[5] Crystal data for **1**: Crystal dimensions 0.60 × 0.50 × 0.50 mm³, $C_{66}H_{24}Cl_{24}Cr_2O_{12}S_{24}$, $M_r = 2733.21$, triclinic, $P\bar{1}$, $a = 12.4074(9)$, $b = 14.554(1)$, $c = 15.270(2)$ Å, $\alpha = 117.193(4)$, $\beta = 97.7640(9)$, $\gamma = 96.0637(8)°$, $V = 2386.0(3)$ Å³, $Z = 1$, $\rho_{calcd} = 1.902\ g\,cm^{-3}$, $2\theta_{max} = 55.1°$, $Mo_{K\alpha}$, $\lambda = 0.71069$ Å, ω scan, 296 K, 10915 independent reflections, number of reflections included in the refinement = 7092 ($I > 4.0\sigma(I_0)$), and $R(wR) = 0.037(0.048)$. The intensity data were collected on a Rigaku mercury CCD area detector. Empirical absorption correction was performed by using the program REQABA.[6a] The structures were solved by direct methods (SIR92).[6b] All the calculations were performed by using the teXsan crystallographic software package from the Molecular Structure Corporation.[6c] Crystallographic data (excluding structure factors) for the structure reported in this paper have been deposited with the Cambridge Crystallographic Data Centre as supplementary publication no. CCDC-165306 (**1**). Copies of the data can be obtained free of charge on application to CCDC, 12 Union Road, Cambridge CB21EZ, UK (fax: (+44) 1223-336-033; e-mail: deposit@ccdc.cam.ac.uk).

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[7] Intermolecular Cl···S contacts; Cl(1)···S(1) 3.541(2) (I···A; $-x-2$, $-y-1$, $-z-2$), Cl(1)···S(2) 3.646(2) (I···A; $+x$, $+y$, $+z$), Cl(5)···S(9) 3.510(1) (II···B; $+x$, $+y-1$, $+z$), Cl(5)···S(10) 3.677 (2) (II···C; $-x-2$, $-y-1$, $-z-1$), Cl(8)···S(5) 3.610(1) (II···B; $+x$, $+y$, $+z$), Cl(12)···S(1) 3.632 (2) (II···C; $+x$, $+y$, $+z$) Å (sum of the van der Waals radii of Cl and S is 3.65 Å).

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[11] The measurement of the resistivity was carried out by the four-probe dc method using gold wire contacted to a gold electrode deposited on the surface of the single crystal by thermal evaporation. The wires were fixed to four gold contacts arranged linearly using gold paint.

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A Pillared-Layer Coordination Polymer Network Displaying Hysteretic Sorption: $[Cu_2(pzdc)_2(dpyg)]_n$ (pzdc = Pyrazine-2,3-dicarboxylate; dpyg = 1,2-Di(4-pyridyl)-glycol)**

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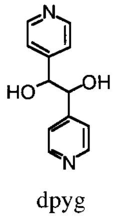
Recently developed porous coordination polymers have added a new dimension to materials-directed coordination chemistry; applications of these compounds range from gas storage and ion exchange to heterogeneous catalysis.[1–4] The key to this success is the establishment of permanent porosity even in the absence of guest molecules as well as inorganic zeolites, to afford the desired robust three-dimensional (3D) frameworks of metal ions and organic ligands. The next challenge is to develop a dynamic porous compound, a so-called third-generation compound,[5] which responds to a specific guest molecule and changes its microcavities into those well-suited for the shape and/or affinity of the guest molecule. Metal complex based compounds in this category are emerging[6–10] but still few. Herein, we have focused on developing the rational design and synthesis of this kind of framework. We have employed a pillared-layer motif because simple modification of the pillar module can control not only the channel size and shape but also the chemical functionality. The prototype structure was obtained by using Cu^{2+}, Na_2pzdc (pzdc = pyrazine-2,3-dicarboxylate), and a series of pillar ligands of pyridine derivatives.[11] We designed the new pillared-layer type coordination polymer with 1,2-dipyridylglycol (dpyg) as a flexible and functional pillar, and examined guest (CH_4, MeOH, and H_2O) inclusion properties.



