Variable Dimensionality from Mononuclear and Trinuclear to One and Two Dimensions: A Series of Copper(II) Compounds with 4,4′-Dipyridine Dioxide

Bao-Qing Ma, Hao-Ling Sun, Song Gao,* and Guang-Xian Xu

State Key Laboratory of Rare Earth Materials Chemistry and Applications & PKU-HKU Joint
Laboratory on Rare Earth Materials and Bioinorganic Chemistry, College of Chemistry and
Molecular Engineering, Peking University, Beijing 100871, P.R. China

Received May 3, 2001

Reaction of 4,4′-dipyridine dioxide (dpdo) and $CuCl_2{\cdot}6H_2O$ in aqueous solution gave an adduct $[Cu(H_2O)_6]Cl_2{\cdot}2dpdo{\cdot}2H_2O$ **1**, which has a hydrogen-bonded three-dimensional network. While substituting $CuCl_2{\cdot}6H_2O$ with $Cu(ClO_4)_2{\cdot}6H_2O$, three pseudopolymorphs, namely, $[Cu(dpdo)_6][ClO_4]_2$ **2**, $[Cu_3(dpdo)_8(H_2O)_6][ClO_4]_6{\cdot}2dpdo{\cdot}6H_2O$ **3**, and $[Cu(dpdo)(H_2O)_4][ClO_4]_2{\cdot}2dpdo$ **4**, were isolated. **2** consists of a mononuclear copper coordinated with six terminal dpdo ligands. Adjacent mononuclear units are overlapped through $\pi-\pi$ stacking of pyridine rings to give a 2D sheet with a triangular channel. **3** forms a trinuclear cluster bridged by two dpdo molecules. The solvate and terminal dpdo molecules are interwoven through hydrogen bonding and $\pi-\pi$ stacking to lead to a rectangular channel with a dimensionality of 12.98 Å × 13.44 Å. **4** has a one-dimensional chain structure bridged by dpdo. Two solvate dpdo ligands link these chains through hydrogen bonding to generate two sets of three-dimensional networks which are interwoven through a common conjunctive point $[Cu(H_2O)_4]^{2+}$, yielding a three-dimensional open framework with triangular channels. ClO_4^- anions are included within these channels in **2**−**4** through weak C−H···O hydrogen bonding. The introduction of the second spacer, 4,4′-bipyridine, generated a 2D architecture $[Cu(dpdo)(4,4'\text{-bipy})][ClO_4]_2{\cdot}2H_2O{\cdot}dpdo$ **5**, which is constructed by 4,4′-bipy and 4,4′-dpdo simultaneously, exhibiting a large channel with approximate dimensionality 11.1 Å × 12.6 Å, in which solvate 4,4′-dpdo ligand and perchlorate anions are accommodated.

Introduction

Supramolecular assembly of organic−metal open frameworks has been mushrooming recently due to their promising applications.[1] The design and synthesis of crystalline host−guest materials possessing large cavities or channels is an important project to be pursued.[2] The assembly principle is to utilize a building block approach to construct a coordination polymer through covalent and/or intermolecular forces under the support of rigid ligands. The ligands containing two 4-pyridyl donors, such as 4,4′-bipyridine,[3] pyrazine,[4] bis(4-pyridyl)ethene,[5] 1,4-bis(4-pyridyl)benzene,[6] 2,4,6-tri(4-pyridyl)-1,3,5-triazine,[7] and 4,4-azobis(pyridine),[8] have been intensively employed and provided a variety of diamond,[9] NbO,[10] α-polonium,[11] ladder,[12] grid,[13] and other topological architectures.[14] In this work, we have chosen 4,4′-dipyridine dioxide (dpdo) as a bifunctional ligand, considering its following advantages, compared with 4,4′-bipyridine: (a) it has a longer spacer that allows for constructing microporous materials with larger cavities or channels; (b) it possesses flexible connection modes that will lead to novel topological architectures; (c) it has a strong capability of forming hydrogen bonding that plays an important role in the assembly of supramolecular compounds; (d) its higher melting point would provide a higher probability of generating

---

* Author to whom correspondence should be addressed. E-mail: gaosong@pku.edu.cn.

(1) (a) Kondo, M.; Yoshitomi, T.; Seki, K.; Matsuzaka, H.; Kitagawa, S. *Angew Chem., Int. Ed. Engl.* **1997**, *36*, 1725. (b) Li, H.; Eddaoudi, M.; O'Keeffe, M.; Yaghi, O. M. *Nature* **1999**, *402*, 276. (c) Yaghi, O. M.; Li, H.; Groy, T. L. *Inorg. Chem.* **1997**, *36*, 4292. (d) Fujita, M.; Kwon, Y. J.; Washizu, S.; Ogura, K. *J. Am. Chem. Soc.* **1994**, *116*, 1151. (e) Kitagawa, S.; Kondo, M. *Bull. Chem. Soc. Jpn.* **1998**, *71*, 1.

(2) (a) Biradha, K.; Hongo, Y.; Fujita, M. *Angew Chem., Int. Ed.* **2000**, *39*, 3843. (b) Noro, S.; Kitagawa, S.; Kondo, M. *Angew Chem., Int. Ed.* **2000**, *39*, 2082.

(3) (a) MacGillivray, L. R.; Subramamian, S.; Zaworotko, M. J. *J. Chem. Soc., Chem. Commun.* **1994**, 1325. (b) Yaghi, O. M.; Li, H. *J. Am. Chem. Soc.* **1995**, *117*, 10401. (c) Carlucci, L.; Ciani, G.; Proserpio, D. M.; Sironi, A. *J. Chem. Soc., Dalton Trans.* **1997**, 1801.

(4) (a) Haynes, J. S.; Retting, S. J.; Sams, J. R.; Thompson, R. C.; Trotter, J. *Can. J. Chem.* **1987**, *65*, 420. (b) Real, J. A.; DeMunno, G.; Munoz, M. C.; Julve, M. *Inorg. Chem.* **1991**, *30*, 2701.

(5) Blake, A. J.; Champness, N. R.; Chung, S. S. M.; Li, W. S.; Schroder, M. *Chem. Commun.* **1997**, 1005.

(6) Fujita, M.; Kwon, Y. J.; Sasaki, O.; Yamaguchi, K.; Ogura, K. *J. Am. Chem. Soc.* **1995**, *117*, 7287.

(7) (a) Abraham, B. F.; Batten, S. R.; Hamit, H.; Hoskins, B. F.; Robson, R. *Angew. Chem., Int. Ed.* **1996**, *35*, 1690. (b) Batten, S. R.; Hoskins, B. F.; Robson, R. *J. Am. Chem. Soc.* **1995**, *117*, 5385.

(8) Carlucci, L.; Ciani, G.; Prosepio, D. M. *New J. Chem.* **1998**, 1319.

(9) (a) Blake, A. J.; Champness, N. R.; Chung, S. S. M.; Li, W.-S.; Schroder, M. *Chem. Commun.* **1997**, 1005. (b) Zaworotko, M. J. *Chem. Soc. Rev.* **1994**, 283.

(10) Power, K. N.; Hennigar, T. L.; Zaworotko, M. J. *Chem. Commun.* **1998**, 595.

(11) (a) Duncan, P. C. M.; Goodgame, D. M. L.; Menzer, S.; Williams, D. J. *Chem. Commun.* **1996**, 2127. (b) Soma, T.; Yuge, H.; Iwamoto, T. *Angew. Chem., Int. Ed.* **1994**, *33*, 1665. (c) Carlucci, L.; Ciani, G.; Proserpio, D. M.; Sironi, A. *Angew. Chem., Int. Ed.* **1995**, 34, 1895.

