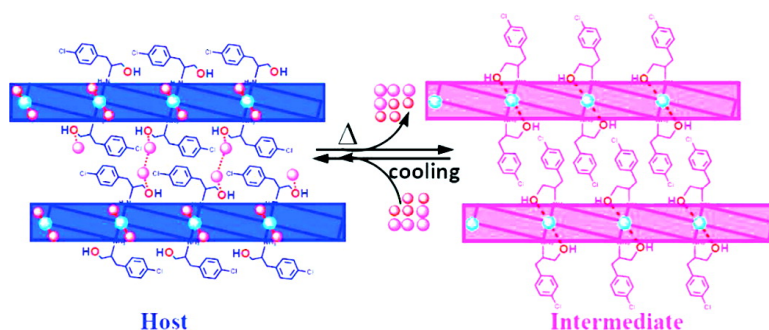


Guest Inclusion and Structural Dynamics in 2-D Hydrogen-Bonded Metal#Organic Frameworks

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Guest Inclusion and Structural Dynamics in 2-D Hydrogen-Bonded Metal–Organic Frameworks

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Hydrogen-bonded coordination networks¹ serve as structurally flexible alternatives to coordination polymers such as metal–organic frameworks (MOFs).² While many MOFs are 3-D frameworks, an interesting goal in supramolecular chemistry is the design and synthesis of lamellar coordination networks that can mimic the structure and properties of naturally occurring clays.³ These 2-D solids take part in host–guest chemistry (e.g., storage and separations), photopolymerization reactions, and catalysis.⁴

Layered solids composed of organic,⁵ metal phosphonates, metal halide anions, and coordination polymer components⁶ have been widely used in the design and synthesis of inorganic/organic lamellar solids, where organic substituents and/or guest molecules are sandwiched between layers. The organic moieties can act as adjustable components to tune the crystal structure and control the physical and chemical properties.⁷

Compared to the widely studied coordination polymers, research on hydrogen bonded coordination frameworks is far less common, especially for materials having guest inclusion.^{4c,7} Hydrogen bonds are comparatively weak, but charge-assisted hydrogen bonds provide strength and allow flexibility in the framework. Flexibility and stabilization of intermediates (e.g., metal ions before and after catalysis) are important when considering the construction of “designer” solid catalysts.

We recently reported the synthesis of hydrogen bonded metal–organic lamellar frameworks based on metal complexes with peripheral carboxylic acids, $\text{Co}(2,4\text{-HPDCA})_2(\text{H}_2\text{O})_2$ or $\text{Ni}(2,4\text{-HPDCA})_2(\text{H}_2\text{O})_2$ ($\text{H}_2\text{PDCA} = 2,4$ pyridine dicarboxylic acid), reacted with organic primary amines. The Cu(II) equivalent of the metal-containing component is shown in Figure 1. A series of architecturally isostructural solids were formed regardless of the nature of the organic amine.³ The solids are very robust due to the presence of “charge-assisted” hydrogen bonds between ammonium and carboxylate moieties. However, no guest inclusion was found in any of the structures.

In this communication, by presenting four new complexes **1–4**, we demonstrate how guest molecules can be trapped in the framework through a simple molecular change (increasing the flexibility of the aromatic ammonium building block), which changes the interlayer packing efficiency. Complexes **1–4** form hydrogen-bonded 2-D structures, and **4** contains an additional substituent that appears to stabilize the metal center during ligand loss at elevated temperatures. These results are supported using single crystal X-ray, powder X-ray, and thermogravimetric analysis (TGA), much of which is provided in the Supporting Information.

Complexes **1–4** were obtained using flexible aromatic primary amines, 4-methylphenylethylamine (for **1**), 4-chlorophenylethylamine (for **2**), 4-bromophenylethylamine, (for **3**), and DL-4-chlorophenylalaninol (for **4**), were allowed to react with 0.5 equiv of $\text{Cu}(\text{HPDCA})_2(\text{H}_2\text{O})_2$ in solution. The metal dicarboxylate ion found in each structure is shown in Figure 1.

