Structure and Charge Control in Metal–Organic Frameworks Based on the Tetrahedral Ligand Tetrakis(4-tetrazolylphenyl)methane

Mircea Dinca, Anne Dailly, and Jeffrey R. Long

Abstract: Use of the tetrahedral ligand tetrakis(4-tetrazolylphenyl)methane enabled isolation of two three-dimensional metal–organic frameworks featuring 4,6- and 4,8-connected nets related to the structures of garnet and fluorite with the formulae Mn₆(ttpm)₃·5DMF·3H₂O (1) and Cu[(CuCl)(ttpm)]₂·CuCl₂·5DMF·11H₂O (2) (H₄ttpm = tetrakis(4-tetrazolylphenyl)methane). The fluorite-type solid 2 displays an unprecedented post-synthetic transformation in which the negative charge of the framework is reduced by extraction of copper(II) chloride. Desolvation of this compound generates Cu₄(ttpm)·0.7CuCl₂ (2d), a microporous material exhibiting a high surface area and significant hydrogen uptake.

Keywords: copper · manganese · metal–organic frameworks · microporous materials · tetrazoles

Introduction

Owing to their porosity and potential utility in a wide variety of applications, especially in gas storage, separations, and catalysis, metal–organic frameworks have attracted considerable recent attention. In particular, reports of frameworks with surface areas well above those of any zeolites,[1] or displaying unprecedented gas separation or catalytic properties,[2] have strengthened the widespread interest in the field. To construct materials with such remarkable properties, researchers must rely on somewhat serendipitous synthetic methods, which more often than not produce materials with no permanent porosity. Although it is not generally possible to predict the stability of a given framework upon guest evacuation, empirical observations show that the vast majority of permanently porous frameworks covalently extend in three dimensions.[4] Surprisingly, however, most known three-dimensional frameworks are based on planar, aromatic bridging ligands that need not assemble into three-dimensional structures. Instead, three-dimensionality in these frameworks is enforced by the metal building units, which usually consist of multinuclear clusters synthesized in situ from single metal-ion precursors.[5] Although mathematical and computational principles have been laid out to understand and sometimes predict the topology of frameworks based on certain cluster building units,[6] the synthetic conditions required to target a given cluster are still poorly understood. As such, the synthesis of three-dimensional frameworks starting from simple, two-dimensional ligands remains largely a matter of trial and error.

A potentially more efficient way to synthesize three-dimensional metal–organic frameworks is to focus on the organic ligands rather than the metal building unit, and to utilize one of the many readily available three-dimensional organic scaffolds, such as tetraphenylmethane, adamantane, or spirane. Indeed, employing a three-dimensional bridging ligand promotes the formation of a three-dimensional framework, regardless of the geometry around the metal building unit. Herein, we show that use of the tetrahedral molecule tetrakis(4-tetrazolylphenyl)methane (H₄ttpm) leads to the formation of two new three-dimensional frameworks with rare 4,6- and 4,8-connected topologies identical to those of garnet (gar) and fluorite (flu).[6] We further show that solvent exchange in the flu-type framework coincides with an anionic-to-neutral post-synthetic transformation that has not been observed in metal–organic frameworks thus far, and that evacuation of this framework pro-
duces a material with permanent porosity and high surface area.

Results and Discussion

The tetrahedral ligand H₄tpm was synthesized by a dipolar [2+3] cycloaddition between Na₃N₃ and tetra(p-cyanophenyl)methane, which in turn was obtained from tetraphenylmethane via tetra(p-bromophenyl)methane.[7] To explore the ability of H₄tpm to promote the formation of porous three-dimensional metal–organic frameworks, we screened synthetic conditions that had previously been effective in the formation of transition-metal–tetrazolate frameworks. Thus, solventothermal reactions between H₄tpm and Mn(NO₃)₂·4H₂O or CuCl₂·2.5H₂O in mixtures of DMF and methanol produced colorless or green crystals of Mn₆(OH)(tpm)₆·5DMF·3H₂O (1) or Cu[(Cu₂Cl)(tpm)₂]₂CuCl₂·5DMF·11H₂O (2), respectively.

