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Rational Synthesis of Stable Channel-Like Cavities with Methane Gas Adsorption Properties: $[\{Cu_2(pzdc)_2(L)\}_n]$ (pzdc = pyrazine-2,3-dicarboxylate; L = a Pillar Ligand)**

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The synthesis and characterization of coordination networks with channel structures that provide new sizes, shapes, and chemical environments are of great current interest.[1–5] This is not only because of their intriguing structural diversity, but also because of their potential for applications in molecular adsorption, ion exchange, and heterogeneous catalysis.[2, 6–10] However, the synthesis of such functional porous networks is often unsuccessful, because of the formation of an interpenetrating structure, which provides only small-sized channels or none at all.[1, 11–17] Another reason could be the deformation of the channel structure on the removal of the included guest molecules.

Although several porous structures have been reported, the methods for synthesizing stable porous networks are still in their infancy. Some successful examples of multidimensional networks that have been synthesized and structurally characterized to date are: $[\{M_2(4,4'\text{-bpy})_3(NO_3)_4\}_n]$ (M = Co, Ni, Zn; 4,4′-bpy = 4,4′-bipyridine),[18] $[\{Ag(teb)(CF_3SO_3)\}_n]$ (teb = 1,3,5-tris(3-ethynylbenzonitrile)benzene),[19] $[\{Zn_2(btc)(NO_3)\cdot(H_2O)(C_2H_5OH)_5\}_n]$ (btc = 1,3,5-benzenetricarboxylate),[1] and $[\{Zn_3(bdc)_3\cdot 2\,CH_3OH\}_n]$ (bdc = 1,4-benzenedicarboxylate).[20]

It has been demonstrated that the pillared-layer structure is effective for the construction of three-dimensional networks with large channels.[21] Although this type of network has been investigated in the hydrogen-bonded assembly of organic molecules, the organic pillared-layer structures obtained are unstable in the absence of included guest molecules.[21, 22] In comparison, coordination networks give more stable struc-

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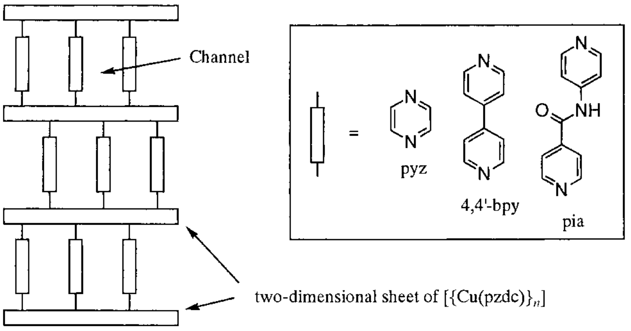
[**] This work was supported by the Kao Foundation for Arts and Science and a Grant-in-Aid for Scientific Research from the Japanese Ministry of Education, Science and Culture.

Supporting information for this article is available on the WWW under http://www.wiley-vch.de/home/angewandte/ or from the author.

tures.[22] We have developed a new method for synthesizing stable pillared-layer structures using coordination networks (Scheme 1), and have succeeded in the syntheses of porous materials with various new channel properties. Complex **1** was prepared by the reaction of $Cu(ClO_4)_2 \cdot 6H_2O$ with Na_2pzdc and pyrazine in water. The crystal structure of this complex was determined by X-ray crystallography, and Figure 1 shows the ORTEP drawing around the Cu^{II} center; three carboxylate oxygen atoms, one nitrogen atom of pzdc, and one nitrogen atom of pyrazine form a distorted square-pyramidal geometry around the Cu^{II} atom.



Scheme 1. Schematic representation of the pillared-layer structures of $[\{[Cu_2(pzdc)_2(L)] \cdot x H_2O\}_n]$. pzdc = pyrazine-2,3-dicarboxylate; **1**: L = pyz, $x = 2$; **2**: L = 4,4′-bpy, $x = 5$; **3**: L = pia, $x = 5$.

