Inorg. Chem. **2005**, *44*, 4912–4914

Inorganic Chemistry
Communication

Microporous Pillared Paddle-Wheel Frameworks Based on Mixed-Ligand Coordination of Zinc Ions

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Received March 25, 2005

The reaction of $Zn(NO_3)_2 \cdot 6H_2O$, various dicarboxylic acids, and either 4,4′-bipyridine or *N*,*N*′-di(4-pyridyl)-1,4,5,8-naphthalenetetracarboxydiimide produces a family of anisotropic, mixed-ligand, open-framework compounds featuring paddle-wheel-type coordination of Zn(II) pairs in two dimensions and pyridyl ligand pillaring in the third. Despite 2-fold interpenetration, the compounds contain channels of molecular dimensions and several are permanently microporous, displaying high internal surface areas.

Much of the current interest in the rapidly growing field of metal-organic-framework (MOF) materials derives from the potential of microporous crystalline versions of these materials to provide interesting solutions to difficult problems in gas storage,[1] sensing,[2] separations,[3] and catalysis.[4] To engender permanent microporosity, synthesis schemes must avoid both channel clogging (e.g., due to excessive framework interpenetration or unfavorable positioning of counterions) and channel collapse (e.g., upon solvent removal). In many cases, metal dimer or cluster/carboxylate linkages have proven to be sufficiently strong to stabilize networks against collapse,[5,6] whereas metal/pyridine linkages, although widely employed, generally have not stabilized open frameworks against channel collapse. A further drawback of pyridine-only frameworks is that ions required for charge compensation may block any channels obtained. We reasoned that both problems might be overcome by combining pyridine coordination with carboxylate coordination in mixed-ligand framework compounds. We further reasoned that mixed coordination could facilitate the incorporation of functionality. Of particular interest to us are redox reactivity and visible-region light collection and re-emission. Additionally, mixed-ligand compounds might be expected to display useful anisotropic optical, guest-transport, and/or other properties.

Here we report the synthesis and characterization of five examples of mixed-ligand MOF materials. The new compounds make use of robust carboxylate paddle-wheel-type coordination[7] of Zn(II) pairs to define perforated 2D sheets that are pillared with more delicate pyridine/Zn linkages to yield open mixed-ligand frameworks. The compounds can be formulated as $Zn_2L_2L' \cdot$solvent [L = fumaric acid (FMA), **1**; 1,4-benzenedicarboxylic acid (BDC), **2**; 2,6-naphthalenedicarboxylic acid (NDC), **3** and **4**; 1,4-biphenyldicarboxylic acid (BPDC), **5**; L′ = 4,4′-bipyridine (BIPY), **1**−**3**; *N*,*N*′-di(4-pyridyl)-1,4,5,8-naphthalenetetracarboxydiimide (DPNI), **4** and **5**].[8]

Colorless compounds **1**−**3** were prepared by heating dimethylformamide (DMF) solutions of $Zn(NO_3)_2 \cdot 6H_2O$, the corresponding acid, and BIPY in sealed vials. Single-crystal X-ray diffraction measurements confirmed that each is comprised of dimeric zinc units ligated by carboxylate-terminated struts in the *x* and *y* directions and pyridine struts

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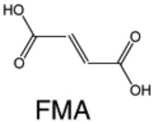
[7] Our disclosure is prompted in part by the very recently reported preparation of Cu and Zn versions of a related *non*interpenetrating microporous compound that utilizes more strongly ligated and more sterically demanding amines as pillars: $M_2(BDC)_2$(1,4-diazabicyclo-[2.2.2]octane) (Kitaura, R.; Iwahori, F.; Matsuda, R.; Kitagawa, S.; Kubota, Y.; Takata, M.; Kobayashi, T. C. *Inorg. Chem.* **2004**, *43*, 6522; Dybtsev, D. N.; Chun, H.; Kim, K. *Angew. Chem., Int. Ed.* **2004**, *43*, 5033). Additionally, a Cu version of **1**, not yet characterized by single-crystal X-ray diffraction, has been described (Seki, K. *Chem. Commun.* **2001**, 1496), as have some *non*porous, multiply interpenetrating, diimine/dicarboxylate coordination polymers (Wang, R.; Han, L.; Jiang, F.; Zhou, Y.; Yuan, D.; Hong, M. *Cryst. Growth Des.* **2005**, *5*, 129; Dalai, S.; Mukherjee, P. S.; Zangrando, E.; Lloret, F.; Chaudhuri, N. R. *J. Chem. Soc., Dalton Trans.* **2002**, 822; Lee, S. W.; Kim, H. J.; Lee, Y. K.; Park, K.; Son, J.-H.; Kwon, Y.-U. *Inorg. Chim. Acta* **2003**, *353*, 151).