(12) (a) Losier, P.; Zaworotko, M. J. *Angew. Chem., Int. Ed.* **1996**, *35*, 2779. (b) Hennigar, T. L.; MacQuarrie, D. C.; Losier, P.; Rogers, R. D.; Zaworotko, M. J. *Angew. Chem., Int. Ed.* **1997**, *36*, 972. (c) Yaghi, O. M.; Li, H.; Groy, T. L. *Inorg. Chem.* **1997**, *36*, 4292.

(13) (a) Hagrman, D.; Zubieta, C.; Rose, D. J.; Zubieta, J.; Haushalter, R. C. *Angew. Chem., Int. Ed.* **1997**, *36*, 873. (b) Blake, A. J.; Hill, S. J.; Hubberstey, P.; Li, W. S. *J. Chem. Soc., Dalton Trans.* **1997**, 913. (c) Lu, J.; Paliwala, T.; Lim, S. C.; Yu, C.; Niu, T.; Jacobson, A. J. *Inorg. Chem.* **1997**, *36*, 923. (d) Tong, M. L.; Ye, B. H.; Cai, J. W.; Chen, X. M.; Ng, S. W. *Inorg. Chem.* **1998**, *37*, 2645.

(14) (a) Tong, M. L.; Chen, X. M.; Yu, X. L.; Mak, T. C. W. *J. Chem. Soc., Dalton Trans.* **1998**, 5. (b) Kiang, Y. H.; Gardner, G. B.; Lee, S.; Xu, Z. T.; Lobkovsky, E. B. *J. Am. Chem. Soc.* **1999**, *121*, 8204.

10.1021/ic0104712 CCC: $20.00

Table 1. Crystal Data and Structure Refinement for **1**−**5**

	1	**2**	**3**	**4**	**5**
formula	$C_{20}H_{32}Cl_2CuN_4O_{12}$	$C_{60}H_{48}Cl_2CuN_{12}O_{20}$	$C_{100}H_{104}Cl_6Cu_3N_{20}O_{56}$	$C_{30}H_{32}Cl_2CuN_6O_{18}$	$C_{30}H_{28}Cl_2CuN_6O_{14}$
fw	327.47	1391.54	2885.35	899.06	831.02
λ (Å)	0.7107	0.7107	0.7107	0.7107	0.7107
T (K)	298	298	298	298	298
space group	$P\bar{1}$ (No. 2)	$P\bar{1}$ (No. 2)	$P2_1/c$ (No. 14)	$P\bar{1}$ (No. 2)	$P2/n$ (No. 13)
a (Å)	6.7319(8)	8.9729(5)	18.3842(8)	5.3540(2)	6.8319(2)
b (Å)	10.2542(13)	11.6632(11)	16.5424(4)	11.8921(4)	11.0582(3)
c (Å)	10.423(4)	14.3691(12)	20.9112(8)	15.2705(6)	21.9995(7)
α (deg)	85.09(2)	104.719(3)	90	110.739(2)	90
β (deg)	72.806(18)	97.282(5)	110.4527(16)	94.0425(19)	97.2546(18)
γ (deg)	89.233(10)	98.254(5)	90	99.2350(18)	90
V (Å^3)	684.8(3)	1418.3(2)	5958.6(4)	888.91(6)	1648.72(8)
Z	1	1	2	1	2
D_{calcd} (Mg/m^3)	1.588	1.629	1.608	1.679	1.674
μ (mm^{-1})	1.059	0.574	0.773	0.855	0.906
R1^a [$I > 2\sigma(I)$]	0.0288	0.0644	0.0731	0.0421	0.0545
wR2^b [$I > 2\sigma(I)$]	0.0771	0.1345	0.1920	0.1033	0.1199

[a] $R1 = \sum||F_o| - |F_c||/\sum|F_o|$. [b] $wR2 = [\sum w(F_o^2 - F_c^2)^2]/\sum[w(F_o^2)^2]^{1/2}$.

compounds with high thermal stability, which is an important precondition in the conversion of the microporous frameworks from laboratory curiosities to practical materials. Only limited compounds on this or related ligands were documented to date.[15] Herein, we describe the synthesis and structures of a series of copper(II) complexes with dpdo. Indeed, they exhibit either strong hydrogen-bonding interactions or open frameworks with large channels as what we expected.

Experimental Section

Materials. 4,4′-Dipyridine dioxide·2H_2O (4,4′-dpdo) was prepared according to the literature method.[16] Other reagents were commercially available and used without further purification.

Synthesis of [Cu(H_2O)$_6$]Cl_2·2dpdo·2H_2O 1. 4,4′-dpdo (1 mmol, 0.224 g) and $CuCl_2$·6H_2O (0.5 mmol, 0.122 g) were mixed in 20 mL of aqueous solution. The mixture was heated for 10 min with stirring and condensed to 10 mL, and then filtered. Upon slow evaporation of filtrate at room temperature, prismatic green crystals were obtained after 10 days.

Synthesis of [Cu(dpdo)$_6$][ClO_4]$_2$ 2 and Synthesis of [Cu_3(dpdo)$_8$(H_2O)$_6$][ClO_4]$_6$·2dpdo·6H_2O 3 and [Cu(dpdo)(H_2O)$_4$][ClO_4]$_2$·2dpdo 4. Method 1. 4,4′-dpdo (1 mmol, 0.224 g) and Cu(ClO_4)$_2$·6H_2O (0.5 mmol, 0.186 g) were mixed in 20 mL of aqueous solution. The mixture was heated for 10 min with stirring and condensed to 10 mL, and then filtered. Upon slow evaporation of filtrate at room temperature, well-shaped orange-red crystals of **2** were observed on the bottom of the reaction vessel after 5 days. Further evaporation left dark red and green crystals, identified as Cu_3(dpdo)$_8$(H_2O)$_6$][ClO_4]$_6$·2dpdo·6H_2O **3** and [Cu(dpdo)(H_2O)$_4$][ClO_4]$_2$·2dpdo **4**. They were mechanically separated and washed with water**.** When the ratio between 4,4′-dpdo and Cu(ClO_4)$_2$·6H_2O was reduced to 2:1, compounds **3** and **4** were obtained as main products. Elemental anal. Calcd for **2** $C_{14}H_{18}CuN_2O_4$: C, 51.76; H, 3.45; N, 12.08. Found: C, 51.10; H, 3.69; N, 11.89. Calcd for **4** $C_{30}H_{28}C_{l2}CuN_6O_{14}$: C, 39.57; H, 3.56; N, 9.34. Found: C, 39.14; H, 3.48; N, 9.02.

Compound **2** also can be obtained by the following method. 4,4′-dpdo (1 mmol, 0.224 g) was dissolved in 30 mL of acetonitrile with heating and stirring. To the above solution was added Cu(ClO_4)$_2$·6H_2O (0.5 mmol, 0.186 g). An orange-red precipitate was formed immediately. DMF was added dropwise to the flurry, and the precipitate dissolved gradually. The resulting solution was filtered, and the filtrate was allowed to stand at room temperature. Plate-shaped crystals were obtained after 2 days. Yield: 76%.