X-ray analysis of a single crystal of 1 revealed a structure in which linear Mn₃ clusters are connected to six distinct ttpm⁴⁻ ligands to form a neutral three-dimensional framework (Figure 1). Here, each trimetallic unit consists of a central Mn⁴⁺ ion octahedrally coordinated by nitrogen atoms from six tetrazolate rings, and two outer Mn⁴⁺ ions, each bridged to the central Mn⁴⁺ ion by three tetrazolate rings and facially coordinated by three solvent molecules.[8] Overall, each trinuclear unit is surrounded by six tetrazolate rings and can thus be described as a six-connected node. Although such linear trimetallic units are common in both tetrazolate- and carboxylate-based frameworks,[9] their unique combination here with the four-connected nodes corresponding to the ttpm⁴⁻ ligands gives rise to a rare 4,6-connected framework with the garnet topology (gar). Notably, this highly-connected topology has, to our knowledge, only been observed once before in the structure of In₃Zn₂(im)₁₂ (im = imidazolate).[10]

X-ray analysis of a single crystal of 2 revealed a structure in which chloride-centered, square-planar [Cu₂Cl]²⁺ units are bridged by eight distinct ttpm⁴⁻ ligands to form a three-dimensional structure (Figure 2). Within a given [Cu₂Cl]²⁺ unit, each Cu²⁺ ion is coordinated by four nitrogen atoms and one chloride anion, whereas pairs of neighboring Cu²⁺ ions are bridged by two tetrazolate rings, such that overall, the cluster can be described as an eight-connected node. The resulting net anionic charge of the framework in 2 is balanced by extraframework Cu²⁺ ions, which are chelated by two nitrogen atoms on adjacent tetrazolate rings. Notably, X-ray analysis also revealed that the structure of 2 includes one full equivalent of CuCl₂, such that the sixth coordination site on the intraframework Cu²⁺ cations is occupied by a solvent molecule 75% of the time and by a chloride anion 25% of the time.

Although square-planar clusters surrounded by eight bridging ligands have been observed previously in the structures of Mn- and Cu-tetrazolate frameworks,[2d,11] and in Fe-, Co-, and Cd-based carboxylate frameworks,[12] their combination here with the tetrahedral four-connected nodes corre-
units showed comparatively higher porosity, samples of Mn₄(bdt)₃ and Zn₃(bdt)₃ (bdt⁻ = 1,4-benzenedimethanetetrazolate) also had a high propensity for collapse upon solvent evacuation.⁹⁶

Unlike 1, crystals of as-synthesized 2 remained intact both during methanol exchange and, more importantly, upon evacuation at 65 °C under reduced pressure. The behavior of 2 towards solvent exchange and guest evacuation is similar to that observed previously for Mn((MnCl)(btt)(CH₃OH))₃ and HCu[(CuCl)(btt)]·3.5HCl (btt⁻ = 1,3,5-benzenetetraazolate).²⁴¹¹a two related frameworks containing analogous square-planar [M₂Cl]⁺⁺ building units. In stark contrast to the btt⁻-based structures, however, initial X-ray analysis of an evacuated crystal of 2 revealed a surprisingly low occupancy of the central Cl⁻ anion. This suggests that methanol exchange could in principle extract CuCl₂ equivalents from 2 to provide a neutral framework with the formula Cu₄(tpm), which would be composed entirely of chloride-voided Cu₄ squares, as described by Equation (1):

\[
\text{Cu}[[\text{Cu}_4\text{Cl}_4](\text{tpm})_2] - 2\text{CuCl}_2 + 2\text{CuCl}_2 
\]

The prospect of effecting an anionic-to-neutral transformation is particularly attractive in 2 because the chloride-deficient Cu₄ squares that would be formed upon extraction of CuCl₂ could potentially serve as strong binding pockets for small molecules, such as O₂, N₂, or H₂. In an effort to probe the possibility of such a transformation, we employed a strategy involving a Soxhlet extraction of CuCl₂ from a fresh sample of 2 with hot methanol. The initially colorless solvent gradually turned green, confirming the extraction of CuCl₂ from the crystals of 2. After five days, methanol-washed single crystals of 2 were collected by filtration and evacuated at 65 °C under reduced pressure to produce Cu₄(tpm)₀.⁷CuCl₂ (2d). As expected, X-ray analysis of an evacuated single crystal of 2d revealed a further decrease of the Cl⁻ occupancy at the central position within the square-planar [Cu₄Cl]⁺⁺ units. Although partially occupied Cl⁻ anions are still bound to outside axial positions of Cu₄ units in 2d, X-ray analysis suggested that the Soxhlet extraction...
eliminated the central Cl$^-$ anion from ca. 50% of the [Cu$_2$Cl]$_{1+}$ clusters. Despite the fact that only a limited amount of CuCl$_2$ was eliminated from 2 under these conditions, the transformation from 2 to 2d represents the first example of a postsynthetic modification in which the charge of the metal–organic framework is reduced.

