for symmetric stretching.[21] The separations (Δ) between $\nu_{asym}(CO_2)$ and $\nu_{sym}(CO_2)$ are 261 and 268 cm^{-1}, respectively. The splitting of $\nu_{asym}(CO_2)$ indicates that the carboxylate groups in **1** function in two different coordination fashions.

An X-ray single-crystal analysis reveals that **1** has a porous three-dimensional framework constructed from fivefold parallel interpenetration of two-dimensional (6,3) nets. Selected bond distances and angles for **1** are listed in Table 1. There are two crystallographically independent copper atoms in **1**, as shown in Figure 1. The Cu(1) atom is trigonally coordinated by two nitrogen atoms from two 4,4′-bpy ligands and one oxygen atom from a pydc ligand. Cu(2), which is located at an inversion center and is coordinated

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to two nitrogen and two oxygen atoms from two pydc ligands, shows a slightly distorted square-planar geometry. The Cu(2)−O(3) and Cu(2)−N(1) distances are 1.967(5) and 1.973(6) Å, respectively, and the O(3a)−Cu(2)−N(1) and O(3)−Cu(2)−N(1) bond angles are 95.6(2) and 84.4(2)°, respectively. In fact, there are also two carboxylate oxygen atoms of pydc ligands from adjacent layers weakly bonded to Cu(2), with a Cu−O distance of 2.689(6) Å in the axial direction [Figure 1 (bottom)], and thus the Cu(2) site can be described as having a "4+2" coordination geometry. The Cu^{II} ion with d^9 configuration tends to have a "4+1" or "4+2" coordination geometry because of a strong Jahn−Teller effect, but the Cu^I ion with d^{10} configuration tends to have a trigonal or tetrahedral coordination geometry. The coordination symmetry of copper(II) ions in combination with charge balance indicates that Cu(1) is monovalent and Cu(2) is divalent.

Table 1. Selected bond distances [Å] and angles [°] for **1**[a]

Cu(1)−N(2)	1.935(6)	Cu(2)−O(3)	1.967(5)
Cu(1)−N(3a)	1.965(6)	Cu(2)−N(1)	1.973(6)
Cu(1)−O(2)	2.074(6)	Cu(1)···Cu(1a)	11.070
Cu(2)−O(3b)	1.967(5)	Cu(1)···Cu(2)	8.935
Cu(2)−O(1)	2.689(6)		
N(2)−Cu(1)−N(3a)	149.9(3)	O(3)−Cu(2)−N(1)	84.4(2)
N(2)−Cu(1)−O(2)	116.0(2)	O(3b)−Cu(2)−N(1b)	84.4(2)
N(3a)−Cu(1)−O(2)	93.1(2)	O(3)−Cu(2)−N(1b)	95.6(2)
O(3b)−Cu(2)−O(3)	180.0(1)	N(1)−Cu(2)−N(1b)	180.0(1)
O(3b)−Cu(2)−N(1)	95.6(2)		

[a] Symmetry codes: a = $x + 1/2, -y + 1/2, z - 1/2$; b = $-x + 2, -y, -z + 1$.