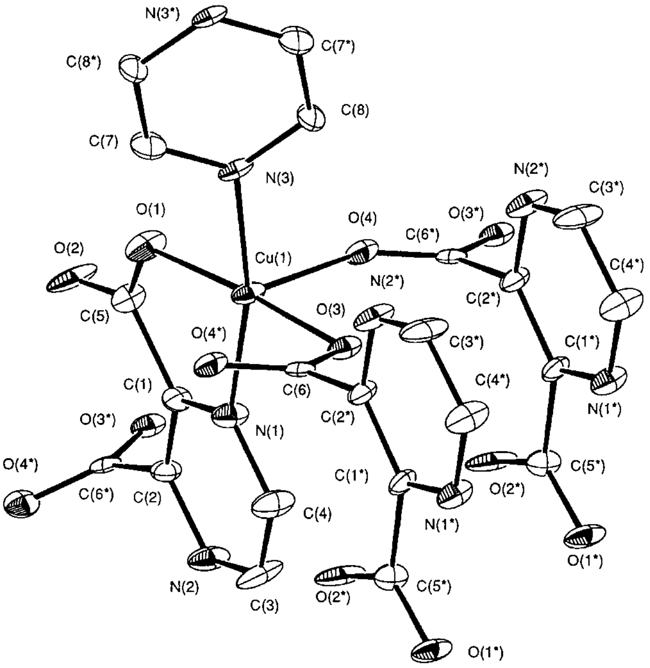


Figure 1. ORTEP drawing of the structure of **1** around the Cu center (30% probability ellipsoids). Hydrogen atoms are omitted for clarity. Selected bond lengths [Å] and angles [°]: Cu(1)–N(1) 1.99(1), Cu(1)–N(3) 2.04(1), Cu(1)–O(1) 1.947(9), Cu(1)–O(3) 1.973(8), Cu(1)–O(4) 2.21(1); N(1)-Cu(1)-N(3) 167.8(5), N(1)-Cu(1)-O(1) 81.9(4), N(1)-Cu(1)-O(3) 95.9(4), N(1)-Cu(1)-O(4) 86.8(4), N(3)-Cu(1)-O(1) 91.0(4), N(3)-Cu(1)-O(3) 90.6(4), N(3)-Cu(1)-O(4) 103.2(4), O(1)-Cu(1)-O(3) 176.0(4), O(1)-Cu(1)-O(4) 90.4(4), O(3)-Cu(1)-O(4) 92.9(4).

This complex consists of a two-dimensional sheet of $[\{Cu(pzdc)\}_n]$ and pillar pyrazine ligands that bridge each sheet. The pzdc unit links the three Cu^{II} atoms; one nitrogen atom from pzdc and one oxygen atom from the carboxylate group chelate with the Cu^{II} atom, while each oxygen atom of the other carboxylate group forms a monodentate ligand with two Cu^{II} atoms. The remaining nitrogen atom from pzdc does not associate with any other atoms. As a result, an extended neutral two-dimensional sheet is formed in the *ac* plane (Figure 2). The sheet has a puckered structure with a thickness of about 7.5 Å; it has has no large cavities, and forms no interpenetrating networks.