Further evidence of CuCl$_2$ elimination from 2 comes, as one may expect, from the significant structural changes caused by the loss of Cl$^-$ from the square-planar [Cu$_4$Cl]$_7$ building units. In this context, the most significant changes were observed in the length of the Cu–N bonds and the trans Cu–Cu distances, which were shortened from 2.036(3) to 1.985(3) and 5.078(2) Å, respectively, in 2, to 1.985(3) and 4.932(2) Å, respectively, in 2d. However, despite a shortening of the distances within the square-planar units, which are situated parallel to the ac plane, the a and c parameters are in fact larger in 2d than in 2, as shown in Table 1. This seemingly counterintuitive observation is due to a reorganization of the tetrahedral ligand, wherein the acute angle between two of the arms widens from 84(1) in 2 to 89(1)$^\circ$ in 2d.

As such, the a and c cell edges are extended, whereas the b parameter is shortened for an overall cell volume augmentation of 3.3% in going from 2 to 2d. In 2d, two types of pores exist: tetragonally-distorted octahedral cage-like pores defined by six [Cu$_4$Cl]$_7$$_+$$^+$$ units and eight ttpm$_4$ ligands and with interior atom-to-atom dimensions of 27.5 x 17.8 x 17.8 Å$^3$, and rhombohedral-shaped two-dimensional channels running parallel to the ac plane, with diagonal atom-to-atom dimensions of 14.1 x 12.6 Å$^2$.

An N$_2$ adsorption isotherm for 2d, shown in Figure 3, revealed a reversible Type I adsorption isotherm with a saturation amount of 640 cm$^3$ g$^{-1}$ at 1 bar. Fits of the isotherm employing the BET and Langmuir models gave apparent surface areas of 2506(2) and 2745(3) m$^2$ g$^{-1}$, respectively. Significantly, these represent the highest surface areas yet reported for a tetrazolate-bridged framework, surpassing the previous record held by Ni$_{2.75}$Mn$_{0.25}$[(Mn$_4$Cl)$_3$(btt)$_8$]$_2$·20CH$_3$OH, which exhibits a BET surface area of 2110(5) m$^2$ g$^{-1}$ and a Langmuir surface area of 2282(8) m$^2$ g$^{-1}$.[14]

The combination of high internal surface area and exposed metal coordination sites suggested that compound 2d might be of interest for hydrogen storage applications. Indeed, its H$_2$ adsorption isotherm at 77 K revealed a reversible uptake of 2.8 wt% at 1.2 bar (Figure 4), representing one of the highest H$_2$ uptakes reported for a metal–organic framework under these conditions.[15] Measurement of an H$_2$ adsorption isotherm at 87 K and fitting of the combined 77 and 87 K isotherms allowed calculation of the isosteric heat of adsorption, which showed a zero-coverage value of 8.4 kJ mol$^{-1}$. This is slightly lower than the value of 9.4 kJ mol$^{-1}$ established for HCu[(Cu$_4$Cl)$_3$(btt)$_8$]·3.5HCl.[11a]

The lower zero-coverage enthalpy of adsorption in 2d is likely a consequence of the reduction in the number of strong H$_2$ binding sites due to the presence of Cl$^-$ anions and the fact that, as evidenced by X-ray crystallography, only 70% of the Cu$_2^{1+}$ sites are available for H$_2$ binding, with Cl$^-$ anions occupying the rest of the available sites. Further H$_2$ adsorption measurements at pressures up to 70 bar revealed an excess H$_2$ uptake of 4.1 wt% at 20 bar and 77 K, as shown in Figure 5. The total uptake of 5.6 wt% at 70 bar (corresponding to a volumetric H$_2$ storage density of 41 g L$^{-1}$), is comparable to the total gravimetric uptakes of Mn$_3$[[Mn$_4$Cl]$_3$(btt)$_8$](CH$_3$OH)$_{10}$] and HCu[(Cu$_4$Cl)$_3$(btt)$_8$]·3.5HCl.[8d,10] which at 70 bar showed total uptakes of 6.7 and 5.6 wt%, respectively, but is lower than the total H$_2$

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**Table 1. Comparison of the tetragonal unit-cell dimensions for 2 and 2d.**

