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Hydrothermal Synthesis of a Metal−Organic Framework Containing Large Rectangular Channels

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The great importance of microporous solids such as zeolites in adsorption, ion exchange, and shape-selective catalysis has stemmed from their ability to reversibly bind molecules and ions within their extended channels.[1] Recently, a major research effort has focused on using the molecular building block approach to generate analogous materials with 3-D organic,[2] metal−organic,[3] and inorganic[4] frameworks. Strategies for the construction of these solids have respectively utilized hydrogen-bonding interactions, metal−ligand coordination, and metal−cluster copolymerization reactions to link their molecular components. A number of such frameworks have been found to exhibit desirable zeolitic properties such as stability and microporosity of the framework,[3a,4] guest exchange,[3c,5] and selective catalytic activity.[6] In this report we present hydrothermal synthesis as a route to accessing crystalline, metal−organic, open frameworks having extended channel systems and composed of uncommon metal coordination. This will be demonstrated by describing the synthesis, structure, and properties of the extended network in crystalline Cu(4,4′-bpy)$_{1.5}$·NO$_3$(H$_2$O)$_{1.25}$.

A mixture of Cu(NO$_3$)$_2$·2.5H$_2$O (0.17 g, 0.74 mmol), 4,4′-bpy (0.17 g, 1.11 mmol), and 1,3,5-triazine (0.040 g, 0.49 mmol) in 15 mL of deionized water was transferred to a stainless steel bomb, which was sealed and placed in a programmable furnace. The temperature was raised to 140 °C at 5 deg/min and held at that temperature for 24 h, then cooled at 0.1 deg/min to 90 °C and held for 12 h, then cooled at the same rate to 70 °C and held for another 12 h, and finally cooled down to room temperature at 0.1 deg/min. The resulting rectangular parallelepiped orange crystals of Cu(4,4′-bpy)$_{1.5}$·NO$_3$(H$_2$O)$_{1.25}$ were collected and washed with deionized water (3 × 5 mL) and ethanol (2 × 5 mL) and then air dried to give 0.25 g (87% yield based on bpy).[7,8] This compound is stable in air and is insoluble in water and common organic solvents.

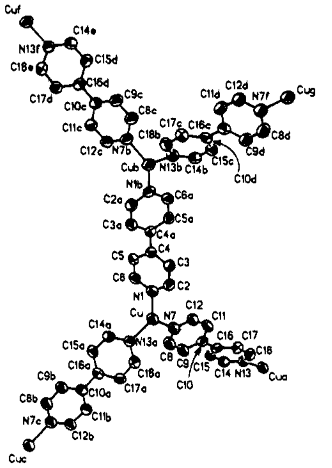

Figure 1. The building block unit including the asymmetric unit present in crystalline Cu(4,4′-bpy)$_{1.5}$·NO$_3$(H$_2$O)$_{1.5}$ with non-hydrogen atoms represented by thermal ellipsoids drawn to encompass 50% of their electron density. Atoms labeled with additional letters a−g are symmetry equivalent to those atoms without such designation.

X-ray structure determination[9] on a single crystal isolated from the reaction mixture was performed to reveal an extended cationic framework constructed from the building unit shown in Figure 1. Here, symmetry equivalent and slightly distorted trigonal planar copper(I) centers (N7−Cu−N1 = 125.4(2)°, N13a−Cu−N1 = 125.7(2)°, and N13a−Cu−N7 = 108.5(2)°) are linked by rod-like 4,4′-bpy ligands to form six porous and identical interpenetrating 3-D networks (shown in Figure 2) with each single network having three different size channels running along the [100], [010], and [001] crystallographic axes with dimensions 26 × 20, 10 × 12, and 43 × 18 Å, respectively. In this structure the planar geometry of the copper centers did not preclude the formation of this 3-D framework. This is due to two opposing rotations within the building unit: the rotation of the two 4,4′-bpy rings with respect to each other (C11−C10−C16−C15 = 31.1(0.2)° and C3−C4−C4a−C5a = 38.1(0.3)°), and similarly the two copper centers Cu and Cub (Cua−Cu−Cub−Cug = 62.3(0.6)°). This arrangement leads to a distorted tetrahedron having Cua, Cuc, Cug, and Cuf as vertices and the midpoint X (not shown) of the line connecting C4 and C4a as its center (Cua−X−Cuc = 71.5(0.7)°, Cua−X−Cug = 120.1(1)°, and Cuc−X−Cug = 142.5(2)°).