Synthesis of [Cu(dpdo)(4,4′-bipy)][ClO_4]$_2$·2H_2O·dpdo 5. The compound was synthesized by adding a Cu(ClO_4)$_2$·6H_2O (0.5 mmol, 0.186 g) aqueous solution to a mixture of an aqueous solution of 4,4′-dpdo (0.5 mmol, 0.112 g) and an ethanol solution of 4,4′-bipy (0.5 mmol, 0.078 g) with stirring and heating. A green precipitate was produced immediately, and the flurry continued to react for 0.5 h. Then, the residues were filtered off and the filtrate was allowed to stand at room temperature. Deep green prismatic crystals were obtained after 1 day (yield: 42% based on dpdo). Element anal. Calcd for $C_{30}H_{28}C_{l2}CuN_6O_{14}$: C, 43.32; H, 3.37; N, 10.11. Found: C, 43.56; H, 3.333; N, 9.85. IR: 3423 s, 3105 s, 3072 s, 3041 s, 3024 s, 2933 m, 2854 m, 1621 m, 1474 vs, 1461 s, 1429 m, 1322 m, 1234 vs, 1187 vs, 1143 vs, 1120 vs, 1089 vs, 1027 vs, 839 vs, 699 m, 636 s, 553 s, 515 m, 485 s cm^{-1}.

Crystallography. A green crystal of **1** (0.30 × 0.30 × 0.23 mm), an orange red crystal of **2** (0.24 × 0.12 × 0.07 mm), a dark red crystal of **3** (0.30 × 0.30 × 0.10 mm), a green crystal of **4** (0.26 × 0.24 × 0.06 mm), and a deep green crystal of **5** (0.26 × 0.20 × 0.14 mm) were selected for the diffraction analysis. For **1**, the data collection was performed on a Siemens P4 X-ray diffractometer with graphite-monochromated Mo Kα radiation (0.71073 Å). For **2**−**5**, the data collections were carried out on a Nonius Kappa CCD diffractometer with graphite-monochromated Mo Kα radiation (0.71073 Å) at 293 K. The structures were solved by direct methods and refined by a full-matrix least-squares technique based on F^2 using the SHELXL 97 program.[17] All non-hydrogen atoms were refined anisotropically, and the hydrogen atoms of water molecules were located from difference electronic Fourier maps, except those of compound **3** were not found. Other hydrogen atoms were placed by calculation positions and refined isotropically. Compound **3** is air unstable and was coated with paraffin oil when data collection was carrying out. Due to the poor quality of the crystal and the presence of a disordered ClO_4^- anion, the structure has a relatively higher *R* factor. The details of crystal data and selected bond lengths and angles for compounds **1**−**5** are listed in Table 1 and Table 2, respectively.

Results and Discussion

Synthesis and Reaction. Reaction of dpdo and $CuCl_2$·6H_2O in aqueous solution gave only one product, an adduct compound [Cu(H_2O)$_6$]Cl_2·2dpdo·2H_2O **1**, whereas three different species, namely, [Cu(dpdo)$_6$][ClO_4]$_2$ **2**, [Cu_3(dpdo)$_8$(H_2O)$_6$][ClO_4]$_6$·2dpdo·6H_2O **3**, and [Cu(dpdo)(H_2O)$_4$][ClO_4]$_2$·2dpdo **4**, were isolated when substituting $CuCl_2$·6H_2O with Cu(ClO_4)$_2$·6H_2O. It indicates that the counterions have an important influence on the formation of solid structures. The reddish, dark red, and

---

(15) (a) Plater, M. J.; Foreman, M. R. St.; Slawin, A. M. Z. *Inorg. Chim. Acta* **2000**, *303*, 132. (b) Long, D. L.; Blake, A. J.; Champness, N. R.; Schroder, M. *Chem. Commun.* **2000**, 1369. (c) Long, D. L.; Blake, A. J.; Champness, N. R.; Wilson, C.; Schroder, M. *J. Am. Chem. Soc.* **2001**, *123*, 3401. (d) Ma, B. Q.; Sun H. L.; Gao, S.; Su, G. *Chem. Mater*. **2001**, *13*, 1946.

(16) Simpon, P. G.; Vinciguerra, A.; Quagliano, J. V. *Inorg. Chem.* **1963**, *2*, 282.

(17) Sheldrick, G. M. *SHELX-97, PC Version*; University of Göttingen: Göttingen, Germany, 1997.

Table 2. Selected Bond Lengths (Å) and Angles (deg) for **1**−**5**

1[a]			
Cu(1)−O(5)	1.9676(14)	Cu(1)−O(4)	1.9681(15)
Cu(1)−O(3)	2.3763(17)	O(1)−N(1)	1.3196(19)
O(2)−N(2)	1.3279(18)		
O(5)−Cu(1)−O(4)a	89.30(7)	O(5)−Cu(1)−O(4)	90.70(7)
O(5)−Cu(1)−O(3)a	92.55(6)	O(4)−Cu(1)−O(3)a	89.57(6)
O(5)−Cu(1)−O(3)	87.45(6)	O(4)−Cu(1)−O(3)	90.43(6)
2[b]			
Cu(1)−O(1)	1.977(3)	Cu(1)−O(5)	1.980(3)
Cu(1)−O(3)	2.323(3)	O(1)−N(1)	1.340(4)
O(2)−N(2)	1.315(4)	O(3)−N(3)	1.322(4)
O(4)−N(4)	1.308(5)	O(5)−N(5)	1.318(5)
O(6)−N(6)	1.349(6)		
O(1)−Cu(1)−O(5)a	91.24(12)	O(1)−Cu(1)−O(5)	88.76(12)
O(1)−Cu(1)−O(3)	84.71(12)	O(5)−Cu(1)−O(3)	86.56(13)
O(1)−Cu(1)−O(3)a	95.29(12)	O(5)−Cu(1)−O(3)a	93.44(13)
N(1)−O(1)−Cu(1)	125.4(2)	N(3)−O(3)−Cu(1)	125.7(2)
N(5)−O(5)−Cu(1)	130.0(3)		
3[c]			
Cu(1)−O(11)	1.915(4)	Cu(1)−O(12)	1.929(4)
Cu(1)−O(10)	1.981(4)	Cu(1)−O(3)	1.995(4)
Cu(1)−O(1)	2.398(4)	Cu(2)−O(13)	1.944(4)
Cu(2)−O(5)	2.012(4)	Cu(2)−O(2)	2.365(4)
O(1)−N(1)	1.318(6)	O(2)−N(2)	1.331(6)
O(3)−N(3)	1.336(6)	O(4)−N(4)	1.333(7)
O(5)−N(5)	1.342(6)	O(6)−N(6)	1.329(6)
O(7)−N(7)	1.312(7)	O(8)−N(8)	1.324(7)
O(9)−N(9)	1.312(6)	O(10)−N(10)	1.335(6)
O(11)−Cu(1)−O(12)	175.80(18)	O(11)−Cu(1)−O(10)	90.33(19)
O(12)−Cu(1)−O(10)	92.51(18)	O(11)−Cu(1)−O(3)	92.50(18)
O(12)−Cu(1)−O(3)	85.07(17)	O(10)−Cu(1)−O(3)	172.24(19)
O(11)−Cu(1)−O(1)	92.33(19)	O(12)−Cu(1)−O(1)	84.40(18)
O(10)−Cu(1)−O(1)	93.86(17)	O(3)−Cu(1)−O(1)	93.24(17)
O(13)−Cu(2)−O(5)a	86.55(16)	O(13)−Cu(2)−O(5)	93.45(16)
O(13)−Cu(2)−O(2)a	83.13(14)	O(5)−Cu(2)−O(2)a	92.80(15)
O(13)−Cu(2)−O(2)	96.87(14)	O(5)−Cu(2)−O(2)	87.20(15)
N(1)−O(1)−Cu(1)	135.8(4)	N(2)−O(2)−Cu(2)	125.5(3)
N(3)−O(3)−Cu(1)	127.0(3)	N(5)−O(5)−Cu(2)	127.8(3)
N(10)−O(10)−Cu(1)	125.6(3)		
4[d]			
Cu(1)−O(4)	1.948(2)	Cu(1)−O(5)	1.967(2)
Cu(1)−O(1)	2.407(2)	O(1)−N(1)	1.334(2)
O(2)−N(2)	1.315(3)	O(3)−N(3)	1.327(3)
O(4)−Cu(1)−O(5)a	93.16(9)	O(4)−Cu(1)−O(5)	86.84(9)
O(4)−Cu(1)−O(1)a	92.70(8)	O(5)−Cu(1)−O(1)a	91.56(6)
O(4)−Cu(1)−O(1)	87.30(8)	O(5)−Cu(1)−O(1)	88.44(6)
N(1)−O(1)−Cu(1)	107.87(13)		
5[e]			
Cu(1)−O(1)	1.968(2)	Cu(1)−N(3)	1.991(3)
O(1)−N(1)	1.337(3)	O(2)−N(2)	1.327(4)
O(1)−Cu(1)−O(1)a	168.43(13)	O(1)−Cu(1)−N(4)b	95.79(6)
O(1)−Cu(1)−N(3)	84.21(6)	N(1)−O(1)−Cu(1)	129.92(18)