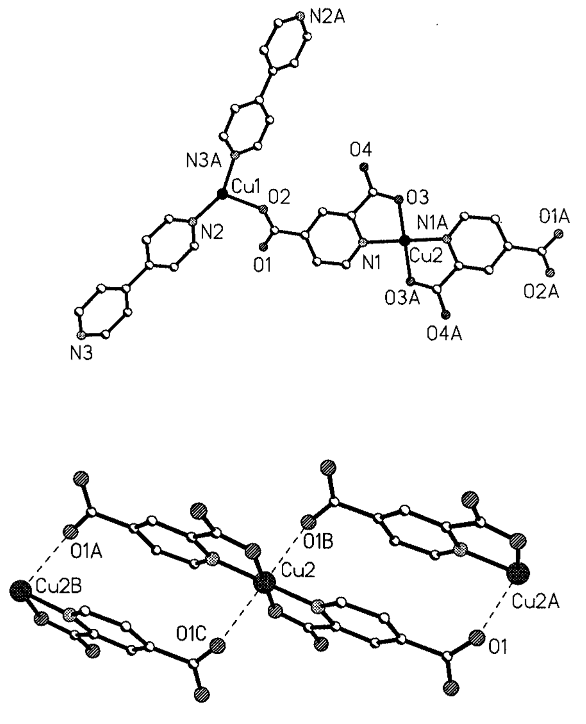
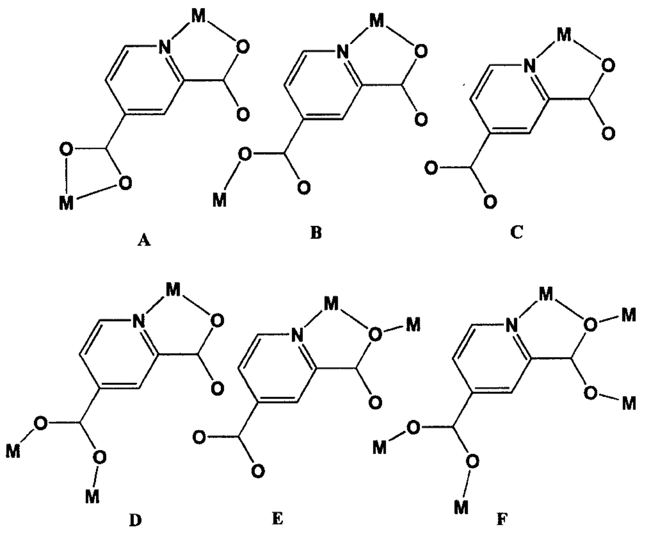


Figure 1. The coordination environments of the copper atoms in **1**

The coordination modes of pydc in its coordination polymers observed up to now are shown in Scheme 1.[18−20] As can be seen, the nitrogen and one of the 2-carboxylate oxygen atoms prefer to chelate one metal atom, and the 4-carboxylate tends to ligate one metal in a bidentate or monodentate mode, to bridge two metal atoms in a carboxylate-*O*,*O′* mode, or be pendent. The coordination mode of pydc in **1** is shown Scheme 1 (b). In addition, we recently found two other coordination modes in cobalt complexes of pydc, as shown in Scheme 1 (e and f).[22]



Scheme 1. Schematic representation of the observed coordination modes of pydc

In **1**, Cu(2) and two pydc ligands form a [Cu^{II}(pydc)$_2$]$^{2-}$ "metal-complex ligand', which bridges [Cu^I(4,4′-bpy)]$_n^{n+}$ zigzag chains to generate a 2-D wave-like (6,3) brick-wall array [Figure 2 (top)]. The tricoordinate nodes are provided by Cu(1) and the dicoordinate nodes are provided by 4,4′-bpy and the [Cu^{II}(pydc)$_2$]$^{2-}$ "metal-complex ligand". The shortest Cu(1)···Cu(1) and Cu(1)···Cu(2) distances are ca. 11.07 and 8.94 Å, respectively. Within the layer, there are large brick-like units (size ca. 18 × 16 Å), each of which is formed by four 4,4′-bpy and two [Cu^{II}(pydc)$_2$]$^{2-}$ "metal-complex ligands". Compared with other known (6,3) networks, the overall structure of **1** is unprecedented, as shown in Figure 2 (bottom). Each single (6,3) network is intertwined with four other networks and the fivefold interpenetration of (6,3) networks results in a 3-D framework. Any two interpenetrating 2-D (6,3) nets in **1** show an interpenetrating mode topologically identical to that of the [Cu$^I_2$(CN){N(CN)$_2$}$_2$]$^-$ polyanion.[23,24] Interpenetration in nature is a space-filling effect to produce dense framework but, surprisingly, the fivefold interpenetration of 2-D (6,3) networks in **1** does not occupy all the voids formed by one independent 2-D network [Figure 3 (top)]. A space-filling plot [Figure 3 (bottom)] clearly shows there are one-dimensional channels running along the *a*-axis direction in **1** which are filled by the guest water molecules. Calculations using PLATON[25] reveal that the free dimensions of these channels in **1** occupy 17.4% of the crystal volume.

