Communication

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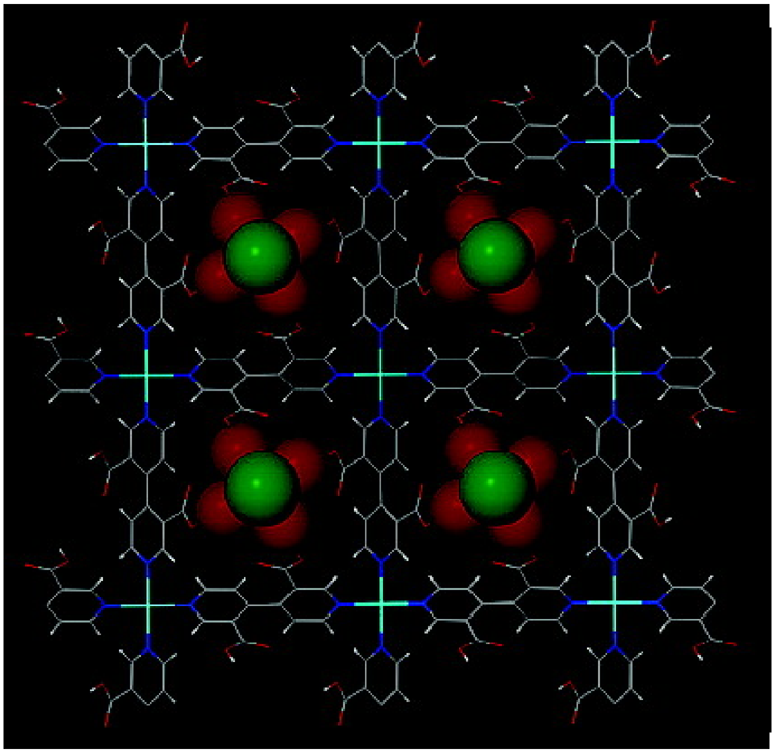

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COMMUNICATIONS

A Metal−Organic Framework Functionalized with Free Carboxylic Acid Sites and Its Selective Binding of a $Cl(H_2O)_4^-$ Cluster

Radu Custelcean* and Maryna G. Gorbunova

Chemical Sciences Division, Oak Ridge National Laboratory, Oak Ridge, Tennessee 37831-6119

Received August 12, 2005; E-mail: custelceanr@ornl.gov

Metal−organic frameworks (MOFs), or coordination polymers, have emerged as a promising new class of materials that can be easily assembled from transition metal cations and organic linkers.[1] These materials often contain crystalline, well-defined cavities or channels that can be used for the inclusion and exchange of various guest species. The advantage of MOFs over analogous inorganic materials is that their cavity size, shape, and functionality can be systematically and predictably adjusted via synthetic modification of the organic component.[2] These unique characteristics offer the prospect for remarkable selectivities[3] and catalytic abilities,[4] which may eventually approach those found in biological systems. One outstanding challenge that has to be met to realize this ambitious goal is the incorporation of binding sites or reactive centers for guest recognition or catalysis in MOFs. Although some steps have been recently taken along this direction by introduction of coordinatively unsaturated metal centers[5] or free OH,[4b] NH_2,[2b,6] and pyridine groups,[7] the functionalization of MOF cavities remains mostly unexplored to date. This can be explained by the tendency of such reactive groups to engage in framework building through coordination or hydrogen bonding, which renders them unusable for guest binding. Motivated by our interest in selective separation of ionic species via host−guest chemistry, we have recently initiated a program targeting MOF hosts functionalized with hydrogen bonding sites[8] for recognition of anions. Here we report the synthesis of the first MOF containing channels functionalized with free −COOH binding sites. This material acts as a selective host for a $Cl(H_2O)_4^-$ cluster, which has been structurally characterized for the first time as part of this study.

Slow diffusion of $CuCl_2$ in MeOH into an aqueous solution of binicotinic acid hydrochloride (BNA·HCl)[9] afforded blue crystals with the composition $[CuCl(BNA)_2]\cdot Cl(H_2O)_4$ (**1**) (Scheme 1), as indicated by X-ray diffraction, TGA, and elemental analysis (Supporting Information).