[a] Symmetry code: a $-x, -y + 1, -z + 1$. [b] Symmetry code: a $-x, -y, -z$. [c] Symmetry code: a $-x + 1, -y, -z$. [d] Symmetry code: a $-x, -y, -z$. [e] Symmetry codes: a $-x + {}^1/_2, y, -z + {}^1/_2$; b $x, y + 1, z$.

green colors for **2**−**4**, respectively, can be attributed to ligand field effects of the Cu ion, due to different numbers of ligands around the copper coordination sphere. The three species can be achieved depending on the ligand:metal molar ratio and the specific solvents used. Under the conditions of lower ligand: metal ratio (≤4:1), compounds **3** and **4** were identified as the main species. With an increase in the ratio up to 6:1, compound **2** dominated. This is related to the fact that the aqua ligand has strong coordination competition for copper with dpdo. The coordination ability of dpdo is relatively weak, compared with its parent 4,4′-bipyridine. Therefore, the concentration of dpdo ligands in the reaction solution has an important effect on the final product. The assumption can be further confirmed by performing the reaction in MeCN solution, which always gave compound **2** in spite of the ligand:metal ratio owing to weak coordination ability of MeCN. All of the products except **3** are air stable.

Ionic Pair. Compound **1** consists of a hydrated $[Cu(H_2O)_6]^{2+}$ cation, two Cl^- anions, two dpdo molecules, and two crystal lattice water molecules. The Cu^{2+} ion is located on an inversion center and has an elongated octahedral environment [Cu1−O5 = 1.9676(14) Å, Cu1−O4 = 1.9681(15) Å, and Cu1−O3 = 2.3763(17) Å]. The two pyridyl rings of dpdo are nearly coplanar, with a twist angle of 1.99°.

Six water molecules of the hydrated $[Cu(H_2O)_6]^{2+}$ cation form single hydrogen bonds with six dpdo ligands [O3···O2a = 2.775(2) Å, O3−H9···O2a = 170(3)°; O5···O1 = 2.600(2) Å, O5−H13···O1= 179(3)°; O4···O2b = 2.727(2) Å, O4−H12···O2b = 153(3)°; a = $x, y + 1, z + 1$; b = $-x + 1, -y, -z$]. One O atom (O1) of the solvate dpdo connects the hydrated Cu ions through single hydrogen bonds, and the other (O2) bridges two discrete $[Cu(H_2O)_6]^{2+}$ cations through double hydrogen bonds. In this way, these discrete hydrate $[Cu(H_2O)_6]^{2+}$ moieties are linked into a 2D sheet in the [101] plane (Figure 1). The remaining hydroxyl groups of six coordinated water molecules yield hydrogen bonds with Cl^- ions or lattice water [O3···Cl1 = 3.2072(17) Å, O3−H10···Cl1 = 172(3)°; O4···O6c = 2.692(2) Å, O4−H11···O6c = 166(3)°; O5···Cl1 = 3.069(2) Å, O5−H14···Cl1 = 175(2)°; c = $-x + 1, -y + 1, -z + 1$]. Thus, each coordinated water molecule is involved in double donor hydrogen bonds. These hydrogen bonds and that formed by Cl^- ion with lattice water [O6···Cl1 = 3.195(2) Å, O6−H15···Cl1 = 160(3)°] link the structure into a three-dimensional network.

Although compound **1** is an ion pair compound, the efficient and rich hydrogen bonds generated through dpdo molecules make it an extended structure.

Mononuclear Unit. Compound **2** consists of a discrete $[Cu(dpdo)_6]^{2+}$ cation and two perchlorate anions (Figure 2). The copper ion lies on an inversion center and is coordinated with six dpdo ligands, forming an elongated octahedron, in which O1, O5, and their symmetry-related oxygen atoms occupy the equatorial positions, and O3 and O3a take up the axial sites. The Cu1−O1, Cu1−O5, and Cu1−O3 bond lengths are 1.977(3), 1.980(3), and 2.323(3) Å, respectively. Two pyridyl groups of the three dpdo ligands (denoted as N1, N3, N5) are twisted by 29.25(21)°, 18.64(25)°, and 14.56(34)°, respectively.

Although it is a mononuclear molecule, the adjacent mononuclear units are connected by symmetry-related dpdo ligands through $\pi-\pi$ stacking with the interplane distances in the range 3.44−3.52 Å, yielding a 2D (3,6) sheet as depicted in Figure 3. A triangular channel, in which perchlorate anions are contained, is produced. ClO_4^- ions contact with dpdo through weak C−H···O hydrogen-bonding interactions with C···O distances and C−H···O angles being within the ranges 3.223−3.394 Å and 127.8−168.6°, respectively.

Trinuclear Cluster. Compound **3** is a linear trinuclear cluster linked by two bridging dpdo ligands shown in Figure 4, in which the central copper ion is located at an inversion center and coordinated with two O atoms from two bridging dpdo molecules [Cu2−O2 = 2.365(4) Å], two monodentate dpdo molecules [Cu2−O5 = 2.012(4) Å], and two water molecules [Cu2−O13 = 1.944(4) Å], also producing an elongated octahedron as observed in **1** and **2**. Each terminal copper atom has a square based pyramidal coordination sphere, in which two water molecules [Cu1−O11 = 1.915(4) Å, Cu1−O12 = 1.929(4) Å] and two monodentate dpdo molecules [Cu1−O3 = 1.995(4) Å, Cu1−O10 = 1.981(4) Å] form the base and the oxygen

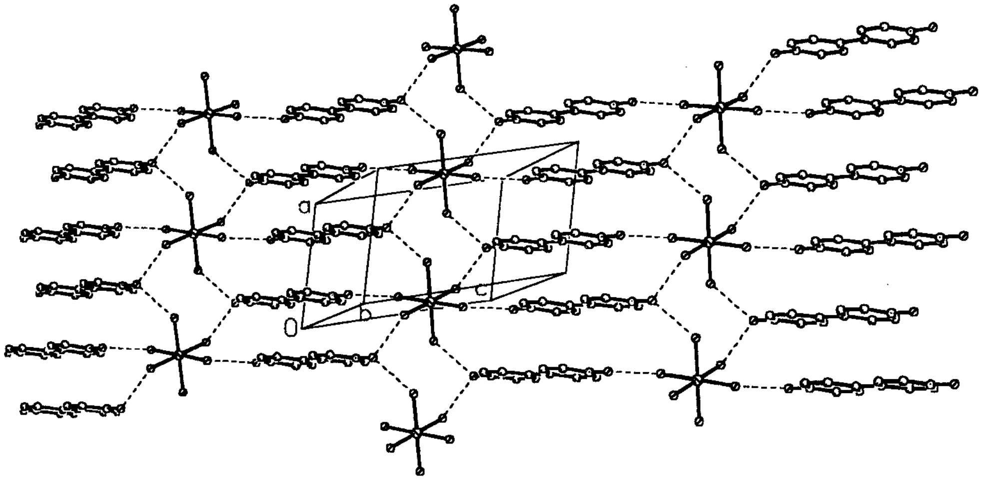


Figure 1. 2D sheet formed by hydrogen bonding between dpdo ligands and hydrated $[Cu(H_2O)_6]^+$ cations in **1**.

