DESIGNING POROSITY IN COORDINATION SOLIDS

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ABSTRACT. Two strategies for producing porous coordination solids are described. The first deals with the construction of rigid metal-organic frameworks using ligands having multidentate functionalities, and shapes that prevent interpenetration. These ligands are chosen to enhance the selective inclusion of certain guest molecules. The second strategy addresses the character of the guest species that occupy the channels of the metal-organic framework. Here, hydrogen-bonded aggregates have been designed as guest species not only to allow the formation of large voids but also to facilitate the removal of inclusions, thus permitting access into the channels by other molecular species.

1. Introduction

The development of strategies for the construction of coordination solids with open-framework structures is at a stage where it is becoming increasing possible to realize target topologies and compositions [1]. Recently, a number of extended open frameworks have been prepared by linking organic ligands to metal ions to give covalent structures that have the same topologies as basic inorganic structures such as SiO_2 [2], rutile [3], PtS [4], CaCuP [5], and $ThSi_2$ [6]. The larger size of the building units in these coordination solids compared to those of their inorganic counterparts creates open space where guest solvent molecules or counterions reside in the crystal. At the outset of this study, attempts to liberate the neutral guests or to exchange the counterions has resulted in the destruction of the metal-organic framework, thus precluding its use as a porous material. We believe that in these cases the energy required to remove the inclusions from the channels by breaking the guest-framework interactions is sufficient to destroy the metal-organic architecture.

To provide solutions to this problem, we have focused our efforts on using building units that are capable of generating strong bonding interactions within the backbone structure of the framework, and on employing guest molecules or ions that are expected to self-aggregate within the channels without forming extensive interactions to the

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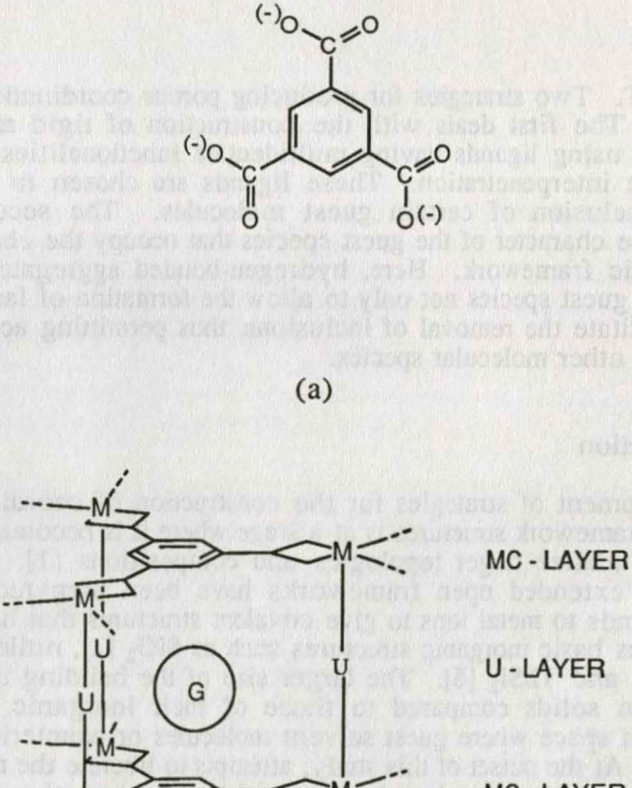
framework. We have demonstrated success in these two areas by using a multi-bidentate ligand, 1,3,5-benzenetricarboxylate (BTC), with cobalt(II) to form a stable open framework, $CoC_6H_3(COO)_2(COOH)(NC_5H_5)_2 \cdot 2/3NC_5H_5$, and by employing large hydrogen-bonded aggregates of nitrate ions and water as guests in the structure of copper(I) bipyridine, Cu(4,4′-bpy)$_{1.5} \cdot NO_3(H_2O)_{1.25}$. In both of these compounds, situations were created where operations such as the removal of the neutral guests or ion exchange of the counterions leave the framework intact. This contribution represents a summary of the synthetic routes developed for the production of these frameworks. The key structural features responsible for the inclusion properties of these solids are also presented.



(a)

(b)

Figure 1. (a) The structural formula of 1,3,5-benzenetricarboxylate, and (b) a schematic representation of its coordination to a metal ion to form alternating metal-carboxylate and spacer unit (U) layers leading to voids where guest inclusions (G) reside.