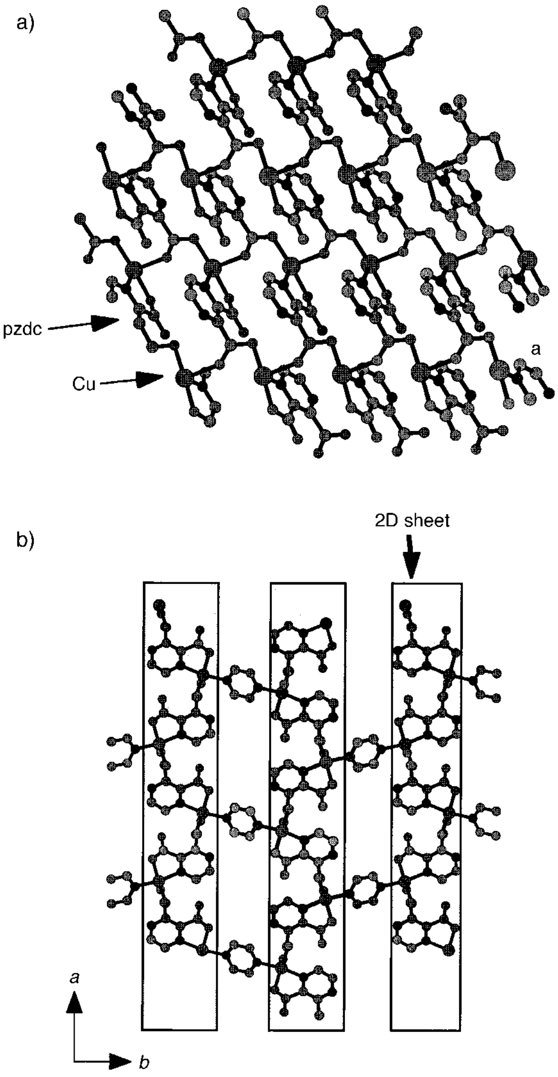


Figure 2. a) View of the two-dimensional sheet. b) Crystal structure of **1** along the *c* axis. Solvent water molecules and hydrogen atoms are omitted for clarity.

Coordination of the pyz ligands to the Cu^{II} atoms provides a pillared-layer structure, in which each two-dimensional sheet is separated by about 3 Å (Figure 2b). The regular arrangement of the pillar ligands along the *a* axis with spacings of 11 Å creates extended channels along the *c* axis with dimensions of about 4 × 6 Å.[23] These channels are occupied by water molecules which are linked with carboxylate oxygen atom (O(2)) through a hydrogen-bonding interaction (O(5)–O(2) 2.91(1) Å).

The dimensions and characteristics of channel structures of this network are apparently controllable depending on the kinds of pillar ligands used. This new adaptable structure prompted us to construct coordination networks with new channel properties in which sizes and chemical environments could be varied. For this purpose, two pillar ligands, 4,4′-bpy and pia were selected; the former provides larger pore sizes, while the latter creates larger channels with specific hydrogen bonding interaction sites for guest molecules. These two complexes were successfully synthesized by using similar procedures for the preparation of **1**, and obtained as microcrystals. The formation of similar pillared-layer networks was confirmed by elemental analyses and X-ray powder diffraction (XRPD) patterns, whose shifts of the (0*n*0) reflections demonstrate the elongated *b* axes of **2** (29.0 Å) and **3** (32.6 Å) compared with that of **1** (19.849(2) Å). These observations are in agreement with the expected elongation of the corresponding pillar ligands. From these results, the channel dimensions of **2** and **3** are estimated to be about 9 × 6 Å and 10 × 6 Å, respectively.

In order to examine the thermal stability of these porous networks, thermal gravimetric (TG) analyses and measurements of the XRPD patterns were carried out. The TG curve of **1** illustrates release of the included water molecules up to 100 °C, followed by release of ligand molecules from 260 to 310 °C. No chemical decomposition was observed between 100 and 260 °C. The structure of this stable phase was studied by measuring the XRPD pattern at 100 °C under reduced pressure. Figure 3 shows the observed XRPD patterns compared with the simulated powder pattern obtained upon removal of water from the single-crystal model of **1**. The good agreement of the peaks in both diagrams demonstrates that the porous network is retained in this phase, indicating that porosity is retained in the absence of the included guest molecules. Similar stability was also observed for complexes **2** and **3**.