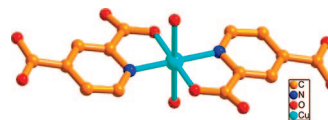


Figure 1. Structure of $\text{Cu}(\text{II})(2,4\text{-PDCA})_2(\text{H}_2\text{O})_2$ dianion, with hydrogen atoms removed.

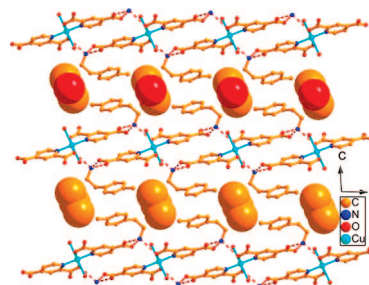


Figure 2. Crystal structure of **1**, showing hydrogen-bonded layers and acetone guests (the latter represented as space filled models).

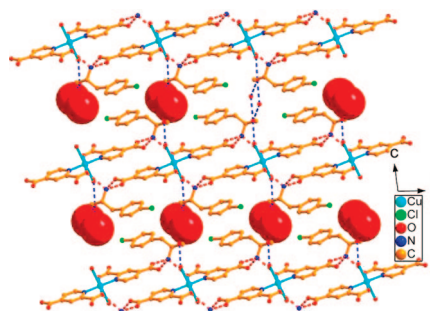


Figure 3. Crystal structure of **4**, showing the same hydrogen-bonded layers as **1–3**, but with water molecules (represented as disordered, space filled models) as guests.

Single crystal X-ray analysis reveals that these four complexes form hydrogen-bonded inorganic–organic layers ($[\text{R}-\text{NH}_3]_2[\text{Cu}(\text{PDCA})]_2$), which exhibit the same hydrogen-bonding patterns as those observed previously (i.e., layers formed *via* ammonium–carboxylate hydrogen bonds).³ However, crystal structures of **1–4** show that these hydrogen bonded frameworks host solvent molecules, Figure 2. The combination of flexible alkyl and aromatic groups in the counterion likely leads to less efficient interlayer packing, thus allowing the inclusion of guests.

In the structures of **1–3**, acetone molecules are found between adjacent layers, while the guest molecules in **4** are water molecules, Figure 3. Interestingly, introducing the $-\text{CH}_2\text{OH}$ group in **4** also results in a very different thermal behavior and in an unusual structural transformation in the solid state.

Powder XRD shows that the host framework in **2** and **3** survives the loss of the acetone guests but changes irreversibly after being

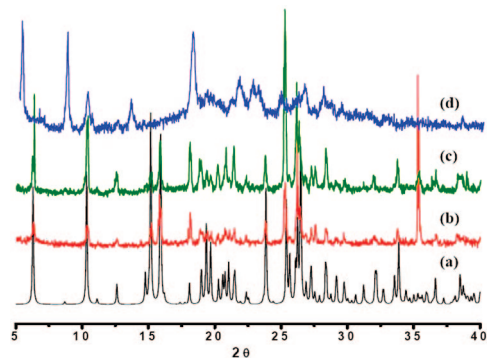


Figure 4. XRD patterns for **3**: (a) simulated, (b) immediately after removal from the mother liquor, (c) after loss of guest molecules, (d) after heating **3** to 130 °C for 16 h.

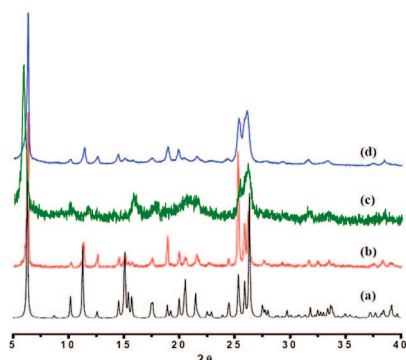


Figure 5. XRD patterns of **4**: (a) simulated, (b) well-ground sample before heating, (c) immediately after heating to 170 °C, (d) 6 h after heating to 170 °C.

heated or dried under vacuum; an example is given in Figure 4 (Complex **1** changes immediately upon loss of acetone). TGA shows that two water molecules [the axial ligands on Cu(II)] are lost upon heating, and the samples become purple in color. However, upon cooling in air, there is reuptake of one water ligand, as demonstrated by a color change to blue and by TGA indicating the loss of only one water molecule upon heating.