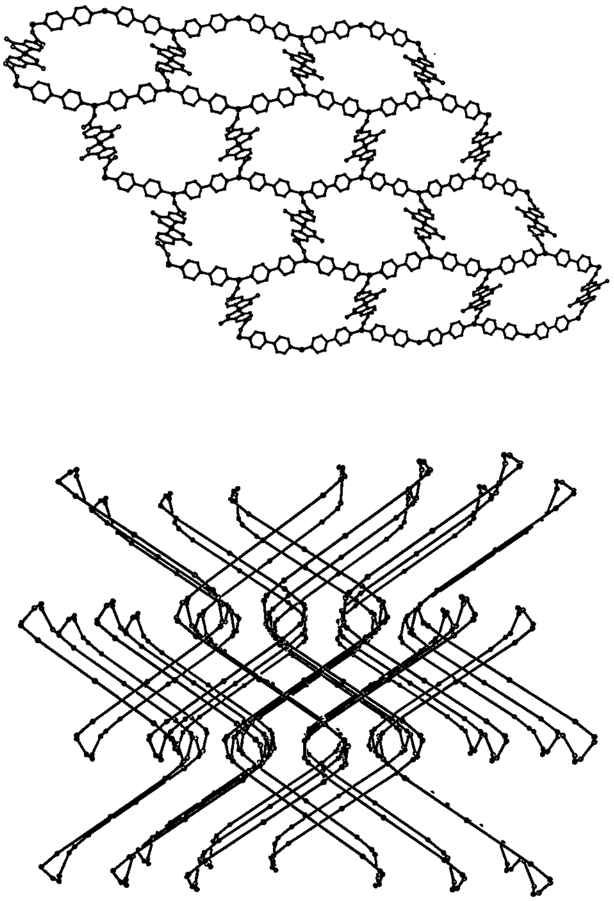


Figure 2. Perspective view of the 2-D (6,3) net in **1** (top) and the fivefold interpenetration of 2-D (6,3) nets (bottom)

Thermogravimetric analysis (Figure 4) in air showed one well-separated weight loss of 9.2% occurring in the temperature range 50−180 °C, corresponding to the removal of water molecules. It should be noted that no weight loss was observed in the temperature range 180−235 °C, indicating the formation of a stable phase formulated as $[Cu^{I}_{2}Cu^{II}(pydc)_{2}(4,4'\text{-}bpy)_{2}]$ (**1′**). The X-ray powder diffraction patterns (Figure 5) of the as-synthesized **1** and calcinated **1′** are similar, although the intensities and widths of some peaks show some differences, indicating that the porous network of **1** is retained after the calcination and removal of the lattice water molecules.

In summary, a new mixed-valence copper(I,II) coordination polymer $[Cu^{I}_{2}Cu^{II}(4,4'\text{-}bpy)_{2}(pydc)_{2}]$ has been hydrothermally synthesized, and is the first porous 3-D framework constructed from fivefold parallel interpenetration of 2-D (6,3) nets. The one-dimensional channels are occupied by guest water molecules. The porous network of **1** is stable after removal of the water molecules, which may be due to the multiple entanglement of the 2-D nets.