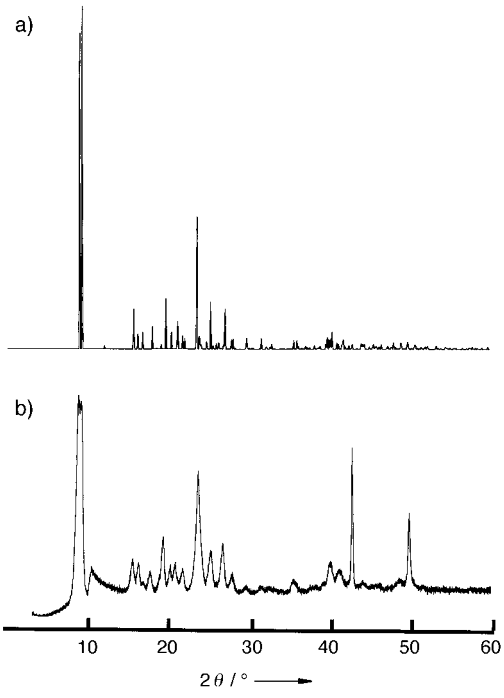


Figure 3. a) Simulated and b) experimental X-ray powder diffraction diagrams of **1** after removal of water.

In order to examine the porous functionality of these synthetic materials, their methane adsorption capabilities were measured. Gas adsorption activity is one of the most attractive properties of porous materials such as zeolites.[24–26] Figure 4 displays the results of the adsorption activity experiments of anhydrous complexes **1**–**3**, which were obtained by drying under vacuum with methane between 1 and 31 atm. A rapid increase in the amount of adsorbed gas is shown by an increase in pressure of up to 5 atm, which represents the diffusion of methane into the channels. These isotherms are of type I according to the IUPAC classification.[27] Approximately 0.8 mmol, 2.5 mmol, and 2.9 mmol of methane were adsorbed per 1.0 g of anhydrous samples of **1**, **2**, and **3**, respectively, at a pressure of 31 atm. The increased methane adsorption activity for **2** and **3** compared to that of **1** is consistent with the larger channel sizes of these complexes. This activity is comparable to that of zeolites[28, 29] and a stable porous network of [M_2(4,4′-bpy)$_3$(NO_3)$_4$] (M = Co, Ni, Zn),[18] which we reported recently.

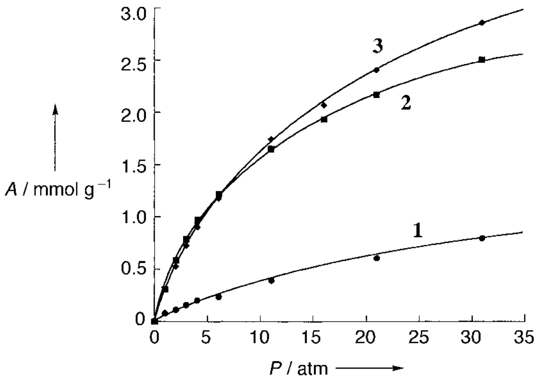


Figure 4. Adsorption isotherms for **1**–**3** obtained with CH_4 between 1 and 36 atm. *A* = absolute adsorption [mmol g^{-1}].

Experimental Section

Synthesis of **1**: Na_2pzdc (0.21 g, 1.00 mmol) in H_2O (20 mL) was slowly added to the H_2O solution (20 mL) containing $Cu(ClO_4)_2 \cdot 6H_2O$ (0.37 g, 1.00 mmol) and pyz (1.0 g, 12.5 mmol). The blue microcrystals obtained were collected by filtration, and dried under reduced pressure for 2 h. Yield 0.26 g (90 %). Elemental analysis calcd for $C_{16}H_{12}Cu_2N_6O_{10}$ (%): C 33.40, H 2.10, N 14.61; found: C 32.78, H 1.57, N 14.34.

Complexes **2** and **3** were prepared analogously in EtOH/H_2O (1/1) media. **2**: Elemental analysis calcd for $C_{22}H_{22}Cu_2N_6O_{13}$ (%): C 37.45, H 3.14, N 11.91; found: C 37.44, H 3.30, N 11.67. **3**: Elemental analysis calcd for $C_{23}H_{23}Cu_2N_7O_{14}$ (%): C 36.90, H 3.10, N 13.10; found: C 37.63, H 3.20, N 12.23.