Though **1–4** are essentially isostructural, **4** behaves differently upon guest/ligand loss. While **1–3** exhibit an irreversible structural change after loss of water ligands, **4** undergoes a reversible structural transformation. XRD of **4** immediately after heating shows an intermediate framework that quickly returns to the original after reuptake of water molecules. Powder XRD and TGA both confirm the return to the original structure. The reformation of the original framework in **4** occurs in as little as 5 min, Figure 5. TGA shows a loss of 3 equiv of water molecules before and after the dehydration/rehydration process. Even after eight cycles of dehydration/rehydration, the powder pattern of **4** shows virtually no change in peak position, although there is some loss of crystallinity.

This structurally dynamic process, where a solid reversibly undergoes loss and reuptake of both guests and ligands, is unprecedented for hydrogen-bonded coordination frameworks. Such processes are known for coordination polymers⁸ and are what Kitagawa termed “Type III” materials.⁹ This supports the idea that hydrogen-bonded networks have great potential for utility in the world of materials chemistry.

What is the reason for the reversible rearrangement of the network? The difference between **1–3** and **4** is the presence of a hydroxyl-containing arm. Presumably, this hydroxyl group moves

to interact with the Cu(II) center, stabilizing an intermediate state, allowing a return to the original framework upon water reuptake. It may also be important to have a metal center, like Cu(II), that can adopt multiple coordination numbers.

What are the implications of these results? If the aim of materials design is for, e.g., catalytic activity, intermediate states for the metal (i.e., before and after coordination of reactants) must be stabilized. A Lewis base containing arm may move about and stabilize the metal centers even in more “fragile” hydrogen-bonded solids. Therefore, an arm that provides a labile Lewis base may allow substrates to access the metal centers during catalysis.

In this communication, we have demonstrated that our lamellar hydrogen-bonded coordination networks can incorporate guest molecules when using a more flexible linker for the associated cation. More importantly, by introducing a $-\text{CH}_2\text{OH}$ group in close proximity to the metal center (in **4**), we are able to produce a structurally dynamic solid that undergoes reversible changes after both guest and ligand loss. These results demonstrate the continuing possibilities of hydrogen-bonded coordination frameworks for functioning as “smart” materials.

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Supporting Information Available: Single crystal X-ray data, TGA, XRD, and experimental details for **1–4**. This material is available free of charge via the Internet at <http://pubs.acs.org>.