Unlike many other solids[10] with interpenetrating networks, the extent of interpenetration in this structure does not fill all the available voids but leaves a significant portion of it in the form of two rectangular extended channels (8 × 6 and 4 × 5 Å) which are occupied by nitrate anions that are hydrogen-bonded to solvent water molecules as shown in Figure 2. This type of framework interpenetration has been observed for another solid,[3a,11] namely, Cu(4,4′-bpy)$_2$·PF$_6$, where there are

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(6) Catalytic activity by crystalline 3-D metal−organic frameworks has not been demonstrated. However, a report on using a 2-D metal−organic framework as a catalyst for cyanosilation of aldehyde has appeared: Fujita, M.; Kwon, Y. J.; Washizu, S.; Ogura, K. *J. Am. Chem. Soc.* **1994**, *116*, 1151−1152.

(7) Anal. Calcd for CuC$_{15}$H$_{14.5}$N$_4$O$_{4.25}$: C, 47.12; H, 3.82; N, 14.65; Cu, 16.62. Found: C, 46.82; H, 3.75; N, 14.23; Cu, 16.35.

(8) The homogeneity of the bulk product was confirmed by comparison of the observed and calculated X-ray powder diffraction patterns. The calculated pattern was produced using the SHELXTL-XPOW program with the single-crystal data.[9]

(9) Single crystals of Cu(4,4′-bpy)$_{1.5}$·NO$_3$(H$_2$O)$_{1.25}$ were analyzed at 20 ± 1 °C: orthorhombic, space group *Fddd*-D_{2h}^{24} (No. 70) with a = 18.272(5) Å, b = 23.498(5) Å, c = 29.935(7) Å, V = 12853(6) Å^3, Z = 32, d_{calcd} = 1.581 g·cm^{-3}, and μ_a(Mo K$\bar{\alpha}$) = 1.39 mm^{-1}. A total of 2230 independent absorption-corrected reflections having 2Θ(Mo K$\bar{\alpha}$) < 45.8° (the equivalent of 0.6 limiting Cu K$\bar{\alpha}$ spheres) were collected on a computer-controlled Nicolet autodiffractometer using full (0.90° wide) ω scans and graphite-monochromated Mo K$\bar{\alpha}$ radiation. The structure was solved using "direct methods" techniques with the Siemens SHELXTL-PC software package as modified at Crystalytics Company. The resulting structural parameters have been refined to convergence {R_1 (unweighted, based on F) = 0.036 for 1404 independent absorption-corrected reflections having 2Θ(Mo K$\bar{\alpha}$) < 45.8° and $I > 3\sigma(I)$} using counter-weighted, full-matrix, least-squares techniques and a structural model which incorporated isotropic thermal parameters for all hydrogen atoms and disordered oxygen atoms O$_{1'}$, O$_{2'}$, O$_{2''}$ and O$_{4''}$ and anisotropic thermal parameters for all remaining non-hydrogen atoms. One of the two crystallographically independent H$_2$O molecules appears to be statistically disordered in the lattice with two alternate orientations for the oxygen atom. The two crystallographically independent NO$_3^-$ anions lie on crystallographic C_2 axes and are also disordered with several preferred orientations in the lattice.

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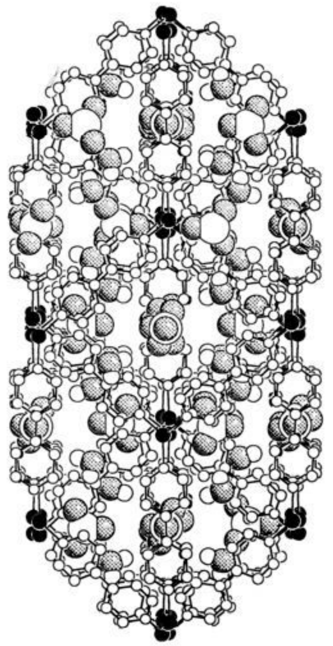

Figure 2. Crystal structure of $Cu(4,4'\text{-bpy})_{1.5}{\cdot}NO_3(H_2O)_{1.25}$ shown approximately down the crystallographic direction [100], which contains six interpenetrating frameworks. Framework atoms: dark spheres, Cu; small open spheres attached to Cu, N; and others, C. The nitrate anions and the water guest inclusions are depicted with large open spheres, N; small shaded spheres, O; small open spheres, H. 4,4′-bpy H's are omitted; all atoms are assigned arbitrary sizes for clarity.

four interpenetrating diamond-like frameworks leaving behind channels (6 × 6 Å) where the PF_6 anions reside.

It is instructive to view the frameworks of the two copper bipyridyl solids in terms of the diamond structure shown in Figure 3a.[12] The framework present in $Cu(4,4'\text{-bpy})_2{\cdot}PF_6$ is related to the diamond structure by replacing each C in diamond with a Cu(I) center and each C−C with 4,4′-bpy, resulting in an open framework with the building unit shown in Figure 3b. The framework making up the structure of $Cu(4,4'\text{-bpy})_{1.5}{\cdot}NO_3(H_2O)_{1.25}$ can be derived from Figure 3b by simply detaching two vertices on every Cu tetrahedron and linking them to another *Cu* center in a newly added *Cubpy* linkage; in this way, every $Cu(bpy)_4$ unit in Figure 3b is converted to a $(bpy)_2$*Cu(bpy)*-$Cu(bpy)_2$ unit to give Figure 3c, which is the building unit of the titled solid.