2. Selective Binding in $CoC_6H_3(COO)_2(COOH)(NC_5H_5)_2{\cdot}2/3NC_5H_5$

Given that carboxylate groups are known to bind to transition metal ions within the same plane as either bidentate or monodentate ligands, we postulated that the reaction of 1,3,5-benzenetricarboxylate (BTC) (Figure 1a) with a first-row transition metal may yield a material composed of metal-carboxylate (MC) layers as shown in Figure 1b. Here, U groups hold adjacent layers and create channels where inclusions reside. Depending on the character of U, suitable environments for accommodating various inclusions (G) could be generated.

2.1. SYNTHESIS

Solid $Co(NO_3)_2{\cdot}6H_2O$ (0.582 g, 2 mmol) and the acid form of BTC (BTCH3) (0.420 g, 2 mmol) were dissolved in 15 mL ethanol, then added to a solution of polyethylene oxide (PEO) (0.250 g, MW = 100,000) in 1,2-dichloroethane (5 mL). The mixture was stirred until a clear solution was obtained. Pyridine was diffused into this solution resulting in the formation of large pink crystals. These were collected and washed successively with 1,2-dichloroethane, ethanol, and acetone to yield 0.85 g of product. (Found; C, 54.99; H, 3.82; N, 7.44; Co, 12.43%: Calculated for $CoC_6H_3(COO)_2(COOH)(NC_5H_5)_2{\cdot}2/3NC_5H_5$; C, 56.11; H, 3.66; N, 7.82; Co, 12.33%.) This material is insoluble in water and common organic solvents. The homogeneity of the bulk product was confirmed by comparison of the observed and calculated powder diffraction pattern, which was produced using the single crystal data.

2.2. SINGLE CRYSTAL X-RAY STRUCTURE

An X-ray crystal analysis study was performed [at 20±1 °C, hexagonal, space group $P6_3/mcm$ - D_{6h}^3 (no. 193) with $a = 16.711(4)$ Å, $c = 14.189(2)$ Å, $V = 3423(1)$ Å^3, and $Z = 6$ for $x = 1$, $d_{calcd} = 1.464$ g cm^{-3}, $d_{found} = 1.48 \pm 0.01$ g cm^{-3}, R_1 (unweighted, based on F) = 0.068 for 552 independent reflections, μ_a ($MoK_{\bar{\alpha}}$) = 0.80 mm^{-1}] to reveal the presence of a neutral porous network represented by the formula, $CoC_6H_3(COO)_2(COOH)(NC_5H_5)_2{\cdot}2/3NC_5H_5$. A single layer of the structure is shown in Figure 2a, where two $BTCH_3$ and one BTC units are coordinated to each of the cobalt(II) centers. The remaining positions on the metal centers are occupied by pyridine molecules which were treated as being statistically disordered with two preferred orientations around the Co-N bond. This arrangement generates extended sheets along the *xy* plane. In the crystal, these sheets stack along the *z* axis to give alternating cobalt-carboxylate and pyridine layers as shown in Figure 2b. Close examination of the remaining space between the sheets reveals the presence of uncoordinated pyridine molecules which occupy the rectangular channels (7 × 10 Å) resulting from the tight fit between the layers. This gives the structure a three-dimensional character in that these closely interacting pyridines running along the third dimension create a rigid channel system; as the layer-layer separation