References

- (a) Beatty, A. *Coord. Chem. Rev.* **2003**, *246*, 131–143. (b) Beatty, A. *CrystEngComm* **2001**, *51*, 1–15. (c) Brammer, L. *Chem. Soc. Rev.* **2004**, *33*, 476–489. (d) Braga, D.; Grepioni, F. *Acc. Chem. Res.* **2000**, *33*, 601–608. (e) May, L. J.; Shimizu, G. K. H. *Z. Kristallogr.* **2005**, *220*, 364–372.
- Rowell, J. L. C.; Yaghi, O. M. *Angew. Chem., Int. Ed.* **2005**, *44*, 4670–4679.
- Beatty, A. M.; Helfrich, B. A.; Hogan, G. A.; Reed, B. A. *Crys. Growth Des.* **2006**, *6*, 122–126.
- (a) Matsumoto, A.; Sada, K.; Tashiro, K.; Miyata, M.; Tsubouchi, T.; Tanaka, T.; Odani, T.; Nagahama, S.; Tanaka, T.; Inoue, K.; Saragai, S.; Nakamoto, S. *Angew. Chem., Int. Ed.* **2002**, *41*, 2502–2505. (b) Nakano, K.; Sada, K.; Nakagawa, K.; Aburaya, K.; Yoswathanant, N.; Tohnai, N.; Miyata, M. *Chem.—Eur. J.* **2005**, *11*, 1725–1733. (c) Reddy, D. S.; Duncan, S.; Shimizu, G. K. H. *Angew. Chem., Int. Ed.* **2003**, *42*, 1360–1364.
- (a) Holman, K. T.; Pivovar, A. M.; Swift, J. A.; Ward, M. D. *Acc. Chem. Res.* **2001**, *34*, 107–118. (b) Holman, K. T.; Pivovar, A. M.; Ward, M. D. *Science* **2001**, *294*, 1907–1911. (c) Beatty, A. M.; Granger, K. E.; Simpson, A. E. *Chem.—Eur. J.* **2002**, *8*, 3254–3259. (d) Beatty, A. M.; Schneider, C. M.; Simpson, A. E.; Zaher, J. L. *CrystEngComm* **2002**, *4*, 282–287. (e) Biradha, K.; Dennis, D.; MacKinnon, V. A.; Sharma, C. V. K.; Zaworotko, M. J. *J. Am. Chem. Soc.* **1998**, *120*, 11894–11903. (f) Yuge, T.; Miyata, M.; Tohnai, N. *Cryst. Growth Des.* **2006**, *6*, 1271–1273. (g) Sada, K.; Inoue, K.; Tanaka, T.; Epergyes, A.; Tanaka, A.; Tohnai, N.; Matsumoto, A.; Miyata, M. *Angew. Chem., Int. Ed.* **2005**, *44*, 7059–7062. (h) Oshita, S.; Matsumoto, A. *Chem.—Eur. J.* **2006**, *12*, 2139–2146.
- (a) Mallouk, T. E.; Gavin, J. A. *Acc. Chem. Res.* **1998**, *31*, 209–217. (b) Mitzi, D. B. In *Functional Hybrid Materials*; Gomez-Romero, P., Sanchez, C., Eds.; Wiley-VCH Verlag GmbH & Co. KGaA: Weinheim, Germany, 2004; pp 347–386. (c) Kitagawa, S.; Kitaura, R.; Noro, S.-I. *Angew. Chem., Int. Ed.* **2004**, *43*, 2334–2375. (d) Song, J. L.; Mao, J. G.; Sun, Y. Q.; Zeng, H. Y.; Kremer, R. K.; Clearfield, A. *J. Solid State Chem.* **2004**, *177*, 633–641.
- (a) Li, Y. Y.; Lin, C. K.; Zheng, G. L.; Cheng, Z. Y.; You, H.; Wang, W. D.; Lin, J. *Chem. Mater.* **2006**, *18*, 3463–3469. (b) Tang, C.-L.; Beatty, A. M. *Chem. Commun.* **2007**, 76–78. (c) Guloy, A. M.; Tang, Z. J.; Miranda, P. B.; Srdanov, V. I. *Adv. Mater.* **2001**, *13*, 833–837. (d) Dalrymple, S. A.; Shimizu, G. K. H. *Chem. Commun.* **2006**, 956–958.
- (a) Chen, C.-L.; Goforth, A. M.; Smith, M. D.; Su, C.-Y.; zur Loye, H.-C. *Angew. Chem., Int. Ed.* **2005**, *44*, 6673–6677. (b) Kawano, M.; Fujita, M. *Coord. Chem. Rev.* **2007**, *251*, 2592–2605. (c) Vittal, J. J. *Coord. Chem. Rev.* **2007**, *251*, 1781–1795. (d) Bradshaw, D.; Warren, J. E.; Rosseinsky, M. J. *Science* **2007**, *315*, 977–980.
- Kitagawa, S.; Uemura, K. *Chem. Soc. Rev.* **2005**, *34*, 109–119.

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