

Preparation of a Chiral, 2-Dimensional Network Containing Metallacrown and Copper Benzoate Building Blocks

Jeffrey J. Bodwin and Vincent L. Pecoraro*

Department of Chemistry, University of Michigan, Ann Arbor, Michigan 48109-1055

Received November 17, 1999

Great attention is presently being focused on the controllable preparation of porous, metal organic solids using a small molecule building block approach.¹ The interest in these materials stems from applications of the solids ranging from sensors to catalysts, either through framework recognition or through reactive guests. The preparation of non-centrosymmetric solids is also desirable since nonlinear optical, ferroelectric, and piezoelectric effects are technologically important.² Beautiful examples now exist of two- and three-dimensional porous lattices that are constructed rationally using molecular units that assemble to form the desired structure in high yields.¹ A supramolecular approach to form metal organic solids has been intensively studied, and recently chiral, acentric networks have been prepared.³ Typically these solids have the metal atom of the framework as their chiral center while the organic ligands used are achiral. While there are exceptions,⁴ this approach usually does not allow for the preparation of chiral solids in bulk. This is because an individual system may form either racemic networks or chiral crystals that must be manually separated. Thus, the search for new chiral synthons that can be woven into 2D or 3D frameworks to generate controllably well-defined chiral solids is an important objective of solid-state chemistry.

One attractive chiral synthon that can be considered for preparation of metal organic solids is metallacrowns.⁵ These polynuclear complexes can be isolated with multiple resolved chiral centers in one-step, high-yield (>70% in gram quantities) benchtop syntheses. The metallacrowns can be prepared as colored, optically active and often paramagnetic molecules. Their sizes and shapes, as 12-MC-4 species, are reminiscent of porphyrins and phthalocyanines; however, unlike these well-

known macrocycles, chirality is easily introduced into the metallacrown.

In order to form 2D or 3D networks one must be able to link each metallamacrocycle. This can be achieved in one dimension through anion bridges between the metals of adjacent metallacrowns. 2D or 3D networks could then be generated either by covalent linkages off of the metallacrown side chains or through metal–heteroatom bonds off of the same side chains or the metallacrown core. One attractive strategy that exploits the latter approach is connecting adjacent metallacrowns using the ubiquitous group of metal carboxylate dimers.

To this end, we have prepared $\{Cu^{II}(NO_3)_2[12-MC_{Cu^{II}}(N(S-\beta\text{-pheHA})^-)_4]Cu_2(\text{benzoate})_4\}_n$, **1**.⁶ Analysis of the non-centrosymmetric (*P*1, No. 1) crystals reveals that the $Cu_2(\text{benzoate})_4$ dimer (Cu_{dimer}) is bound in axial positions to two adjacent metallacrowns through the carbonyl oxygen of the hydroximate ligand at a distance of 2.24 Å.⁷ The $MC-Cu_{\text{dimer}}$ repeat unit is illustrated in Figure 1. A linear chain is generated by the $[MC-Cu_{\text{dimer}}]_n$ interaction with the metal–oxygen connectivity pattern $[Cu-Cu-O-Cu-O-Cu-O-Cu-O]_n$. The metallacrowns are also linked through a bridging nitrate anion that is oriented nearly perpendicular to the chain axis. The $MC-MC$ separation through the bridging nitrate is 7.27 Å ($Cu-O_{NO_3} = 2.46$ and 3.13 Å) and through the Cu_{dimer} is 7.13 Å ($Cu-O_{MC} = 2.24$ Å each). The Cu_{dimer} and the NO_3^- bridges generate a chiral 2D layer with each of the β -carbon atoms in the *S* configuration. A second nitrate is bound to the metallacrown ($Cu-O_{NO_3} = 2.53$ Å) for charge balance but does not bridge.

Examination of the solid perpendicular to this layer reveals channels with 8 Å × 9 Å dimensions.⁸ The ceiling and floor of the channels are formed by the faces of the metallacrowns. In contrast, walls are generated by overlap of the aromatic rings. This neutral 2D framework contains a guest benzoic acid that is tightly hydrogen bonded to a proton of a water molecule bound to a ring $Cu(II)$ and to the amine nitrogen of the chiral ligand. While the individual metallacrown is soluble in alcohols, water, and *N,N*-dimethylformamide and the copper benzoate dimer is soluble in alcohols and acetone, **1** is soluble in methanol, water,