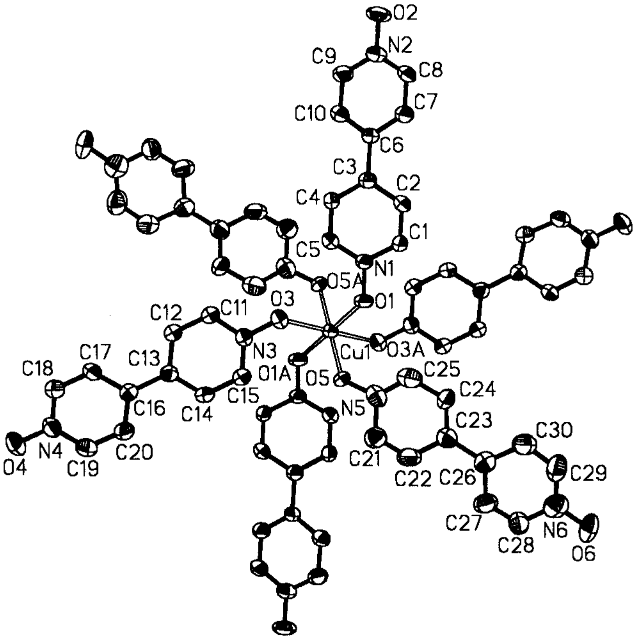


Figure 2. Molecular structure of **2**.

atom from the bridging dpdo occupies the apex position [Cu1−O1 = 2.398(4) Å]. These distances are comparable to the corresponding values in an elongated octahedral Cu environment. Cu1 ion protrudes out the base plane 0.0907 Å. All of the N−O−Cu angles range from 125.5° to 135.8°. The dihedral angle between the Cu1−O1−O2 and Cu2−O2−O1 planes is 118.9°, close to a cis connection mode for the dpdo bridge.

For these bifunctional ligands, such as pyrazine, bipyridine, and 1,2-bis(4-pyridyl)ethane, they usually formed extended structures or mononuclear compounds. No oligonuclear clusters have been reported so far.[18] To the best of our knowledge, compound **3** represents the first case of cluster structures. dpdo ligands in **3** fall into three groups: two bridging, six terminal, and two uncoordinated ones. The dihedral angles of their pyridyl groups are in the range 4.59(22)−21.86(17)°. No significant differences are observed among the three kinds of forms. It was noted that **3** contains the three forms simultaneously, a rare case for dpdo compounds.[15] Even for 4,4-bipy complexes, the coexistence of three forms of one ligand was also rarely found.[19] The terminal and central coppers are linked through a dpdo bridge with a long Cu1···Cu2 separation, 12.977 Å.

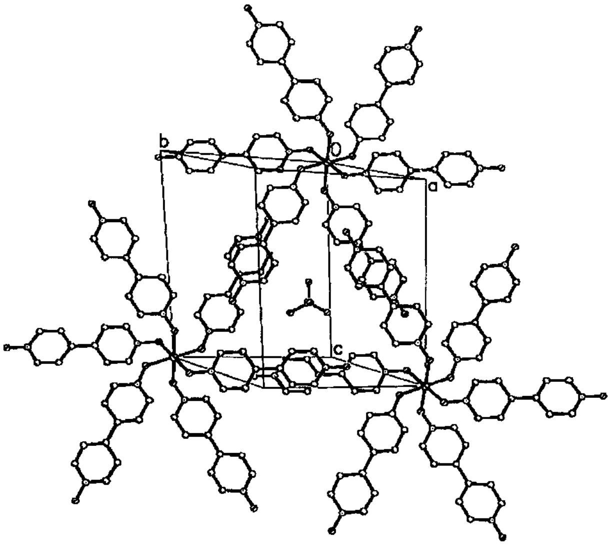


Figure 3. 2D sheet formed through intermolecular $\pi-\pi$ interactions in **2**.

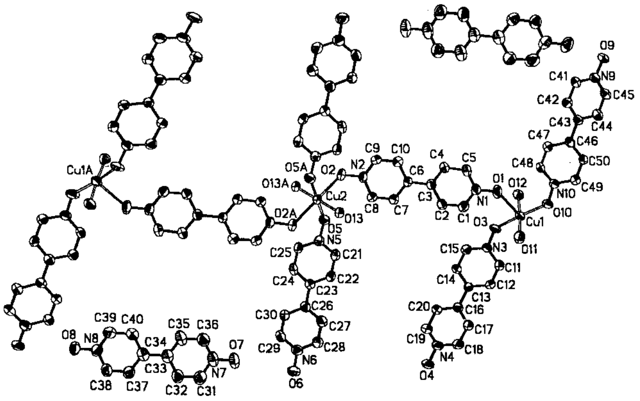


Figure 4. Molecular structure of **3**.

The trinuclear cluster has a fish-bone-like motif. The solvate dpdo is parallel to the bridging dpdo and located near the distal end of terminal ones. It yields significant hydrogen bonding

---

[18] Tong, M. L.; Lee, H. K.; Chen, X. M.; Huang, R. B.; Mak, T. C. W. *J. Chem. Soc., Dalton Trans.* **1999**, 3657.

[19] Yaghi, O. M.; Li, H.; Groy, T. L. *Inorg. Chem.* **1997**, *36*, 4292.

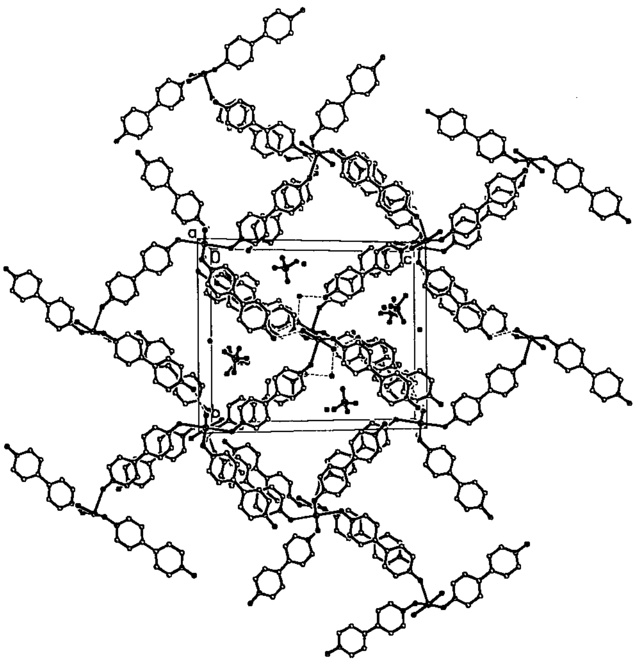


Figure 5. 2D sheet with rectangular channel yielded through hydrogen bonding and $\pi-\pi$ interactions in **3**.