10.1021/ic050452i CCC: $30.25

approximately in the z direction.[9] Crystallography also established (for all five MOFs) 2-fold interpenetration (Figure 2). Although interpenetration reduces the void volume, it likely increases the volumetric surface area. Void volumes for **1**−**3**, as calculated by PLATON from the crystal structures, are 20, 28, and 42%, respectively.

Thermogravimetric analyses (TGA) of compounds **1**−**3** showed initial mass losses that are consistent with solvent loss as calculated from structural data (Table 1). Solvent loss starts at ambient temperature and is complete at ca. 140−200 °C, depending on the compound. Further loss, due to framework decomposition, starts at 380−400 °C. TGA with evacuated frameworks show, as expected, only the higher temperature weight loss. A single-crystal structure of **1** in evacuated form indicates a 3% volume reduction.[10] Powder X-ray diffraction (PXRD) patterns of the evacuated frameworks point to a high degree of crystallinity and, for all but **3**,[11] give patterns similar to but not quite identical with those of freshly synthesized material. Notably, resolvation reverses the changes, implying that porosity is retained upon evacuation, but with slight alterations in the framework structure. Further evidence of persistent microporosity is provided by N_2 adsorption measurements. Figure 3 shows the behavior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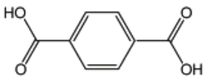
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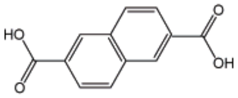
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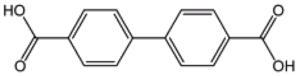
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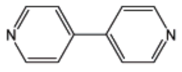
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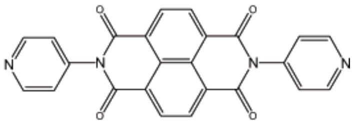
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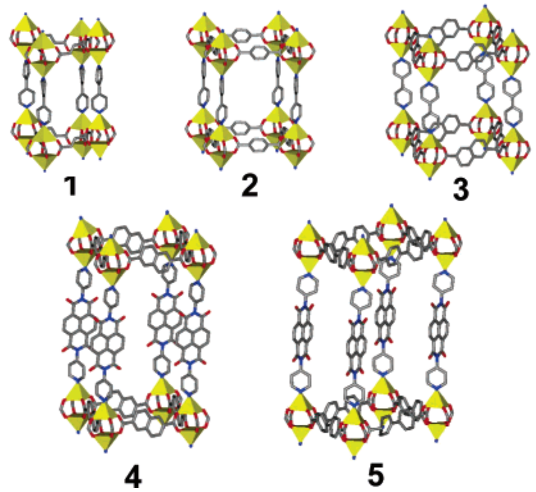

Figure 1. Single network units for compounds **1**−**5.** The yellow polyhedra represent the zinc ions. Carbon: gray. Oxygen: red. Nitrogen: blue.

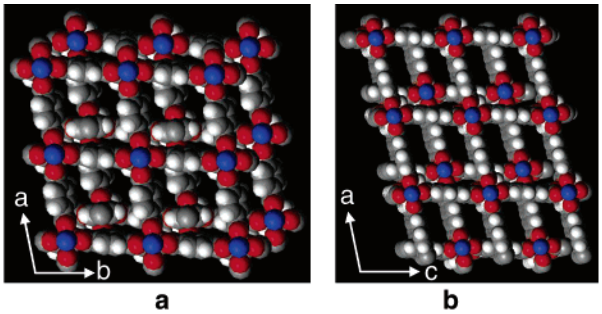

Figure 2. Space-filling diagram of compounds **2** (a) and **4** (b) showing the 2-fold interpenetration and remaining channels along the pyridyl pillar direction.

Table 1. Channel Parameters and Thermal Data for Compounds **1**−**5**

compd	n_{solvent} (DMF)[a]	V_{free}(Å^3)/Zn_2 unit	TGA calcd/found (%)
1	0.50	104.0	6.62/6.50
2	1.61	227.6	16.04/17.53
3	3.15	446.9	24.33/22.43
4	6.51	1005.8	32.67/32.50
5	10.50	1522.1	

[a] Number of DMF molecules, n, estimated from the number of excluded electrons per unit cell after application of SQUEEZE.[9]

