Coordination Polymers Composed of Copper(II), Trimesic Acid, and Imidazole: 3D Architecture Stabilized by Hydrogen Bonding

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Coordination polymers are a family of materials composed of 1D chains, 2D sheets, and 3D networks of metal-organic building blocks connected via coordinate and hydrogen bonds. Recently, they have received considerable attention because of their potential in chemical separation technologies and heterogeneous catalysis, as well as their potentially unusual magnetic and electronic properties.[1] Porous coordination polymers are particularly attractive synthetic goals because they have the potential to utilize reactive species along pore walls, that is, transition metals, for catalysis.[2] Although there have been many reports of coordination polymers that contain channels or pores, compounds that maintain their structure after guest molecules have been removed are far fewer.[3] Coordination polymers that make use of aromatic carboxylates as bridging units have been synthesized and structurally characterized as chains,[4] sheets,[5] interpenetrating networks,[6] polyhedra,[7] and open networks.[8] Here, we report the syntheses and structures of two coordination polymers formed in aqueous solution at room temperature with copper(II), trimesic acid (TMA), and either imidazole (Im) or *N*-methylimidazole (Me-Im), and we report the dependence of their stability on hydrogen bonding.

Coordination polymers $\{[Cu_3(TMA)_2(Im)_6(H_2O)]\cdot 7H_2O\}_n$ (**1**) and $\{[Cu_3(TMA)_2(Me\text{-}Im)_6(H_2O)]\cdot 16H_2O\}_n$ (**2**) were synthesized by adding an aqueous solution of copper(II) sulfate to a slightly basic (pH $\leq$ 8) solution of TMA, followed by addition of solid Im or Me-Im (Scheme 1). X-ray quality single crystals of **1** and **2** were obtained in moderate yield by slow evaporation of the filtered reaction mixtures. Both **1** and **2** are insoluble in water and common organic solvents.

A single-crystal X-ray diffraction study of **1** revealed that it is made up of infinite sheets of Cu^{2+} cations connected by TMA^{3-} anions.[9] Although the asymmetric unit contains three crystallographically distinct Cu^{2+} ions, there are two types of copper coordination geometries. The first is distorted trigonal bipyramidal where the Cu^{2+} ions are coordinated by three carboxylate oxygen atoms in the trigonal plane and two Im nitrogen atoms in the axial positions. These trigonal bipyramidal moieties are joined by two bridging carboxylate ligands to form dimeric units (Figure 1a).[10] The second distinct coordination geometry is a distorted square pyramidal mononuclear copper unit (Figure 1b). The copper ion in the monomeric unit is coordinated by two carboxylate oxygen atoms and two Im nitrogen atoms in the equatorial plane, and by a H_2O molecule in a long [2.264(2) Å] axial bond.[10]

The dimeric units are connected to the monomeric units via the TMA ligands, creating a two-dimensional sheet with an unprecedented structure (Figure 2). Three types of rings are evident in the sheets of **1**: (1) the small rings formed by the carboxylate-bridged dimeric units, (2) slightly larger rings formed when two dimeric units are linked together, and (3) the largest rings created between monomer-linked chains of dimers. These large rings can be viewed in isolation as two dimeric units and two monomeric units connected to form a large ring, with one of the coordinated H_2O molecules pointing into the ring, and the other into the next ring.

Scheme 1
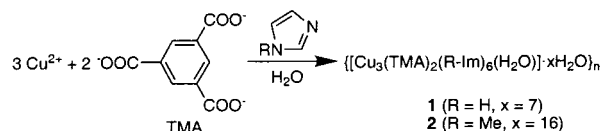
The stacked 2D sheets are held together via hydrogen bonds and $\pi-\pi$ interactions to create a 3D network. The closest distance between sheets in **1** is approximately 6.0 Å. The intersheet hydrogen bonding illustrated in Figure 3a is between the axial Im ligands of the dimeric units and carboxylate oxygen atoms of the neighboring sheet. The Im ligands coordinated to the monomeric units are not involved in intersheet hydrogen bonding. The Im ligands on adjacent sheets are interdigitated, producing a modified zipper effect (Figure 3a),[11] giving rise to $\pi-\pi$ interactions between Im rings.[12] Im ligands coordinated to dimeric units of adjacent sheets have centroid−centroid distances of 4.1 Å and are offset by 41°, while slightly longer distances between Im rings coordinated to monomer units on adjacent sheets (4.7 Å centroid vector, 38° offset) suggest a smaller $\pi-\pi$ contribution.[13]

Large H_2O-filled channels that run the length of the crystal lattice are apparent when **1** is viewed down the crystallographic *c* axis. The channels, which are roughly oval in shape with dimensions of 10.9 × 6.6 Å^2, contain seven uncoordinated H_2O molecules per formula unit. The H_2O molecules are held in place by hydrogen bonds with the Im ligands of the monomeric units and with carboxylate oxygen atoms. The H_2O molecules also hydrogen bond to each other, creating ribbonlike chains that fill the channels (Figure 4). Square pyramidal Cu^{2+} ions of the

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(2) Barton, T. J.; Bull, L. M.; Klemperer, W. G.; Loy, D. A.; McEnaney, B.; Misono, M.; Monson, P. A.; Pez, G.; Scherer, G. W.; Vartuli, J. C.; Yaghi, O. M. *Chem. Mater.* **1999,** *11,* 2633−2656.