[O7$\cdots$O11a = 2.520 Å; O8$\cdots$O12b = 2.554 Å; a = $-x + 1$, $-y + 1$, $-z$; b = $x + 1$, $0.5 - y$, $1.5 + z$] and $\pi-\pi$ interactions [center-to-center and interplane distances being 4.326 and 3.421 Å, respectively] with the bridging dpdo of adjacent trinuclear cluster. One end terminal dpdo (denoted as N4) is overlapped with a central one (N6) through intermolecule hydrogen bonds [O6$\cdots$O11a = 2.651 Å; O4$\cdots$O13 = 2.590 Å; a = $-x + 1$, $-y + 1$, $-z$; b = $x + 1$, $0.5 - y$, $1.5 + z$] and $\pi-\pi$ interactions [center-to-center and interplanar distances being 3.808 and 3.422 Å, respectively]. Meanwhile, another one generates the $\pi-\pi$ interactions [center-to-center and interplane distances being 4.374 and 3.487 Å, respectively] with a neighboring central terminal dpdo (N6). In this way, these adjacent fish-bone units are connected by intermolecular $\pi-\pi$ interactions, giving a 2D (4,4) sheet (Figure 5). A large rectangular channel with dimensionality of 12.98 Å × 13.44 Å, parallel to the [100] direction, is produced, in which water molecules and perchlorate anions are accommodated through O$-$H$\cdots$O hydrogen bonding or weak C$-$H$\cdots$O hydrogen bonding.

One-Dimensional Polymer. Compound **4** contains one Cu ion, four water molecules, three 4,4′-dpdo ligands, and two ClO_4^- anions. One 4,4′-dpdo molecule functions as a bridge to connect two Cu ions, leading to a 1D covalently linked chain running along the [100] direction. Each Cu^{2+} ion is located on a symmetry center and octahedrally coordinated with four aquo ligands [mean Cu$-O_{aqu}$ = 1.958(2) Å] and two 4,4′-dpdo oxygen atoms [Cu$-$O1 = 2.407(2) Å] in trans position. The N1$-$O1$-$Cu1 bond angle is 107.87(13)°. Thus, a zigzag Cu$-$4,4′-dpdo$-$Cu chain with a Cu$\cdots$Cu separation of 11.83 Å is formed.

These adjacent zigzag chains are further connected through hydrogen bonding [O5$\cdots$O1a = 2.736 Å, O5$-$H4$\cdots$O1a = 163.43°; a = $-x - 1$, $-y$, $-z$] between the bridging 4,4′-dpdo ligands and coordinated water molecules of neighboring chains, leading to a 2D structural motif in the $a-b$ plane as illustrated in Figure 6. These 2D sheets are linked into a 3D network through double hydrogen bonds [O4$\cdots$O3b = 2.630 Å, O4$-$H1$\cdots$O3b = 173.16°; O5$\cdots$O3 = 2.613 Å, O5$-$H3$\cdots$O3 = 163.68°; b = $x + 1$, y, z] produced by a single hydroxyl group of four coordinated water molecules and one noncoordinated 4,4′-dpdo molecule, forming a large channel parallel to the [110] direction with Cu$\cdots$Cu separations through double hydrogen bonds being 16.0 Å (Figure 8a). Alternatively, the three-dimensional network may be regarded as a result of interweaving the two sets of sheets. One is that mentioned above (Figure 6), and the other is generated by the uncoordinated 4,4′-dpdo and hydrated Cu(II) ions through hydrogen bonding along the [111] direction as shown in Figure 7. Meanwhile, these 2D sheets (Figure 6) are also connected by another solvated 4,4′-dpdo through single hydrogen bonding [O4$\cdots$O2 = 2.548 Å, O4$-$H2$\cdots$O2 = 151.11°] with coordinated water molecules and two end oxygen atoms along the [001] direction, leading to a one-dimensional channel with intermetal connections 11.83 Å × 16.50 Å (Figure 8b). It is notable that these hydrogen-bonding interactions are considerably strong, which facilitate to cosolidify the framework backbone. In addition, these metal$-$metal distances are significantly larger than those organized by 4,4′-bipy, such as $[Zn(H_2O)_4(4,4'\text{-bipy})][NO_3]_2\cdot4,4'$-bipy, $[Cu(4,4'\text{-bipy})(H_2O)_2(ClO_4)_2]\cdot4,4'$-bipy, and $[Cu(4,4'\text{-bipy})(H_2O)_2(BF_4)_2]\cdot4,4'$-bipy.[20]

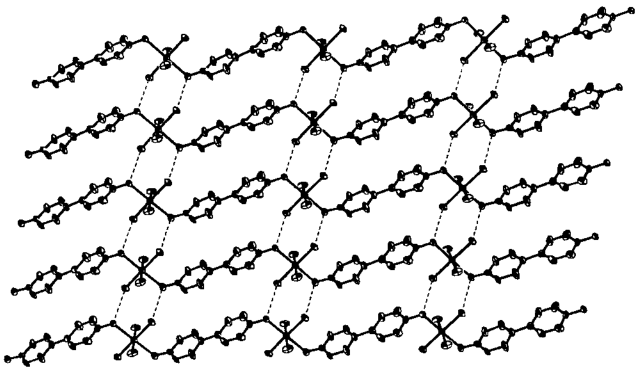


Figure 6. 2D sheet formed through hydrogen bonding between bridging 4,4′-dpdo ligands and coordinated water molecules in the [110] plane in **4**.

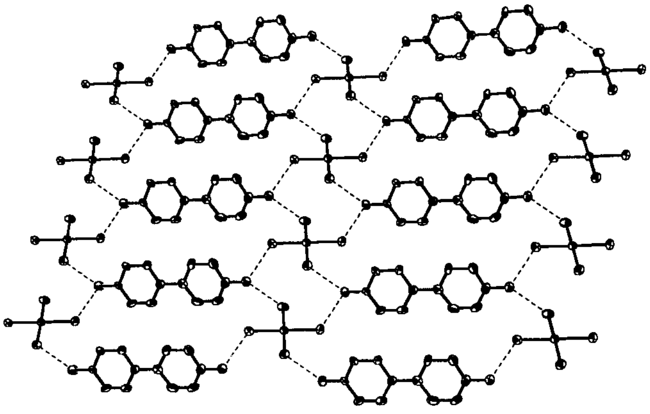


Figure 7. 2D sheet formed through hydrogen bonding between one solvated 4,4′-dpdo ligand (N3) and coordinated water molecules in the [111] plane in **4**.

An interesting feature is that the whole structure may be described as a three-dimensional net fused by two three-dimensional open frameworks as shown in Figure 8a,b. The two sets of networks cross over to yield a triangular channel

---

[20] (a) Carlucci, L.; Ciani, G.; Proserpio, D. M.; Sironi, A. *J. Chem. Soc., Dalton Trans.* **1997**, 1801. (b) Blake, A. J.; Hill, S. J.; Hubberstey, P.; Li, W. S. *J. Chem. Soc., Dalton Trans.* **1997**, 913. (c) Chen, X. M.; Tong, M. L.; Luo, Y. J.; Chen, Z. N. *Aust. J. Chem.* **1996**, *49*, 835.