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(8) A mixture of $Zn(NO_3)_2 \cdot 6H_2O$ (0.1 mmol), dicarboxylic acids (0.1 mmol), and BIPY or DPNI (0.05 mmol) was placed in a small vial containing 10 mL of DMF. The vial was sealed and heated in an oil bath at 80 °C for 48 h and allowed to cool to room temperature. The crystals suitable for X-ray diffraction were collected by filtration, washed with DMF, and dried in air. Elemental analysis for evacuated samples. Calcd (%) for **1** ($C_{18}H_{19}Zn_2N_2O_{8.5}$): C, 41.25; H, 2.50; N, 5.35. Found: C, 41.02; H, 2.55; N, 5.35. Calcd (%) for **2** ($C_{26}H_{18}Zn_2N_2O_9$): C, 50.30; H, 2.90; N, 4.52. Found: C, 49.03; H, 2.40; N, 4.22. Calcd (%) for **3** ($C_{30}H_{22}Zn_2N_2O_9$): C, 52.63; H, 3.22; N, 4.09. Found: C, 52.71; H, 2.96; N, 4.05. Calcd (%) for **4** ($C_{48}H_{28}Zn_2N_4O_{14}$): C, 56.77; H, 2.78; N, 5.52. Found: C, 56.20; H, 2.72; N, 5.51.

(9) Crystal data. Compound **1**: $C_{19.5}H_{15.5}Zn_2N_{2.5}O_{8.5}$, $M = 551.58$, monoclinic, $C2/m$, $a = 13.446(2)$ Å, $b = 11.584(2)$ Å, $c = 14.040(2)$ Å, $\beta = 105.407(2)°$, $U = 2108.2(5)$ Å^3, $Z = 4$, $D_c = 1.738$ mg m^{-3}, $\mu = 2.330$ mm^{-1}, $F(000) = 1112$, GOF = 1.120. R1 and wR2 are 0.0740 and 0.1793 respectively for 153 parameters and 1901 reflections [$I \geq 2\sigma(I)$]. Compound **2**: $C_{26}H_{16}Zn_2N_2O_8$, $M = 615.15$, triclinic, $P\bar{1}$, $a = 10.886(3)$ Å, $b = 10.919(3)$ Å, $c = 14.091(3)$ Å, $\alpha = 89.294(4)°$, $\beta = 89.081(4)°$, $\gamma = 79.691(3)°$, $U = 1647.6(7)$ Å^3, $Z = 2$, $D_c = 1.240$ mg m^{-3}, $\mu = 1.496$ mm^{-1}, $F(000) = 620$, GOF = 1.004. R1 and wR2 are 0.0726 and 0.1739 respectively for 415 parameters and 4077 reflections [$I \geq 2\sigma(I)$]. Compound **3**: $C_{34}H_{20}Zn_2N_2O_8$, $M = 715.26$, triclinic, $P\bar{1}$, $a = 12.976(2)$ Å, $b = 13.110(2)$ Å, $c = 13.926(2)$ Å, $\alpha = 85.310(2)°$, $\beta = 70.710(2)°$, $\gamma = 84.193(2)°$, $U = 2221.5(4)$ Å^3, $Z = 2$, $D_c = 1.069$ mg m^{-3}, $\mu = 1.118$ mm^{-1}, $F(000) = 724$, GOF = 0.766. R1 and wR2 are 0.0950 and 0.2404 respectively for 489 parameters and 4990 reflections [$I > 2\sigma(I)$]. Compound **4**: $C_{48}H_{24}Zn_2N_4O_{12}$, $M = 979.45$, monoclinic, $P2_1$, $a = 12.994(2)$ Å, $b = 22.318(2)$ Å, $c = 13.091(2)$ Å, $\beta = 102.582(2)°$, $U = 3705.1(6)$ Å^3, $Z = 2$, $D_c = 0.878$ mg m^{-3}, $\mu = 0.689$ mm^{-1}, $F(000) = 992$, GOF = 0.938. R1 and wR2 are 0.0492 and 0.1085 respectively for 597 parameters and 15 936 reflections [$I \geq 2\sigma(I)$]. Compound **5**: $C_{52}H_{28}Zn_2N_4O_{12}$, $M = 1031.52$, triclinic, $P\bar{1}$, $a = 15.164(2)$ Å, $b = 15.173(2)$ Å, $c = 22.273(2)$ Å, $\alpha = 82.987(1)°$, $\beta = 78.446(1)°$, $\gamma = 72.771(1)°$, $U = 4784.9(7)$ Å^3, $Z = 2$, $D_c = 0.716$ mg m^{-3}, $\mu = 0.535$ mm^{-1}, $F(000) = 1048$, GOF = 0.867. R1 and wR2 are 0.0365 and 0.0827 respectively for 631 parameters and 14 485 reflections [$I > 2\sigma(I)$]. The data were collected on a SMART CCD 1000 with Mo Kα radiation ($\lambda = 0.710\,73$ Å) at 120 K. The structures were solved by direct methods and refined by a full matrix least-squares technique based on F^2 using SHELXL 97 program. Modeling of solvent molecules except **1** proved to be impossible because of severe disorder. To solve the structures, therefore, the SQUEEZE subroutine in the PLATON software package was applied to mask the electron density in the cavities.