A unique character of the framework of $Cu(4,4'\text{-bpy})_{1.5}{\cdot}NO_3(H_2O)_{1.25}$ is the trigonal planar geometry of the copper(I) center; a search of the literature[13] yielded no molecular or extended solid compounds of this kind having such coordination. Attempts to prepare this compound outside the bomb by using the same reaction in water at room temperature or by refluxing for 24 h did not succeed. It appears that hydrothermal conditions are essential for dissolving 4,4′-bpy and achieving the reduced product.

The lability of the hydrogen-bonded inclusions was examined by thermal gravimetric analysis of a 21.631 mg microcrystalline sample, which revealed that the water guests are liberated at 120 °C, as indicated by a weight loss of 6% corresponding to 1.25 H_2O per formula unit. We have begun to study the ion-exchange properties of this material as the results from single-crystal X-ray data showed disordered nitrate ions, indicating that they are loosely bound to the framework. Infrared and elemental microanalysis data reveal that most of the nitrate ions can be exchanged in aqueous media with other simple ions such as SO_4^{2-} and BF_4^-. Currently, we are evaluating whether this material undergoes ion exchange with strong bases such as SCN^-, CN^-, OH^-, and MoO_4^{2-}. Nevertheless, we have observed that the framework is stable up to 180 °C under an inert atmosphere and for hours at 70 °C in water.

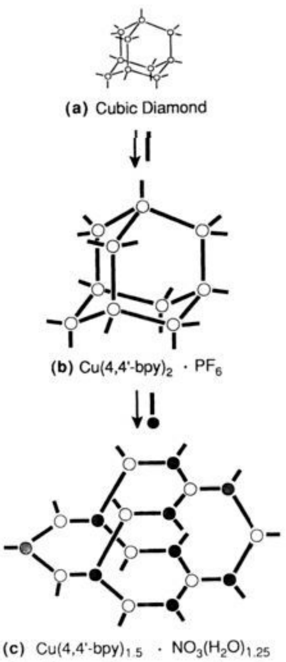

Figure 3. Schematic illustration presenting the structural analogy recognized between diamond and two new Cu(4,4′-bpy) solids. The length of the rod-like 4,4′-bpy ligand (shown as dark lines) allows the formation of open frameworks b and c that are based on tetrahedral coordination of Cu(I). The Cu(I) centers in parts b and c are distinguished as open and dark spheres for clarity.[12]

The results of this study show that hydrothermal synthesis is a viable route to accessing zeolite-like materials in crystalline form and having components that are not generally observed otherwise. Further experimentation aimed at the application of this synthetic method to the production of similar frameworks having larger channels is already in progress.

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Supporting Information Available: Crystallographic data for $Cu(4,4'\text{-bpy})_{1.5}{\cdot}NO_3(H_2O)_{1.25}$ including crystal structure analysis reports and tables of intensity collections, positional parameters, thermal parameters, and interatomic distances and angles (21 pages); listing of observed and calculated structure factors (6 pages). This material is contained in many libraries on microfiche, immediately follows this article in the microfilm version of the journal, can be ordered from the ACS, and can be downloaded from the Internet; see any current masthead page for ordering information and Internet access instructions.

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(10) Such as organic acids,[10a,b] metal−organic species,[10c−e] and inorganic species.[10f] (a) Benzene-1,3,5-tricarboxylic acid: Duchamp, D. J.; Marsh, R. E. *Acta Crystallogr.* **1969**, *B25*, 5−19. (b) Adamantane-1,3,5,7-tetracarboxylic acid: Ermer, O. *J. Am. Chem. Soc.* **1988**, *110*, 3747−3754. (c) $Zn(4,4'\text{-bpy})_2SiF_6{\cdot}2H_2O$: Gable, R. W.; Hoskins, B. F.; Robson, R. *J. Chem. Soc., Chem. Commun.* **1990**, 1677−1678. (d) $Ag_2CO_2(CH_2)_2CO_2$: Michaelides, A.; Kiritsis, V.; Skoulika, S.; Aubry, A. *Angew. Chem., Int. Ed. Engl.* **1993**, *32*, 1495−1497. (e) $Ag_2(pyz)_3{\cdot}2BF_4$: Carlucci, L.; Ciani, G.; Proserpio, D. M.; Sironi, A. *J. Am. Chem. Soc.* **1995**, *117*, 4562−4569. (f) Cu_2O: Wells, A. F. *Structural Inorganic Chemistry*, 4th ed.; Clarendon Press: Oxford, U.K., 1975; p 102.

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(12) This analogy does not take packing of tetrahedra and topology into consideration.

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