dpyg

$[\{[Cu_2(pzdc)_2(dpyg)]\cdot 8H_2O\}_n]$ (**1**) was synthesized by the reaction of $Cu(ClO_4)_2\cdot 6H_2O$ with Na_2pzdc and dpyg in H_2O/EtOH media. The molecular structure of **1** was determined by X-ray crystallography, and Figure 1 shows the structure around the Cu^{II} centers. Each Cu^{II} atom is five-coordinate, residing in a distorted trigonal-bipyramidal environment, surrounded by three O atoms from three pzdc ligands, and two N atoms from a dpyg and a pzdc ligand. The $Cu_2(\mu\text{-}O)_2$ units are linked by the pzdc ligands to give a neutral two-dimensional layer in the *bc* plane (Figure 2a). The dpyg

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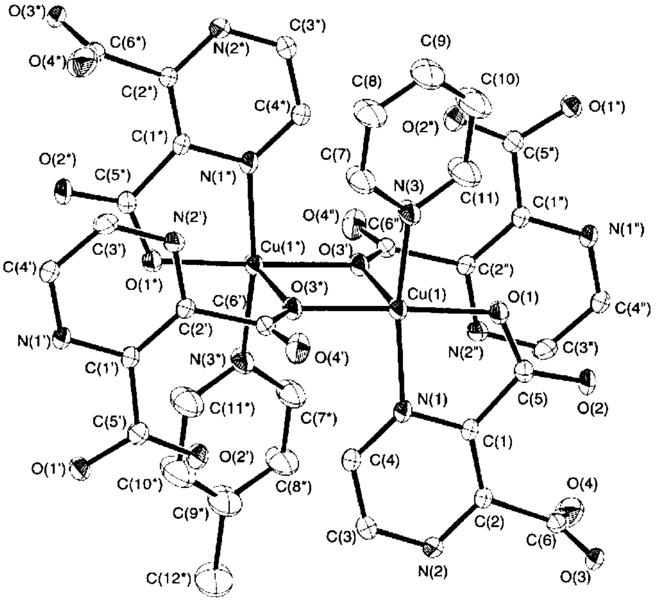

Figure 1. Molecular structure of the dicopper sites of **1** (ORTEP drawing with 30% probabilities). Hydrogen atoms and OH groups are omitted for clarity. Selected bond lengths [Å] and angles [°]: Cu(1)-O(1) 1.928(4), Cu(1)-O(3′) 1.973(3), Cu(1)-O(3*) 2.494(4), Cu(1)-N(1) 2.022(4), Cu(1)-N(3) 2.003(4); O(1)-Cu(1)-O(3′) 172.3(2), O(1)-Cu(1)-O(3*) 96.1(2), O(1)-Cu(1)-N(1) 81.8(2), O(1)-Cu(1)-N(3) 90.6(2), O(3′)-Cu(1)-O(3*) 77.5(1), O(3′)-Cu(1)-N(1) 94.3(2), O(3′)-Cu(1)-N(3) 94.1(2), O(3*)-Cu(1)-N(1) 94.6(2), O(3*)-Cu(1)-N(3) 94.0(2), N(1)-Cu(1)-N(3) 169.0(2).

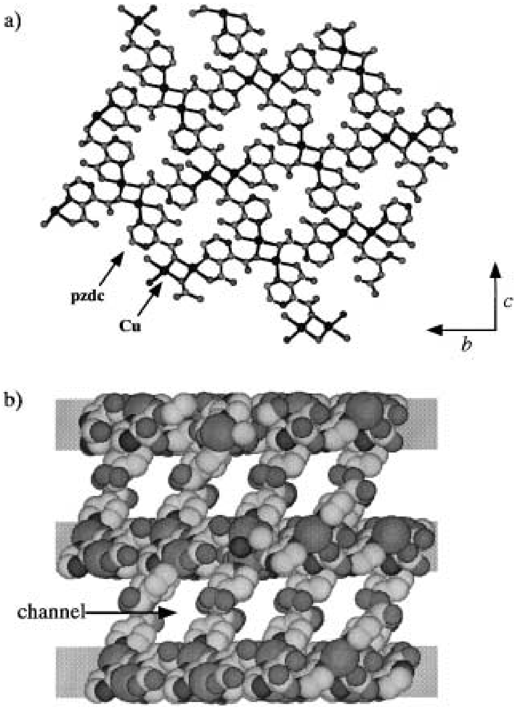

Figure 2. View of the two-dimensional sheet (a) and channel structure (b) of **1**. Solvent water and hydrogen atoms are omitted for clarity.