(3) For examples see: (a) Noro, S.; Kitagawa, S.; Kondo, M.; Seki, K. *Angew. Chem., Int. Ed.* **2000,** *39,* 2082−2084. (b) Li, H.; Eddaoudi, M.; O'Keeffe, M.; Yaghi, O. M. *Nature* **1999,** *402,* 276−279.

(4) (a) Plater, M. J.; Foreman, M. R. S.; Coronado, E.; Gomez-Garcia, C. J.; Slawin, A. M. Z. *J. Chem. Soc., Dalton Trans.* **1999,** 4209−4216. (b) Yaghi, O. M.; Li, H. L.; Groy, T. L. *J. Am. Chem. Soc.* **1996,** *118,* 9096−9101.

(5) Choi, H. J.; Suh, M. P. *J. Am. Chem. Soc.* **1998,** *120,* 10622−10628.

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(7) (a) Eddaoudi, M.; Kim, J.; Wachter, J. B.; Chae, H. K.; O'Keeffe, M.; Yaghi, O. M. *J. Am. Chem. Soc.* **2001,** *123,* 4368−4369. (b) Moulton, B.; Lu, J. J.; Mondal, A.; Zaworotko, M. J. *Chem. Commun.* **2001,** 863−864.

(8) Reineke, T. M.; Eddaoudi, M.; Fehr, M.; Kelley, D.; Yaghi, O. M. *J. Am. Chem. Soc.* **1999,** *121,* 1651−1657.

(9) Crystal data for **1**: triclinic, space group $P\bar{1}$, blue, *a* = 10.049(2) Å, *b* = 14.290(3) Å, *c* = 18.843(7) Å, α = 75.896(17)°, β = 77.73(2)°, γ = 77.018(7)°, 173(2) K, *Z* = 2, R1 = 0.0565, wR2 = 0.1467, and GOF = 1.014.

(10) The bond distances in **1** are typical for copper(II) with carboxylates and *N*-heterocycles. For example, [Cu(OAc)$_2$(py)]$_2$: Melnik, M. *Coord. Chem. Rev.* **1982,** *42,* 259−293.

(a)

(b)
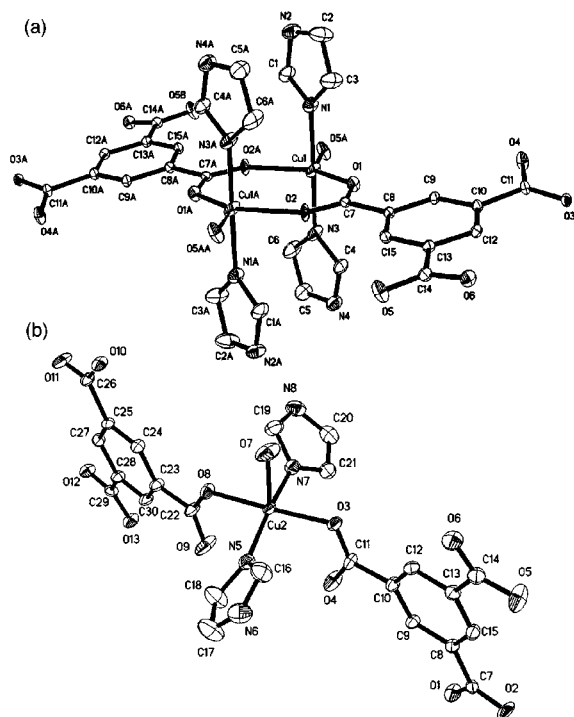
Figure 1. Structures represented as 30% thermal ellipsoids (H atoms omitted for clarity) of (a) the bis(μ-carboxylato) dicopper "dimeric unit" and (b) the mononuclear copper "monomeric unit" that comprise the building blocks of **1**.
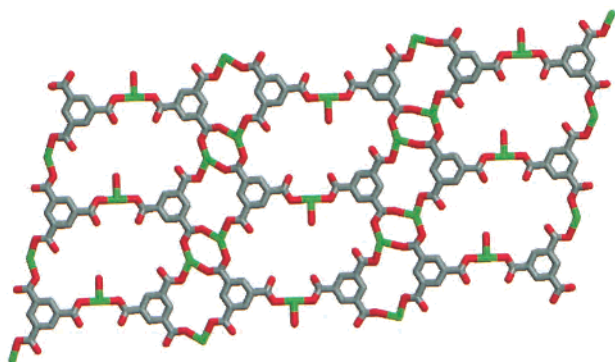

Figure 2. Sheet of **1** containing chains of dimeric units connected by monomeric units to create the 2D network. Hydrogen atoms, Im ligands, and uncoordinated H_2O molecules have been removed for clarity (red, O; gray, C; green, Cu).

monomeric units line the channel walls, raising the possibility that **1** may have potential as a catalyst. Thermal gravimetric (TG) experiments showed that all of the uncoordinated H_2O can be removed by heating **1**, and it does not decompose until it has been heated above 200 °C. Powder XRD spectra of hydrated and dehydrated **1** are nearly identical, supporting the notion that the crystal lattice remains intact after the uncoordinated H_2O molecules are removed.