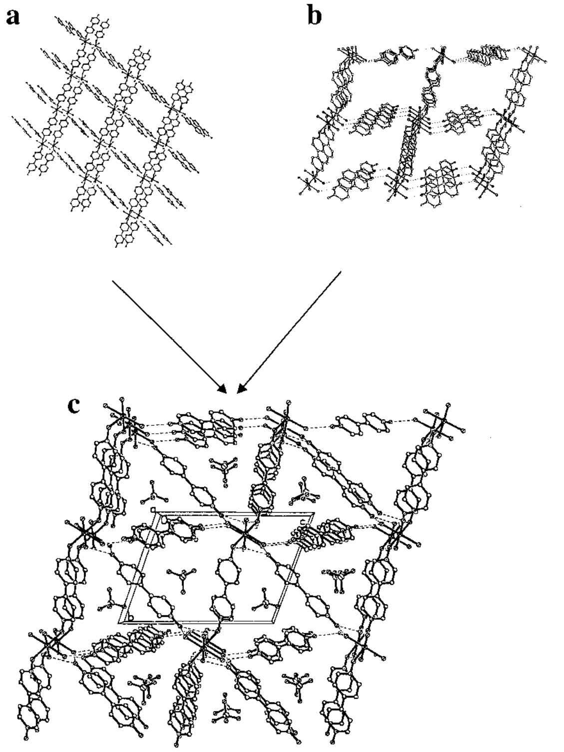


Figure 8. (a) 3D network generated through covalent chain and one solvate dpdo ligand (N3) with a large channel parallel to the [110] direction. (b) 3D network generated through covalent chain and one solvate dpdo ligand (N2) with a large channel parallel to the [100] direction. (c) A 3D framework interwoven by two sets of networks (Figure 8a,b) in **4**. ClO_4^- anions are included within these channels.

(Figure 8c). ClO_4^- anions are anchored within these channels through weak C−H···O hydrogen bonding with the C···O distances being within the ranges 3.287−3.373 Å.

Two pyridyl groups of three 4,4′-dpdo ligands are completely coplanar. No significant $\pi-\pi$ stackings are found between these 4,4′-dpdo molecules. All the four coordinated water molecules form double acceptor hydrogen bonds with three 4,4′-dpdo molecules.

A striking feature of compound **4** lies in its 3D interwoven network formed by strong, rich, and efficient hydrogen bonding. It also indicates that the dpdo ligand is a good candidate to assemble organic−inorganic hybrid open frameworks involving hydrogen bonding.

Two-Dimensional Sheet. From **1** to **4**, the compounds display ion pair, mononuclear, trinuclear, and 1D motifs, respectively. Subsequently, we attempted to prepare the 2D or 3D compounds by increase of the ligand/metal ratio (≥10:1), but failed. So, the second ligand, 4,4′-bipy, having stronger coordination ability, was introduced to increase the dimensionality. It turned out that compound **5** was obtained. It consists of a 2D microporous open framework formed by a parallelogram cavity as illustrated in Figure 9. The Cu moiety has a planar square coordination geometry with N_2O_2 donors and has a weak bonding interaction with the water molecules in axial positions [Cu1−O3a = 2.638(3) Å], giving a 4 + 2 environment. The Cu ions are bridged by 4,4′-bipy along the [010] direction [Cu1−N4b = 1.989(4) Å, Cu1−N3 = 1.991(3) Å], yielding a linear chain. These adjacent chains are further linked through 4,4′-dpdo in a zigzag form [Cu1−O1 = 1.968(2) Å], leading to a 2D sheet in the (011) plane with an interlayer separation of 6.83 Å, in which the 4,4′-dpdo adopts a trans connection fashion. Thus, a large channel parallel to the crystallographic [100] axis with approximate dimensionality 11.1 Å × 12.6 Å between the neighboring metal centers remains, in which one solvate dpdo ligand and two ClO_4^- anions are accommodated (Figure 10a). Allowing for the van der Waals radii, the free pore volume of the structure is 40.6% based on the literature calculation

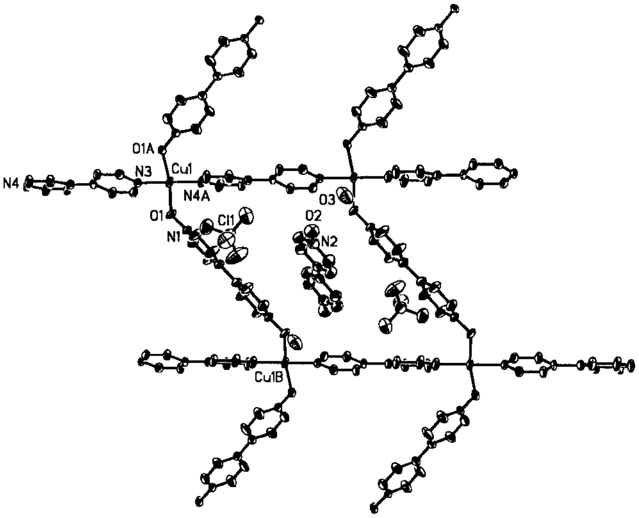


Figure 9. An ORTEP drawing of a parallelogram unit in **5**.

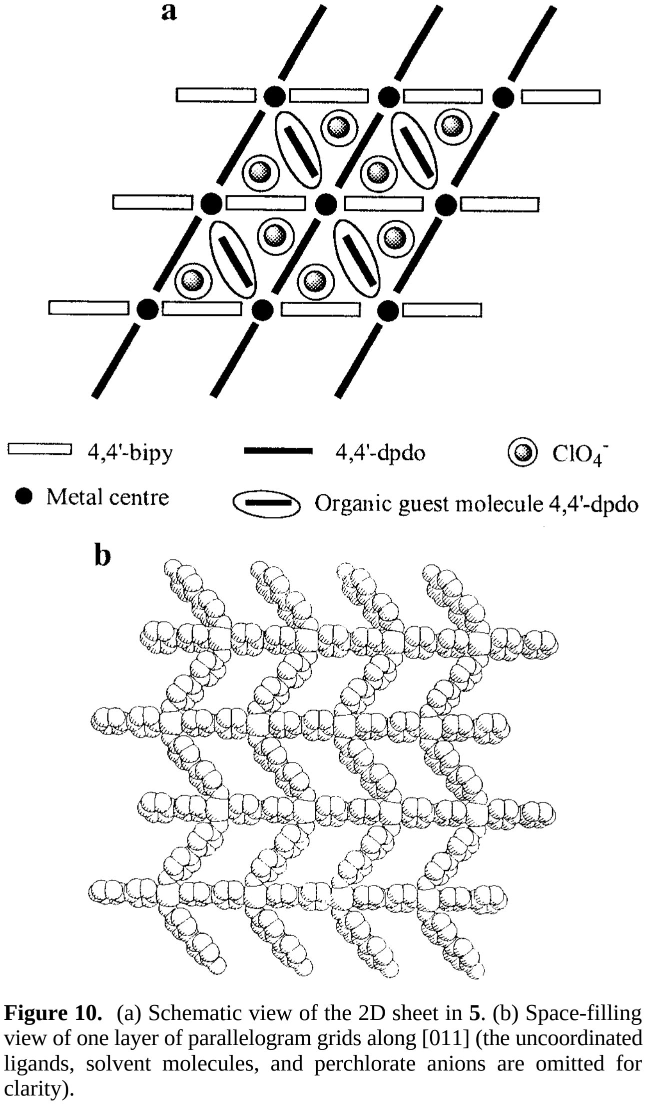


Figure 10. (a) Schematic view of the 2D sheet in **5**. (b) Space-filling view of one layer of parallelogram grids along [011] (the uncoordinated ligands, solvent molecules, and perchlorate anions are omitted for clarity).

approach,[21] which is considerably large among microporous networks.[22] The parallelogram units do not arrange in the common stacked form observed in the network built with linear ligand,[23] but array in an interlaced fashion, leading to a less common parallelogram grid (Figure 10b).