ligand acts as a pillar; $Cu_2(\mu\text{-}O)_2$ units in the adjacent layers are linked to form a three-dimensional pillared-layer structure (Figure 2b). The OH groups are disordered because of the racemic nature of the dpyg ligands. The framework provides interlayer spaces (ca. 33% porosity), resulting in microchannels with a cross section of 4×6 Å in size.[12] Interestingly, all the OH groups of the dpyg ligands are not utilized for the coordination framework but for coordinating guest molecules in the channel. As a result, **1** includes water molecules, which are hydrogen-bonded to the OH groups as well as to the nearest neighbor water molecules.

The thermogravimetric profile of **1** shows that the on-set of the release of the crystalline water molecules occurs at 60 °C, and that the structure decomposition occurs at 220 °C. No weight change was observed between 140 °C and 220 °C, where a guest-free phase (anhydrous **1**, therefore apohost **2**), is maintained. Figure 3 shows the X-ray powder diffraction (XRPD) patterns of **1** and **2**. The XRPD pattern of **2** has sharp diffraction peaks, indicating that the porous framework is maintained even without guest molecules. The initial framework of **1** undergoes a slight change to become that of **2**; for instance, a peak (100) at 6.80° for **1** moves to 7.10° for **2**, exhibiting a slight decrease in the layer distance. In practice, the original framework is completely reformed when immersed in H_2O or MeOH. It should be emphasized that this transformation of crystal **2** to crystal **1** occurs even when exposed to H_2O or MeOH vapor. Consequently, this structural change can take place reversibly in the process of evacuation under reduced pressure/exposure to the guest vapors.

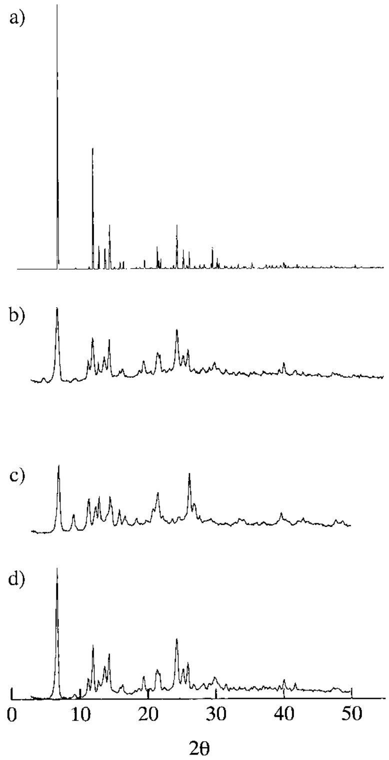

Figure 3. a) Simulated XRPD pattern upon removal of the water molecules from the single crystal. Observed XRPD patterns of as-synthesized sample **1** (b), anhydrous sample **2** (dried at 110 °C under reduced pressure for 5 h) (c), and MeOH immersed sample after drying (d)

We measured the adsorption isotherms for CH_4, H_2O, and MeOH to examine the porous properties. The adsorption isotherm of CH_4 for **2** at 298 K reveals no uptake into the micropores at all, indicating that the channel of **2** is not large enough to incorporate CH_4 molecules (3.8×3.8 Å). On the other hand, MeOH, irrespective of its similar size to that of CH_4, can be adsorbed, as well-illustrated in Figure 4. The isotherm shows a sudden rise at point A (relative pressure, P/P_o, is 0.23) and attains a saturated level (ca. 6.2 mmol g^{-1}) at point B ($P/P_o = 0.5$). On the other hand, the desorption isotherm does not trace the adsorption one any more, instead, showing an abrupt drop at point C ($P/P_o = 0.1$). This hysteretic profile between the adsorption and desorption isotherms was reproducible many times. This sharp adsorption jump/desorption drop with the hysteresis indicates the occurrence of a framework transformation in the crystal state, which should permit guest inclusion.[13, 14] The BET surface area calculated from the adsorption isotherm in the region between zero and point A is 37 m^2 g^{-1}. Thus only surface adsorption for MeOH as well as CH_4 occurs before the point A. Then, after point A, MeOH molecules can diffuse into the channels, whereas CH_4 molecules do not. This is chiefly associated with the hydrogen bonding interaction between the MeOH molecules and the OH groups of the dpyg ligands; the attractive force should be strong enough to transform the channel structure to allow the incorporation of the guest molecules. The structural distortion is confirmed by the XRPD measurements shown in Figure 3. A similar adsorption isotherm with a hysteresis profile is observed in the case of H_2O vapor. The estimated micropore volume from the MeOH adsorption isotherm is 0.25 mL g^{-1},[15] indicating that MeOH vapor is included in the porous network.