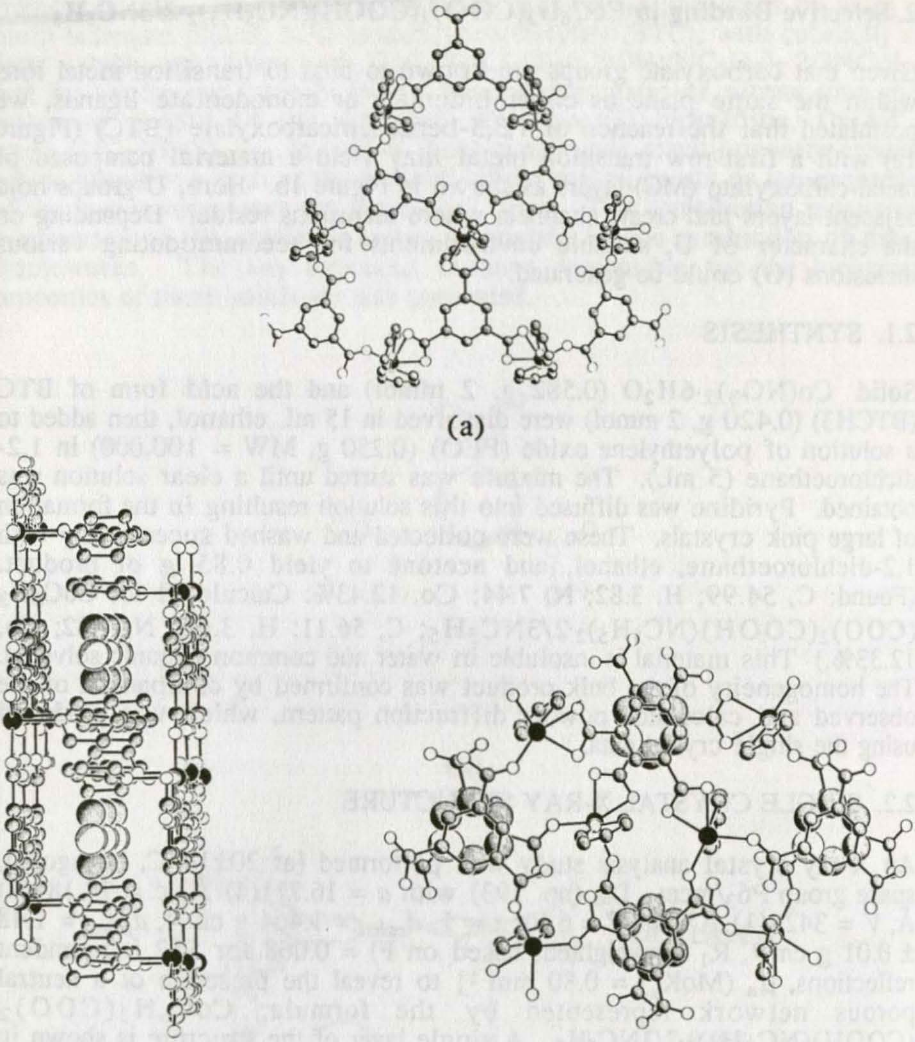


Figure 2. (a) A single layer of the extended porous network of $CoC_6H_3(COO)_2(COOH)(NC_5H_5)_2 \cdot 2/3\ NC_5H_5$. The metal-carboxylate layer is shown approximately along the *xy* plane with the spheres: dark, Co; open, O; partially shaded, N; and shaded, C. Only one of the two preferred orientations about the Co-N bond is shown for the statistically disordered coordinated pyridine molecules. The hydrogen atoms on the pyridines and btc units are omitted for clarity. (b) A perspective drawing perpendicular to the *z* axis. Here, the pyridine guest molecules are represented in the space-filling van der Waals radii to show their occupation of the channels within the structure. (c) A view of the structure along the *z* axis showing the π-stacking of the pyridine guests with the benzene rings of the btc units.

distance and the channel structure remain unaltered upon removal or inclusion of guests.

2.3. SELECTIVE BINDING STUDIES

Thermal gravimetric analysis performed on a crystalline sample showed cleanly at 190 °C a weight loss of 11.7%, corresponding to the loss of the pyridine guests occupying the channels (2/3 NC_5H_5 per formula unit), followed at 350 °C by another weight loss for a total 45.5%, corresponding to the remaining pyridine molecules bound to the metal centers within the framework (2 NC_5H_5 per formula unit). This material does not lose its crystallinity upon removal of the pyridine inclusions. Heating to 200 °C for six hours showed that the positions and intensities of the most intense lines (002), (003), (004), (005) and (006) remain unchanged relative to those observed for the unheated sample of the solid. Elemental microanalysis for the heated material (Found; C, 52.38; H, 3.46; N, 6.84%: Calculated for $CoC_6H_3(COO)_2(COOH)(NC_5H_5)_2$; C, 53.66; H, 3.32; N, 6.59) point to the absence of pyridine guests.

Examination of the single crystals with an optical microscope at 60 °C under 0.001 mm Hg pressure showed that they retain their morphology and crystallinity upon loss of the pyridine guests. Based on infrared data, we found that solid samples of this material, where the pyridine guests have been removed, selectively absorb aromatic molecules such as benzene, nitrobenzene, cyanobenzene, and chlorobenzene but not acetonitrile, nitromethane, or 1,2-dichloroethane. We believe that the remarkable selectivity of this open framework towards aromatic molecules is a direct consequence of their π-stacking with the carboxylate units present within the sheets as shown in Figure 2c. The use of multidentate ligands, coupled with our ability to functionalize the framework contribute greatly to the unusual thermal stability exhibited by this material.

3. Hydrothermal Synthesis of $Cu(4,4'\text{-bpy})_{1.5}{\cdot}NO_3(H_2O)_{1.25}$

Hydrogen-bonded aggregates of nitrate-water can be used as inclusion to support the formation of open structures with copper(I) and 4,4'-bipyridine(4,4'-bpy). However, hydrothermal conditions have to be used due to the poor solubility of 4,4'-bpy in water at room temperature.