To explore the importance of hydrogen bonding in the tertiary structure of **1**, we synthesized **2** by substituting Im with Me-Im

(11) Coordination polymers with interdigitated sheets have been reported. For example, see: Yaghi, O. M.; Li, G. M.; Li, H. L. *Nature* **1995**, *378*, 703−706.

(12) $\pi-\pi$ contacts between coordination polymer chains involving histamine were recently reported. Min, K. S.; Suh, M. P. *J. Solid State Chem.* **2000**, *152*, 183−190.

(13) The offset angle is defined as the angle between the normal of the Im ring plane and the centroid vector. Janiak, C. *J. Chem. Soc., Dalton Trans.* **2000**, 3885−3896.

(14) Crystal data for **2**: monoclinic, space group *C*2/*c*, blue, $a = 31.476(8)$ Å, $b = 10.0561(19)$ Å, $c = 19.549(3)$ Å, $\beta = 90.210(17)°$, 173(2) K, *Z* = 8, R1 = 0.0825, wR2 = 0.2033, GOF = 1.207.
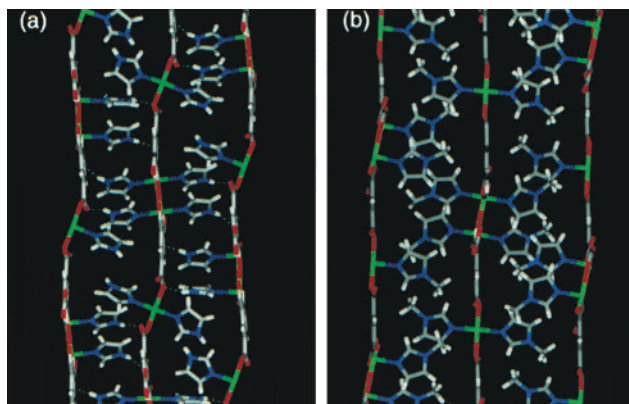
Figure 3. Intersheet contacts composed of (a) hydrogen bonds and $\pi-\pi$ interactions for **1** and (b) only weak $\pi-\pi$ interactions for **2** (red, O; white, H; gray, C; blue, N; green, Cu).
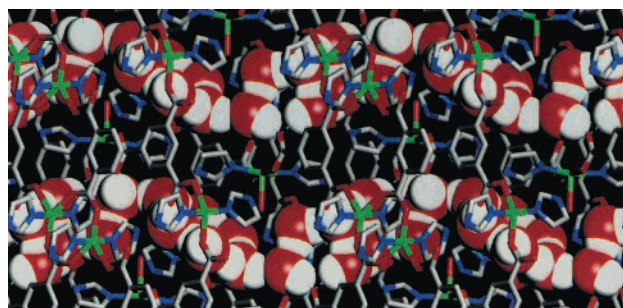
Figure 4. View of ribbonlike chains of H_2O molecules (CPK spheres) that reside in the channels of **1** (same color scheme as Figure 3).

(Scheme 1). The X-ray crystal structure of **2** was determined,[14] and it is remarkably similar to the structure of **1**, with the important exception of the hydrogen bonding between sheets (Figure 3b). The intersheet distance in **2** is approximately 8.2 Å, weakening any $\pi-\pi$ interactions, and because Me-Im cannot participate in hydrogen bonding, there are no intersheet hydrogen bonding contacts. Perhaps as a consequence of the larger intersheet distances and the absence of hydrogen bonding with Im, **2** contains nine additional H_2O molecules per formula unit. Interestingly, **2** is not as stable as **1**. Crystals of **2** quickly lose solvent and crumble at room temperature in the open air while **1** remains crystalline indefinitely under the same conditions. Furthermore, powder XRD results of **2** before and after dehydration are considerably different, adding support to the conclusion that the hydrogen bonding between sheets in **1** is of critical importance in stabilizing the tertiary structure.

We have synthesized two new copper(II) coordination polymers that have nearly identical structures and contain very large H_2O-filled channels. Hydrogen bonding between sheets in **1** serves to stabilize its 3D structure, even after the guest H_2O molecules have been removed. However, the lack of intersheet hydrogen bonding in **2** destabilizes its tertiary structure, leading to decomposition upon loss of H_2O.