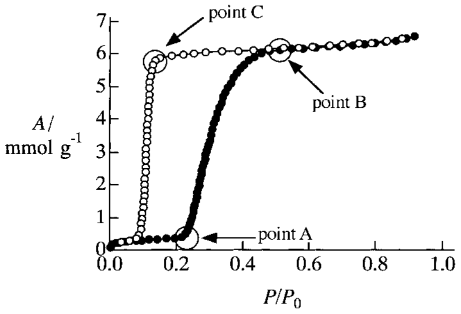

Figure 4. Methanol adsorption (filled circles) and desorption (open circles) isotherms at 298 K. A = absolute absorption.

The use of a pillared layer motif for the rational synthesis of a novel coordination polymer that displays a hysteretic isotherm, which is based on the response of the flexible and dynamic framework to specific guest molecules, opens up a new field in porous coordination materials.

Experimental Section

1: $Cu(ClO_4)_2 \cdot 6H_2O$ (0.37 g) in H_2O/EtOH (1:1; 100 mL) was slowly added to a solution of dpyg (0.21 g) and Na_2pzdc (0.21 g) in H_2O/EtOH (1:1; 100 mL). The blue microcrystals obtained were collected by filtration, and dried under reduced pressure for 5 h. Finally, apohost **2** was obtained. Yield 0.37 g (55 %). Elemental analysis calcd for $C_{24}H_{16}Cu_2N_6O_{10}$ (%): C 42.67, H 2.39, N 12.44; found: C 41.22, H 2.31, N 12.48.

X-ray structure determination of **1**: Measurements were recorded on a Rigaku mercury CCD diffractometer with graphite-monochromated $Mo_{K\alpha}$ radiation. All calculations were performed by using the teXsan crystallographic software package from the Molecular Structure Corporation. Crystal data: $C_{24}H_{12}Cu_2N_6O_{18}$, $M_r = 799.48$, monoclinic, space group $P2_1/c$ (no. 14), $a = 13.1990(9)$, $b = 13.631(2)$, $c = 9.650\ (3)$ Å, $\beta = 104.556(1)^\circ$, $V = 1680.5(4)$ Å^3, $T = 298$ K, $Z = 2$, $\rho_{calcd} = 1.580$ g cm^{-3}, $\lambda(Mo_{K\alpha}) = 0.71069$ Å, $F(000) = 800$, $\mu(Mo_{K\alpha}) = 13.4$ cm^{-1}, $2\theta_{max} = 55.2^\circ$, 3719 reflections measured, 2638 observed ($I > 2.00\sigma(I)$), 215 parameters; $R = 0.071$, $R_w = 0.095$. Crystallographic data (excluding structure factors) for the structure reported in this paper have been deposited with the Cambridge Crystallographic Data Centre as supplementary publication no. CCDC-168595. Copies of the data can be obtained free of charge on application to CCDC, 12 Union Road, Cambridge CB21EZ, UK (fax: (+44)1223-336-033; e-mail: deposit@ccdc.cam.ac.uk).

Gas adsorption measurements: The sorption isotherm measurements for MeOH and H_2O were performed at 298 K by using an automatic volumetric adsorption apparatus (BELSORP18; BEL inc). A known weight (200–300 mg) of the as-synthesized sample was placed in the quartz tube, then, prior to measurements, the sample was dried under high vacuum at 373 K for 5 h to remove the solvated water molecules. The adsorbate was placed into the sample tube, then the change of the pressure was monitored and the degree of adsorption was determined by the decrease of the pressure at the equilibrium state.

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