X-ray structure determination of **1**: All measurements were made on a Rigaku AFC7R diffractometer with graphite-monochromated $Mo_{K\alpha}$ radiation and a 12 kW rotating anode generator. The unit cell constant was obtained from a least-squares refinement using the setting angles of 25 carefully centered reflections with 2θ values in the range of $20.03° < 2\theta < 24.34°$. The structure was solved by direct methods and refined by the block-diagonal least-squares method. Hydrogen atoms except for those in water molecules were placed at calculated positions, but their parameters were not refined. The final refinements were carried out using full-matrix least-squares techniques for non-hydrogen atoms. All calculations were performed using the TEXSAN crystallographic software package of Molecular Structure Corporation. Crystal data: $C_{16}H_{12}Cu_2N_6O_{10}$, $M_r = 575.40$, orthorhombic, space group $P2_1/c$, $a = 4.693(3)$, $b = 19.849(2)$, $c = 11.096(2)$ Å, $\beta = 96.90(2)^\circ$, $V = 1026.1(6)$ Å^3, $Z = 2$, $\rho_{calcd} = 1.862\,g\,cm^{-3}$, $\lambda(Mo_{K\alpha}) = 0.71069$ Å, $F(000) = 576$, $\mu(Mo_{K\alpha}) = 21.43\,cm^{-1}$, $T = 25\,^\circ C$, $2\theta_{max} = 55.1^\circ$, 2447 reflections measured, 934 observed ($I > 2.00\sigma(I)$), number of parameters 155; $R = 0.062$, $R_w = 0.062$. Crystallographic data (excluding structure factors) for the structure reported in this paper have been deposited with the Cambridge Crystallographic Data Center as supplementary publication no. CCDC-103110. 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 adsorption isotherms of CH_4 gas were measured according to the reported procedure.[18, 24, 25] The apparatus was equipped with a Cahn R-100 electrobalance contained within a SUS steel pressure chamber which was connected with two separate lines for evacuation and adsorbate gas pressurization. Prior to adsorption measurement, in order to remove the solvated water molecules, the sample (50–80 mg) was dried under reduced pressure at 25 °C until no further weight loss was observed. The adsorbate CH_4 was dosed into the adsorption chamber, then the change of the weight of the sample was monitored. The entire adsorption isotherms were determined by increasing the adsorbate gas pressure to a maximum of 31 atm.

Received: June 2, 1998
Revised version: August 24, 1998 [Z11933IE]
German version: *Angew. Chem.* **1999**, *111*, 190–193

Keywords: copper · crystal engineering · gas adsorption · microporosity · solid-state structures

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Formation of Supramolecular Polymers from Homoditopic Molecules Containing Secondary Ammonium Ions and Crown Ether Moieties**

Nori Yamaguchi and Harry W. Gibson*

Chemists are extending the concept of self-organizing noncovalent interactions into the field of material science to control and engineer linear and network supramolecular polymers.[1] Such interactions permit reversibility in the polymeric materials at the molecular level to afford thermodynamically controlled suprastructures.[2] This factor is advantageous for producing polymers with the potential for commercial use, since kinetically induced defects in conventional covalently bonded polymers are irreversible.

Strong associations between self-organizing building blocks promote the construction of well-defined supramolecular polymeric materials with properties comparable to covalent polymers.[3] This prompted us to utilize a simple system with dibenzylammonium hexafluorophosphate and dibenzo-[24]crown-8 (DB24C8) units, between which the association constant is desirably high ($K_a = 2.7 \times 10^4\,M^{-1}$ in [D$_3$]chloroform at 25 °C).[4] Association of homoditopic molecules that contain such complimentary units spontaneously leads to reversible chain extension in 1:1 stoichiometric solutions to form linear supramolecular polymers based on pseudorotaxane formation.

The synthetic methodologies employed for the homoditopic molecules are depicted in Scheme 1 and the constructions

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[**] This work was supported by the National Science Foundation (CHE95-21738). The authors thank Prof. H. Marand for his helpful discussions on the thermal analyses of the supramolecular polymers. Mass spectra were provided by the Washington University Mass Spectrometry Resource, an NIH Research Resource (Grant No. P41RR0954).