(10) Unit cell for **1** after evacuation: $a = 13.462(6)$ Å, $b = 11.314(6)$ Å, $c = 14.037(4)$ Å, $\alpha = 90.000°$, $\beta = 105.407(2)°$, $\gamma = 90.000°$, $U = 2045.1(4)$ Å^3.

(11) Additionally, N_2 adsorption measurements with **3** yield a lower than anticipated surface area (100 m^2/g), suggesting that channel collapse occurs.

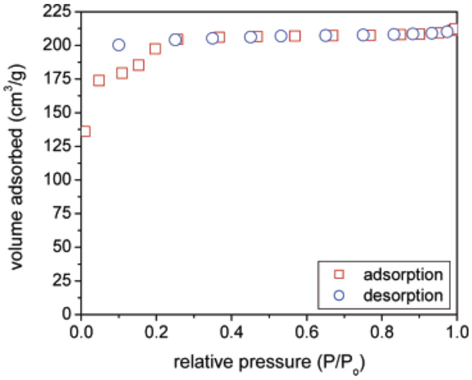

Figure 3. N_2 adsorption and desorption isotherms for **2** at 77 K.

of **2**. Obtained is an approximate type I Langmuir isotherm and a Brunauer−Emmett−Teller (BET) surface area of 660 m^2/g. Clearly evident, however, is a slight hysteresis, possibly reflecting the dynamic structural change in the PXRD pattern. Similar hysteretic behavior and a similar BET surface area (700 m^2/g) have been noted by Seki for a copper analogue of **2**.[12] Notably, however, the most compact of the compounds, **1**, did not take up nitrogen.[13]

Compared with cubic MOFs comprising a single ligand type, mixed-ligand MOFs should, in principle, be obtainable in much greater variety. Toward that end, two additional MOFs, both featuring DPNI in place of BIPY, were prepared by a method analogous to that for **1**−**3**. Single-crystal structures of $Zn_2(NDC)_2(DPNI)\cdot n$DMF (**4**) and $Zn_2(BPDC)_2(DPNI)\cdot n$DMF (**5**) show the compounds to be isoreticular with **1**−**3**. The guest-accessible volumes (PLATON) for **4** and **5** are 54 and 64%, respectively. TGA and PXRD show that both compounds are stable in evacuated form up to 400 °C. N_2 adsorption measurements confirm the permanent microporosity of **4** and give a BET surface area of 420 m^2/g.[14]

Interestingly, compounds **4** and **5** are yellow despite the off-white color of the free ligand, and both are weakly photoluminescent. In light of previous work with discrete supramolecular assemblies,[15] we anticipated that DPNI-containing MOFs might be redox active. Preliminary studies with **4** established that it is readily reducible by tetrahydrofuran solutions of lithium naphthalenide. Accompanying the reduction is a change in color to dark green/brown. The change is reversed upon exposure to air. PXRD measurements show that the framework structure is retained following reduction and reoxidation. Solid-state electrochemical measurements (carbon paste in contact with water as the solvent[16]) yield an E_f of ∼−0.7 V vs ferrocene. The anticipated chemical similarity of Zn(II)-bound BIPY to the well-known organic redox reagent methyl viologen (*N*,*N*′-methyl-4,4′-bipyridine) prompted us to examine **2** briefly as well. This compound proved to be similarly reducible and reversibly turns violet. Although not yet explored, partial reduction of the available mixed-ligand MOFs could reasonably be expected to yield porous materials displaying anisotropic conductivity. Framework reduction obviously also offers a mechanism for doping with specific cations.

In summary, a family of anisotropic open-framework compounds has been obtained based upon paddle-wheel-type coordination of Zn(II) pairs in two dimensions and pyridyl ligand pillaring in the third. The mixed-ligand approach has been used to tune channel dimensions, to introduce otherwise unstable metal/pyridine linkages, and to engender framework redox reactivity. Work in progress is focused on preparing and evaluating preferentially oriented membrane-embedded collections of mixed-ligand MOF crystallites.

Acknowledgment. We gratefully acknowledge the Office of Science, U.S. Department of Energy (Grant DE-FG02-01ER15244), and the Materials Research Center at Northwestern University for financial support of our research.

Supporting Information Available: CIF files, preparation, TGA analysis, and XRPD patterns for freshly prepared and evacuated samples **1**−**5**. This material is available free of charge via the Internet at http://pubs.acs.org.

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(13) **1** also resisted chemical reduction.

(14) In contrast to **1**−**4**, compound **5** has yet to be obtained in a large enough quantity in pure form for adsorption measurements. Under the various synthesis conditions examined, macroscopic preparations of **5** typically were contaminated with what appeared to be a cubic MOF of BPDC.

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