<table>
<thead>
<tr>
<th></th>
<th>2</th>
<th>2d</th>
<th>Difference (%)[2]</th>
</tr>
</thead>
<tbody>
<tr>
<td>a [Å]</td>
<td>15.501</td>
<td>16.091</td>
<td>0.59 (3.8)</td>
</tr>
<tr>
<td>c [Å]</td>
<td>29.401</td>
<td>28.189</td>
<td>-1.214 (~4.1)</td>
</tr>
<tr>
<td>V [Å$^3$]</td>
<td>7064</td>
<td>7299</td>
<td>235 (3.3)</td>
</tr>
</tbody>
</table>

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**Figure 3. Isotherm for the adsorption of N$_2$ within 2d at 77 K.**

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**Figure 4. Isotherms for the excess uptake of H$_2$ within 2d at 77 K (●, ○) and at 87 K (▲, □). Filled and empty symbols represent adsorption and desorption data, respectively, whereas the lines correspond to the virial fits to the two adsorption isotherms.**
uptake of 9.4 wt % observed for Zn₆O(1,4-benzenedicarboxylate), under these conditions.\textsuperscript{[2d]}

Experimental Section

General: All reagents were obtained from commercial vendors and, unless otherwise noted, were used without further purification. Methanol was distilled over Mg/I₂ prior to use. The compound tetra(p-cyanophenyl)methane was synthesized according to a previously published procedure.\textsuperscript{[3]} \textbf{Caution!} Although we did not encounter any incident while handling the compounds described herein, metal azides and tetrazoles are potentially explosive and should be handled with great care.

Tetrakis[2-(5,5-dimethyl-2,2'-bipyridine)cobalt(III)](1H-tptm) (2): A mixture of tetra(p-cyanophenyl)methane (0.02 g, 0.15 mmol), Na₂N₃ (1.2 g, 18 mmol), and triethylamine hydrochloride (2.5 g, 18 mmol) in toluene (25 mL) and methanol (5 mL) was heated at reflux in a 100 mL round-bottomed flask for 4 d. Upon cooling to room temperature, an aqueous solution of NaOH (25 mL, 0.1 M) was added, and the mixture was stirred for 30 min. The aqueous layer was treated with dilute HCl (ca. 0.5 M, 1 mL) until no further precipitate formed. The precipitate was then collected by filtration, dried in air, and dissolved in aqueous NaOH (1 M). The resulting clear, colorless solution was titrated with dilute HCl (ca. 0.2 M, 1 mL) until the pH of the solution was 4. The ensuing precipitate was washed with distilled water (3×150 mL), dried in air to afford 0.75 g (70 %) of product as a white powder.\textsuperscript{[4]}

Conclusion

The foregoing results show that use of predesigned three-dimensional organic ligands can circumvent the formation of low-dimensional systems, enabling isolation of metal–organic frameworks with rare, highly-connected three-dimensional topologies. Herein, two contrasting examples serve to reiterate that predicting the stability of any given framework to desolvation remains a great challenge, but that targeting three-dimensional systems by using this strategy can be an effective way for discovering new materials with permanent porosity. Future efforts will focus on further developing the coordination chemistry of three-dimensional bridging ligands such as H₄tptm and its adamantane-centered analogue. In addition, the unprecedented capability of the [Cu₂Cl]²⁺ tetrazolate clusters to eliminate chloride anions will be explored in the context of sequestering small molecules for potential applications in their storage, activation, and catalytic transformation.

Gas adsorption measurements: Gas adsorption isotherms for pressures in the range 0–1.2 bar were measured by using a Micromeritics ASAP2020 instrument. High pressure H₂ adsorption isotherms were measured on a HyEnergy PCTPro-2000 instrument using ultrahigh purity He (UHP grade 5.0, 99.999 % purity) was used for all measurements at 77 K in liquid nitrogen baths by using UHP-grade gas sources. H₂ was stored in a nitrogen-filled glove bag and quickly rinsed with anhydrous DMF. A C H T U N G T R E N N U N G

X-ray structure determinations (see Table S1 in the Supporting Information): Crystals of 1, 2, and 3 were mounted on a modified Oxford Xcalibur diffractometer, to prevent contamination of the samples during the evacuation process, or of the feed gases during the isothermal measurement. The total amount of hydrogen stored in 2d was calculated as previously described.\textsuperscript{[24]}