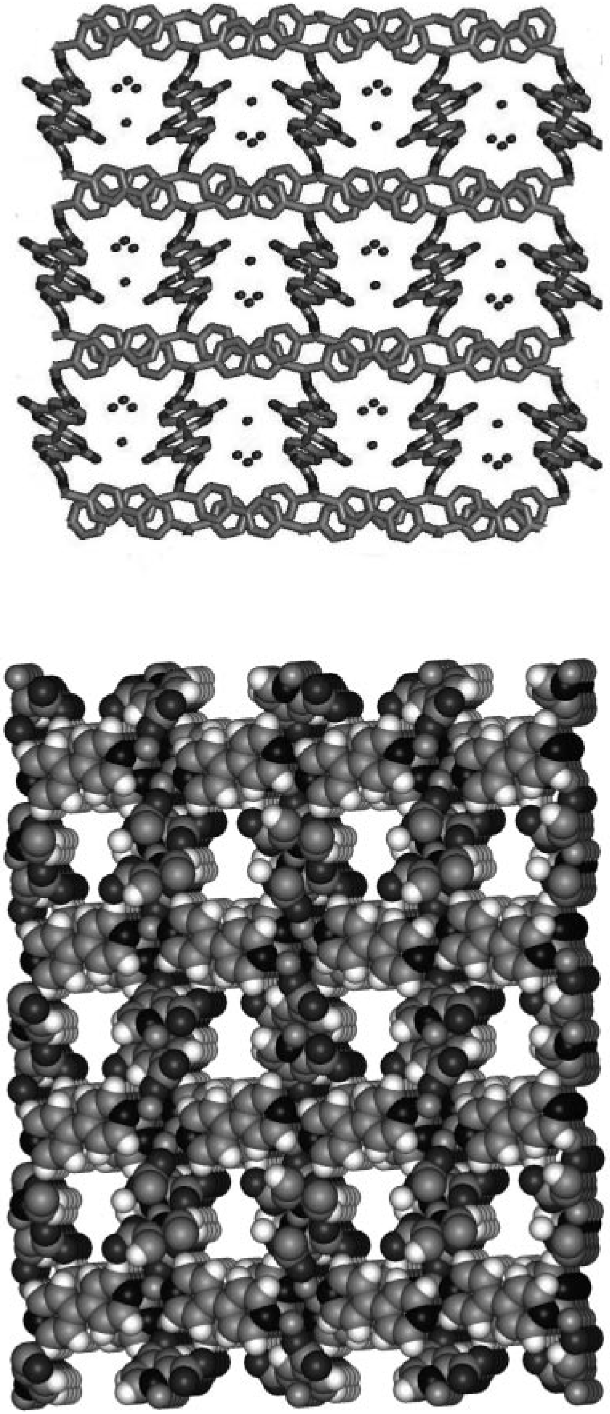


Figure 3. Plots of the 3-D array of **1** viewed along the *a*-axis: (top) ball-and-stick model showing the guest water molecules; (bottom) space-filling model omitting the guest water molecules

Experimental Section

General Remarks: Elemental analyses were performed on a Perkin−Elmer 240 elemental analyzer. The FT-IR spectra were recorded from KBr pellets in the range 400−4000 cm^{-1} on a Nicolet 5DX spectrometer. Thermal gravimetric analyses (TGA) were performed under a static air atmosphere with a Perkin−Elmer 7 thermogravimetric analyzer at a heating rate of 10 °C min^{-1}. The