Single-crystal X-ray diffraction analysis showed that **1** is a cationic MOF exhibiting a perfect square-grid topology, with the Cu^{2+} and BNA acting as nodes and linkers, respectively (Figure 1). The coordination around copper is square pyramidal with four pyridine groups occupying the basal plane (Cu−N = 2.04 Å) and one chloride occupying the apical position (Cu−Cl = 2.60 Å). The $C4$ symmetry on the copper centers is propagated throughout the crystal and translates into the chiral $P4$ space group. The square grids are linked along the c axis by weaker Cu−Cl (2.99 Å) and C−H···O (H···O = 2.34 Å, C−H−O = 157.6°) interactions, in an edge-to-edge fashion, thus generating one-dimensional hourglass-shaped channels with minimum and maximum cross-sections of 6.5 and 8.8 Å.

The most remarkable feature of **1** is that the carboxylic groups do not coordinate the copper centers, as one would normally expect, nor do they hydrogen bond among themselves or to the pyridine N atoms. Instead, they remain available to functionalize the channels of **1**. The presence of COOH groups was supported by their characteristic infrared bands: a strong peak at 1722 cm^{-1} and a broad absorbance in the range of 2500−3000 cm^{-1} corresponding to the C═O and O−H stretching vibrations, respectively. With its free carboxylic groups, **1** is unique among similar MOFs built from pyridine−carboxylate ligands, in which the carboxylic groups are invariably involved in the network assembly through coordination to the transition metal center or hydrogen bonding.[10] The present results can be rationalized by the acidic conditions (pH = 1.6) used

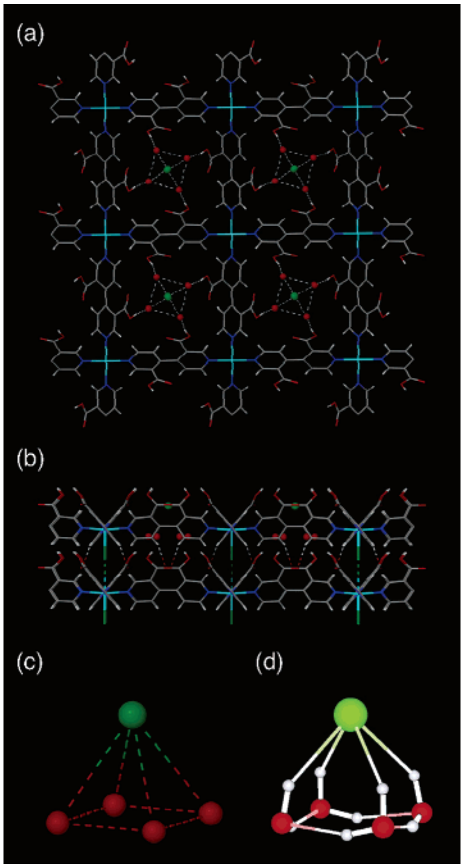
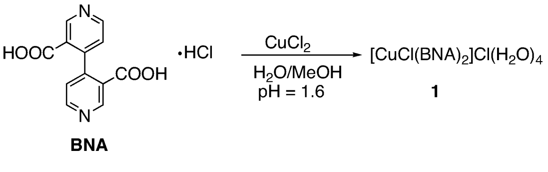


Figure 1. Structure of **1**. (a) View down the c axis showing the square grid network containing channels decorated with COOH groups that bind $Cl^-(H_2O)_4$ clusters. (b) Orthogonal view showing the weaker Cu−Cl and CH···O interactions between the grids by dotted lines. (c) Observed structure of the $Cl^-(H_2O)_4$ cluster in the crystal. (d) Calculated structure of the $Cl^-(H_2O)_4$ cluster. Cu is shown in cyan, N in blue, O in red, C in gray, H in white, and Cl in green.