3.1. SYNTHESIS

A mixture of $Cu(NO_3)_2{\cdot}2.5H_2O$ (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 deionized water (15 mL) 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°/min and held at that temperature for 24 h, then cooled at 0.1°/min to 90 °C and held for 12 h, followed by further cooling at the same rate to 70 °C and held for another 12 h, and finally cooled down to room temperature at 0.1 °C/min. The resulting rectangular parallelepiped orange crystals of Cu(4,4'-

bpy)$_{1.5}$·$NO_3(H_2O)_{1.25}$ were collected and washed with deionized water (3 × 5 mL) and ethanol (2 × 5 mL), then air-dried to give 0.25 g of product (87% yield based on bpy). This compound is stable in air and is insoluble in water and common organic solvents.

3.2. SINGLE CRYSTAL X-RAY STRUCTURE

X-ray structure determination performed on a single crystal [at 20±1 °C, orthorhombic, space group *Fddd* (No. 70) with a = 18.272(5) Å, b = 23.498(5) Å, c = 29.935(7) Å, V = 12853(6) Å^3, and Z = 32, d_{calcd} = 1.581 g cm^{-3}, R_1 (unweighted, based on F)=0.036 for 1404 independent reflections, μ_a (MoK$_{\alpha}^{-}$ = 1.39 mm^{-1}] isolated from the reaction mixture reveal an extended cationic framework constructed from the building unit shown in Figure 3a. 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 with each single network (shown in Figure 3b) having three different size channels running along the [100], [010] and [001] crystallographic axes with dimensions 26 × 20 Å, 10 × 12 Å and 43 × 18 Å, respectively. The overall structure contains six-interpenetrating frameworks. 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 Å and 4 × 5 Å) which are occupied by nitrate anions that are hydrogen-bonded to solvent water molecules.

3.3. ION-EXCHANGE STUDIES

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. 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^-.

4. Summary

This work demonstrates the importance of using multi-bidentate ligands in the formation of stable metal-organic frameworks capable of maintaining their porous structure in the absence of inclusions. The selective binding of aromatic solvents to the cobalt-carboxylate framework indicates that specific features can be built into the structure to generate environments capable of accommodating with discrimination a variety of guests. The large hydrogen-bonded aggregates observed as inclusions in the open structure of copper(I) bipyridine point to a possible relationship between the size of the guest and the size of the channels ultimately produced in the crystal. It appears that liberation of water from these aggregates allows easier access to

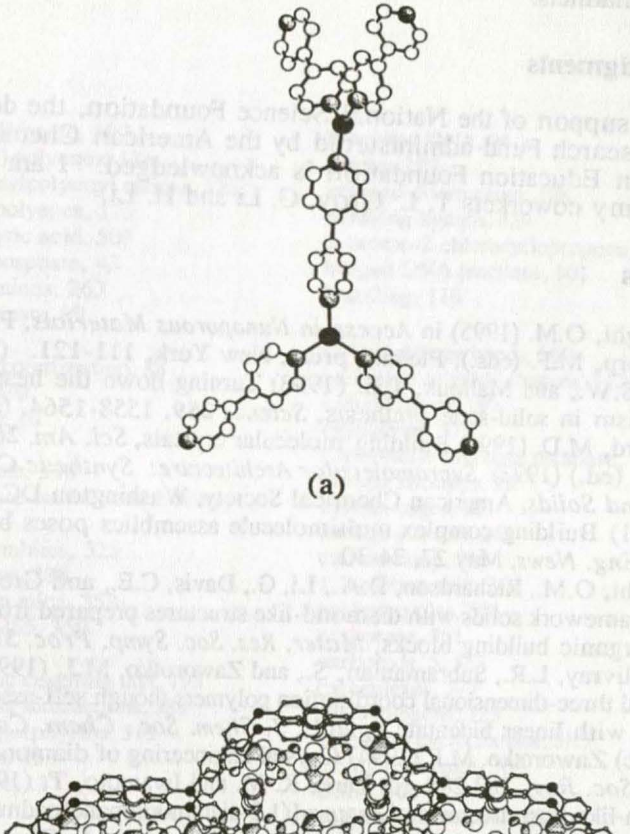


Figure 3. (a) The building block unit present in crystalline Cu(4,4'-bpy)$_{1.5}$·NO$_3$(H$_2$O)$_{1.5}$ (open spheres, C; shaded spheres, N; dark spheres, Cu). (b) The structure of a single framework shown approximately down the crystallographic direction [100]. The framework is represented as a line drawing and the nitrate anions and the water guest inclusions are depicted with large open spheres, O; large shaded spheres, N; small shaded spheres, H. The 4,4′-bpy hydrogens are omitted and all atoms are assigned arbitrary sizes for clarity.

the channels and thus more facile ion-exchange of the nitrate ions residing within those channels.

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