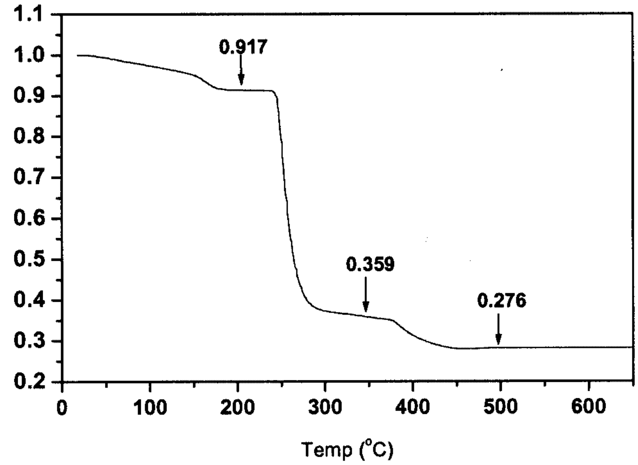


Figure 4. TGA curve of **1** in air

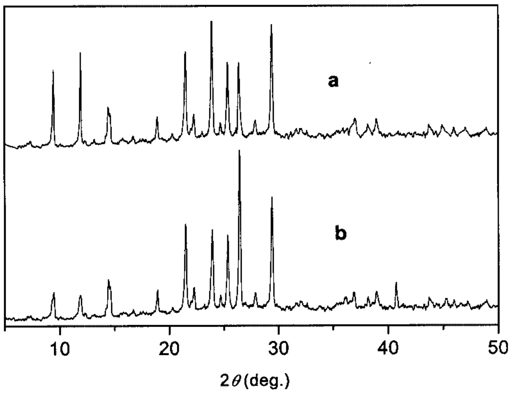


Figure 5. The X-ray powder-diffraction patterns of the as-synthesized **1** (top) and calcinated **1′** (bottom)

XRPD patterns were recorded on a Rigaku D/Max 3III diffractometer with a scanning rate of 4 °min^{-1}.

Preparation: A mixture of $Cu(MeCO_2)_2{\cdot}H_2O$ (0.075 g, 0.5 mmol), H_2pydc (0.042 g, 0.25 mmol), 4,4′-bpy (0.039 g, 0.25 mmol), NaOH (0.02 g, 0.5 mmol) and water (10 mL) in a molar ratio 1.5:1:1:2:2200 was stirred for 20 min in air, then transferred and sealed into a 23 mL Teflon-lined stainless steel container, which was heated to 160 °C for 72 hours. After cooling to room temperature at a rate of 5 °C per hour, dark-brown block crystals of **1** were recovered in 45% yield based on 4,4′-bpy. $C_{34}H_{30}Cu_3N_6O_{12}$ (905.3): calcd. C 45.11, H 3.34, N 9.28; found C 45.06, H 3.37, N 9.22. IR (KBr): $\tilde{\nu}$ = 3444bs, 3096w, 1634s, 1607s, 1552s, 1486m, 1415m, 1373s, 1339s, 1262m, 1091w, 818m, 782w, 732w, 694w cm^{-1}.

X-ray Crystallographic Study: Diffraction data were collected at 293 K on a Siemens R3 diffractometer (Mo-K_α, λ = 0.71073 Å). Lorentz-polarization and absorption corrections were applied. The structure was solved by direct methods (SHELXS-97) and refined by the full-matrix least-squares technique (SHELXL-97).[26] Analytical expressions of neutral-atom scattering factors were employed, and anomalous dispersion corrections were incorporated. In all cases, all non-hydrogen atoms were refined anisotropically and the hydrogen atoms of the organic ligands were placed geometrically. The crystallographic data for **1** are listed in Table 2.

Table 2 Crystal and structure refinement for complex **1**

Empirical formula	$C_{34}H_{30}Cu_3N_6O_{12}$
Molecular weight	905.27
Temperature (K)	293(2)
Wavelength (Å)	0.71073
Crystal system	Monoclinic
Space group	*C*2/*c*
a (Å)	8.058(5)
b (Å)	24.64(2)
c (Å)	19.203(16)
β (°)	95.75(1)
V (Å^3)	3794(5)
Z	4
Density (Mg/m^3)	1.548
μ (mm^{-1})	1.731
F(000)	1784
Absorption correction	Empirical
Max. and min. Trans.	0.4663 and 0.4133
Refl. Ind.	2978
Refinement method	Full-matrix least-squares on F^2
Data/restraints/parameters	2978/0/246
Ggoodness-of-fit on F^2	1.076
R_1	0.0679
wR_2	0.2178
$\Delta\rho_{max}/\Delta\rho_{min}$ (e·A^{-3})	1.131and −0.442

CCDC-192197 contains the supplementary crystallographic data for this paper. These data can be obtained free of charge at www.ccdc.cam.ac.uk/conts/retrieving.html [or from the Cambridge Crystallographic Data Centre, 12, Union Road, Cambridge CB2 1EZ, UK; fax: (internat.) +44-1223/336-033; E-mail: deposit@ccdc.cam.ac.uk].

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