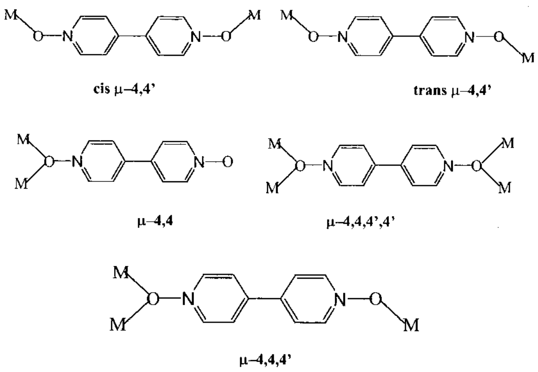
The uncoordinated 4,4′-dpdo molecule as a guest inclinedly interpenetrates within the channel with 51.4° between the molecular plane and the layer plane. It is anchored in the cavity by stronger hydrogen bonding with a water molecule [O3···O2 = 2.675 Å; O3−H2···O2 = 165.35°] and significant $\pi-\pi$ stacking with the 4,4′-dpdo edge (interplane distance 3.33 Å). That the compound selectively includes 4,4′-dpdo rather than 4,4′-bipy under the existence of both reveals the fact that the former has a strong capability of forming hydrogen bonds. Two 4,4′-dpdo ligands (denoted as N1, N2) are related with an inversion center, and two pairs of pyridyl groups are coplanar, whereas that of 4,4′-bipy intersects at 15.57(6)°. This difference may be attributed to the host−guest interactions. The planar arrangement favors two dpdo molecules to participate in the $\pi-\pi$ stacking.

A thermal gravimetric analysis shows a weight loss at 147 °C, corresponding to the loss of two water molecules per formula unit (observed 4.16%; calculated 4.33%). The uncoordinated and coordinated ligands are lost simultaneously at 340 °C, indicating higher thermal stability of the compound. This can be ascribed to the stronger host−guest interactions. Although the removal of water molecules makes the hydrogen bonding of uncoordinated 4,4′-dpdo ineffective, the $\pi-\pi$ stacking between uncoordinated and coordinated 4,4′-dpdo and the weak C−H···O hydrogen bonding generated through uncoordinated 4,4′-dpdo and 4,4′-bipy (O2···H11 = 2.904 Å, C11−H11···O2 = 155.71°) are still operative and cause the host and guest to hold together tightly.

It is noted that compound **5** is the first two-dimensional network bridged from dual N,N′ and O,O′ donors and also serves as the first case of assembling the microporous framework clathrated large organic molecule by linear and angular spacers. Although a number of open frameworks having rigid and large cavities were reported, the studies were mainly restricted to the assembly based on the single supporting ligand, and very few frameworks housed larger organic guest molecules.[24]

The Features of 4,4′-dpdo. Compared with 4,4′-bipy, the features of dpdo for the use of constructing supramolecular frameworks are striking and significant. (a) Bridging mode: 4,4′-bipy has only one linear bridging mode, whereas, at least in principle, there might be five kinds of connection modes for 4,4′-dpdo as listed in Scheme 1. The cis and trans modes have been observed in **3**, **4**, and **5**, respectively. We believe that other modes will emerge with the increasing number of dpdo complexes. (b) Hydrogen bonding: 4,4′-bipy usually forms single hydrogen bonds, while dpdo may form double hydrogen bonds, and hydrogen-bonding modes are more rich and various. Even when it is coordinated to metal ions, its remaining lone pair of electrons may form hydrogen bonds with neighboring hydrogen-bond donors, leading to an extended structure. Additionally, these hydrogen-bonding interactions are considerably strong due to the participation of the strongly polarized NO group. Most of them fall in the range 2.65−2.75 Å. (c) Thermal stability: The melting point of dpdo is ca. 100 °C higher than that of bipy. It is more likely to obtain the stable solid framework for the higher melting point precursor. The higher thermostabilization is a precondition of converting microporous frameworks to practical functional materials.[25]

Scheme 1. Possible Bridging Modes for the dpdo Ligand



Conclusion

The series of copper complexes **1**−**5** with the dpdo ligand have been prepared and structurally characterized. They showed ion pair, mononuclear, trinuclear, 1D, and 2D structural motifs, respectively. That is, we have succeeded in the assembly of supramolecular compounds from lower to higher dimensionality. They possess hydrogen-bonded supramolecular architecture or microporous open frameworks. The features of the dpdo ligand—strong hydrogen-bonding ability, longer spacer, and flexible connection modes—have been fully embodied in these compounds. Compound **3** exhibits the first cluster structure for bifunctional 4-pyridyl ligands, and compound **5** gives a rare example of a microporous framework constructed by mixed rodlike ligands.

We must mention that the introduction of a NO group into the crystal engineering plays a significant role in tailoring the topology and architecture of solid materials. The reported the auxiliary pillars constructing the open frameworks have been mainly focused on the N,N′ donors containing 4-pyridyl groups.[26] Initially, it is likely that the interest can be stimulated to develop a novel family of O,O′-rodlike supporting spacers based on numerous bidentate 4-pyridyl ligands. The further synthesis for the related compounds based on this kind of O,O′-bifunctional ligand is under way.

Acknowledgment. Financial support was provided by the National Natural Science Foundation of China (No. 20023005, 29831010), National Key Project for Fundamental Research (G1998061305), and the Excellent Young Teachers Fund of MOE, P.R.C.

Supporting Information Available: Four figures of molecular and crystal structures for **1**, **4**, and **5**. An X-ray crystallographic file, in CIF format. This material is available free of charge via the Internet at http://pubs.acs.org.

IC0104712

---

(21) Yaghi, O. M.; Davis, C. E.; Li, G.; Li, H. *J. Am. Chem. Soc.* **1997**, *119*, 2861.

(22) Biradha, K.; Domasevitch, K. V.; Hogg, C.; Moulton, B.; Power, K. N.; Zaworotko, M. J. *Cryst. Eng.* **1999**, *2*, 37 and references therein.

(23) Carlucci, L.; Ciani, G.; Proserpio, D. M. *New J. Chem.* **1998**, 1319.

(24) (a) Tong, M. L.; Chen, X. M.; Yu, X. L.; Mak, T. C. W. *J. Chem. Soc., Dalton Trans.* **1998**, 5. (b) Kiang, Y. H.; Gardner, G. B.; Lee, S.; Xu, Z. T.; Lobkovsky, E. B. *J. Am. Chem. Soc.* **1999**, *121*, 8204. (c) Biradha, K.; Donmasevitch, K. V.; Moulton, B.; Seward, C.; Zaworotko, M. J. *Chem. Commun.* **1999**, 1327. (d) MacGillivray, L. R.; Groeneman, R. H.; Atwood, J. L. *J. Am. Chem. Soc.* **1998**, *120*, 2676.

(25) Yaghi, O. M.; Li, H.; Davis, C.; Richardson, D.; Groy, T. L. *Acc. Chem. Res.* **1998**, *31*, 474;

(26) Hagrman, P. J.; Hagrman, D.; Zubieta, J. *Angew. Chem., Int. Ed.* **1999**, *38*, 2638 and references therein.