Figure 5. Isotherms for the adsorption of H₂ within 2d at 77 K. Empty and solid symbols represent excess and total uptake, respectively.
and cooled in a dinitrogen stream. Lattice parameters were initially
determined from a least-squares analysis of more than 100 centered reflec-
tions; these parameters were later refined against all data. None of the
crystals showed significant decay during data collection. The raw inten-
sity data were converted (including corrections for background, Lorentz,
and polarization effects) to structure factor amplitudes and their c's by
using the SAINT 7.07b program. An empirical absorption correction was
applied to each data set by using SADABS. Space-group assignment was
based on systematic absences, E-statistics, and successful refinement of
the structures. Structures were solved by direct methods with the aid of
SHELXTL 5.0 software package. Hydrogen atoms were inserted at ideal-
ized positions and refined by using a riding model with an isotropic ther-
amal parameter 1.2 times that of the attached carbon atom. To determine
the correct stoichiometry for 1 and 2d, the occupancies and thermal pa-
rameters of extraframework Cu and Cl atoms were refined freely. The
disorder evidenced in the electron-density map prevented the refinement
of solvent molecules within the pores of these three compounds. As such,
all peaks with electron densities larger than one electron were refined as
partially occupied oxygen and carbon atoms. The poor quality of the dif-
fraction data and extreme disorder of the bound and guest solvent mole-
cules led to relatively large R and wR values for the structure of 1.
However, the connectivity and structure of the skeleton within 1 was un-
equivocally determined by using this dataset. CCDC-690344, -690345,
and -690346 contain the supplementary crystallographic data for this
paper. These data can be obtained free of charge from The Cambridge
Crystallographic Data Centre via www.ccdc.cam.ac.uk/data_request/cif.

Other physical measurements: IR spectra were collected on a Nicolet
Avatar 360 FTIR spectrometer with an attenuated total reflectance ac-
cessory. 1H NMR spectra were obtained by using a Bruker AVQ-400 in-
strument, Carbon, hydrogen, and nitrogen atom analyses were obtained
from the Microanalytical Laboratory of the University of California, Ber-
keley. Powder X-ray diffraction patterns were recorded by using CuKα ra-
diation (λ = 1.5406 Å) on a Bruker D8 Advance diffractometer.

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structure of 1.

[1] a) H. K. Chae, D. Y. Sibiero-Pérez, J. Kim, Y. Go, M. Eddaoudi,
b) G. Férey, C. Mellot-Draznieks, C. Serre, F. Millange, J. Dutour,
c) S. Kitagawa, R. Kitaura, J. Mater. Chem. 2004, 14, 7896;
d) S. Ma, H.-C. Yuan, X.-H. Jia, J.-S. Chang, S. H. Jhung, G. Férey,
Adv. Funct. Mater. 2007, 17, 1255; g) S. Horike, M. Dincé, K.
Matsuda, S. Kitagawa, Nat. Mater. 2007, 6, 142; d) S. Ma, D. Sun, X.-
S. Wang, H.-C. Zhou, Angew. Chem. Int. Ed. 2007, 46, 2458; e) S.
Hasegawa, S. Horike, R. Matsuda, S. Furukawa, K. Mochuzaki, Y.
Kinoshita, S. Kitagawa, J. Am. Chem. Soc. 2007, 129, 2607; f) J. Y. Lee,
g) S. Horike, M. Dincé, K. Tanaki, J. R. Long, J. Am. Chem. Soc. 2008,
130, 5854.
Ed. 2000, 39, 2270; b) G. Férey, C. Serre, C. Mellot-Draznieks, F.
Millange, S. Sürblé, J. Dutour, I. Margiolaki, Angew. Chem. 2004,
116, 6456; Angew. Chem. Int. Ed. 2004, 43, 6296; c) V. A. Blatov, L.
Carlucci, G. Ciani, D. M. Proserpio, CrystEngComm 2004, 6, 377;
d) O. Delgado-Friedrichs, M. O’Keeffe, O. M. Yaghi, Phys. Chem.
[8] The poor quality of the X-ray diffraction data and extreme disorder
of the solvent molecules did not allow determination of whether the bound
solvent molecules in 1 are DMF or water.
Sci. USA 2006, 103, 10186.
[11] a) M. Dincé, W. S. Han, Y. Liu, A. Dailly, C. M. Brown, J. R. Long,
Angew. Chem. 2007, 119, 1441; Angew. Chem. Int. Ed. 2007, 46,
2008, 47, 11.
116, 699; Angew. Chem. Int. Ed. 2004, 43, 971; b) S. Ma, H.-C.
Zhou, J. Am. Chem. Soc. 2006, 128, 11172; c) L. Xie, S. Liu, C. Gao,
Commun. 2007, 2467.
Chem. 2008, 47, 5355; c) X.-S. Wang, S. Ma, K. Rauch, J. M. Sim-
Eubank, T. Bousquet, L. Wojtas, M. J. Zaworotko, M. Eddaoudi, J.
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