Scheme 1



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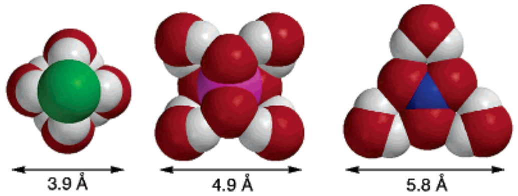

Figure 2. Structures of $Cl(H_2O)_4^-$ (left), $SO_4(H_2O)_4^{2-}$ (center), and $NO_3(H_2O)_3^-$ (right) clusters optimized at the B3LYP/6-31G* level.

for the synthesis of **1** and the presence of Cl^- and water solvent, which are both better hydrogen bonding acceptors for the COOH group[11] and thus inhibited the formation of COOH···HOOC interactions. That the pH is a critical parameter for the introduction of free, uncoordinated COOH groups was demonstrated by reducing the amount of HCl used in the synthesis to only a half equivalent relative to BNA, which in addition to **1** as the major product resulted in the formation of $[Cu(BNA^-)_2]\cdot 7H_2O$ (**2**), in which all carboxylic groups are engaged in the network formation through coordination and hydrogen bonding (Supporting Information) and thus are not available as binding sites.

The channels of the cationic framework in **1** are occupied by square pyramid-shaped $Cl(H_2O)_4^-$ clusters (Figure 1c) anchored to the channel walls by strong hydrogen bonds between the COOH groups and the water (O···O 2.71 Å, H···O 1.89 Å, O−H···O 166.0°). The chloride sits on the 4-fold rotation axis passing through the center of the channel and interacts with the four water molecules within the cluster (Cl···O 3.34 Å) and more weakly with the water in the adjacent cluster in the channel (Cl···O 3.54 Å).[12] There is also strong hydrogen bonding among the four H_2O molecules, with O···O separations of 2.84 Å.[13] Figure 1d shows a model of this cluster optimized[14] at the B3LYP/6-31G* level, which displays Cl···O (3.31 Å) and O···O (2.79 Å) distances similar with those observed by X-ray in the crystal. This *C*4-symmetrical structure has been predicted theoretically as the lowest-energy isomer of $Cl(H_2O)_4^-$,[15] but has not been structurally characterized to date. Its inclusion in the channels of **1** appears to be the result of the good size, symmetry, and functionality match between the MOF host and the $Cl(H_2O)_4^-$ guest.

Preliminary competition experiments indicated preferential inclusion of Cl^- in **1**, in the presence of other anions. Thus, replacing the initial $CuCl_2$ with $Cu(NO_3)_2$, $Cu(ClO_4)_2$, or $CuSO_4$ resulted in the exclusive inclusion of Cl^- (from BNA·HCl) as evidenced by the FTIR spectra of the resulting materials. When $CuBr_2$ or CuF_2 salts were used, however, the inclusion of both Cl^- and Br^- or F^- was observed, with Cl^-/Br^- and Cl^-/F^- molar ratios of 2:1 and 2.3:1, respectively.[16] We rationalize these results based on the size and symmetry match between $Cl(H_2O)_4^-$ and **1**; with its small size and *C*4 symmetry, this cluster fits well inside the channels of **1**, compared with the oxoanion−$(H_2O)_n$ clusters[17] that are too large and symmetry mismatched for optimal interaction with the COOH groups (Figure 2). On the other hand, Br^- and F^- form clusters that are similar in size and shape with $Cl(H_2O)_4^-$,[15] which may account for the reduced selectivity within the halide series.

We have reported here the first synthesis of an MOF containing channels functionalized with free carboxylic groups. The key factors for the formation of this functional MOF appear to be the low pH and the aqueous conditions employed in the synthesis, which prevented the COOH groups from participating in the metal coordination or self-association by hydrogen bonding. While further studies are necessary to establish the generality of this approach, it is clear that the availability of free carboxylic sites may confer unique functionality on this class of materials, as demonstrated here by the selective inclusion of the $Cl(H_2O)_4^-$ cluster.

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Supporting Information Available: Synthetic procedures, X-ray crystallographic data including CIF files for **1** and **2**. This material is available free of charge via the Internet at http://pubs.acs.org.

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