- (1) (a) Yaghi, O. M.; Li, H.; Davis, C.; Richardson, D.; Groy, T. L. *Acc. Chem. Res.* **1998**, *31* (8), 474. (b) Kumar, R. K.; Balasubramanian, S.; Goldberg, I. *Chem. Commun. (Cambridge)* **1998**, 1435. (c) Hasegawa, I.; Hibino, K.; Takei, K. *Appl. Organomet. Chem.* **1999**, *13*, 549. (d) Gudbjartson, H.; Birada, K.; Poirier, K. M.; Zaworotko, M. J. *J. Am. Chem. Soc.* **1999**, *121*, 2599. (e) Kiang, Y.-H.; Gardner, G. B.; Lee, S.; Xu, Z.; Lobkovsky, E. B. *J. Am. Chem. Soc.* **1999**, *121* (36), 8204. (f) Yaghi, O. M.; O'Keeffe, M.; Kanatzidas, M. J. *Solid State Chem.* **2000**, *152*, 1 and subsequent articles in this issue.
- (2) (a) Halasyamani, P. S.; Poeppelmeier, K. R. *Chem. Mater.* **1998**, *10* (10), 2753–2769. (b) Shii, Y.; Motoda, T.; Kai, F.; Nakashima, T.; Tsuchagues, J.-P.; Matsumoto, N. *Inorg. Chem.* **1999**, *38*, 3513–3522.
- (3) (a) Lin, W.; Evans, O. R.; Xiong, R.-G.; Wang, Z. *J. Am. Chem. Soc.* **1998**, *120* (50), 13272–13273. (b) Olenyuk, B.; Whiteford, J. A.; Stang, P. J. *J. Am. Chem. Soc.* **1996**, *118* (35), 8221–8230. (c) Evans, O. R.; Wang, Z.; Lin, W. *Chem. Commun. (Cambridge)* **1999**, 1903–1904.
- (4) Biradha, K.; Seward, C.; Zaworotko, M. J. *Angew. Chem., Int. Ed.* **1999**, *38*, 492–495; Seo, J. S.; Whang, D.; Lee, H.; Jun, S. I.; Oh, J.; Jeon, Y. J.; Kim, K. *Nature* **2000**, *404*, 982–986.
- (5) (a) Pecoraro, V. L.; Stemmler, A. J.; Gibney, B. R.; Bodwin, J. J.; Kampf, J. W.; Wang, H. *Prog. Inorg. Chem.* Karlin, K., Ed.; Pergamon Press: New York, 1996; Vol. 45, Chapter 2, p 83. (b) Pecoraro, V. L.; Bodwin, J. J.; Cutland, A. D. *J. Solid State Chem.* **2000**, *152*, 68. (c) Stemmler, A. J.; Barwinski, A.; Baldwin, M. J.; Young, V., Jr.; Pecoraro, V. L. *J. Am. Chem. Soc.* **1996**, *118*, 11962. (d) Stemmler, A. J.; Kampf, J. W.; Pecoraro, V. L. *Angew. Chem.* **1996**, *35*, 2841. (e) Halfen, J. A.; Bodwin, J. J.; Pecoraro, V. L. *Inorg. Chem.* **1998**, *37*, 5416–5417. (f) Stemmler, A. J.; Kampf, J. W.; Kirk, M. L.; Atasi, B. H.; Pecoraro, V. L. *Inorg. Chem.* **1999**, *38*, 2807.

- (6) Four equivalents of (*S*)- β -phenylalaninehydroxamic acid and 12 equiv of sodium benzoate were dissolved in methanol with stirring. Seven equivalents of copper nitrate hemipentahydrate was added and the reaction mixture stirred for 1 h before being filtered. Slow evaporation of the solvent at room temperature yielded green plates in 55% yield. Dried crystals decompose sharply from 257° to 260 °C. Elemental anal. for $C_{66}H_{68}O_{27}N_{11}Cu_7$ found (calcd): C = 41.66 (41.90), H = 3.64 (3.62), N = 8.35 (8.14), Cu = 23.4 (23.51).
- (7) X-ray diffraction data were collected on a SMART CCD diffractometer at 158 K on a green plate with dimensions 0.06 mm × 0.10 mm × 0.42 mm; 18335 independent reflections were collected over the range 1.91–26.44°; triclinic, *P*1 (No. 1). Unit cell: $a = 10.9445$ Å, $b = 14.2679$ Å, $c = 16.0910$ Å, $\alpha = 90.476^\circ$, $\beta = 101.819^\circ$, $\gamma = 93.738^\circ$. GOF = 1.045. Final $R = 0.0822$. Absolute structure factor = 0.05(2). All non-hydrogen atoms were refined anisotropically, with hydrogens being allowed to ride on idealized positions.
- (8) Cavity size was determined by subtracting a van der Waals radius of 2.5 Å from various atom–atom distances across the cavity.

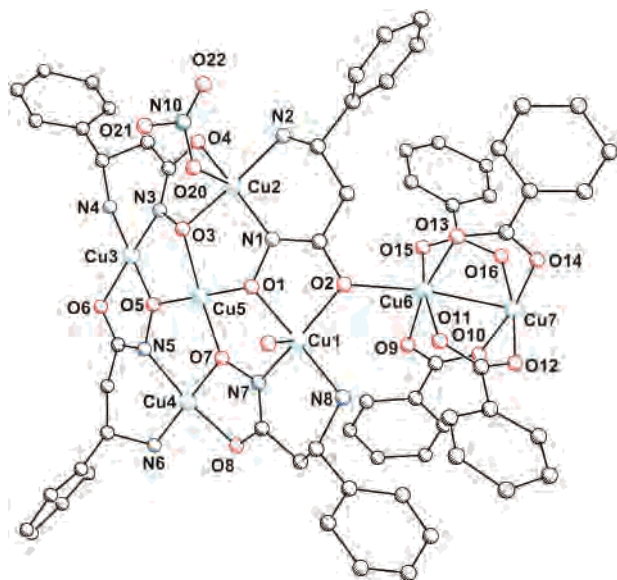


Figure 1. Unique repeat unit of $\{\text{Cu}(\text{NO}_3)_2[12\text{-MCu}^{\text{II}}\text{N}(\text{s}-\beta\text{-pheHA})\text{-4}]\}\text{-}\{\text{Cu}_2(\text{benzoate})_4\}$, **1**, with all heteroatoms numbered. The nonbridging nitrate, benzoic acid guest, and all solvents have been omitted for clarity.

and dimethylformamide but insoluble in ethanol, acetone, and less polar solvents such as diethyl ether, chloroform, and benzene. Methods of characterization which involve dissolution of the sample, such as UV–visible, CD, or mass spectroscopy, yield data which is consistent with dissociation of this 2-dimensional network but not destruction of the metallacrown and copper benzoate dimer components.⁹ Thermogravimetric analysis of the sample reveals that after initial 6% loss of solvent mass (consistent with 3 methanols and 1 water from the crystal structure) between room temperature and 110 °C, the sample is stable up to 220 °C, at which point it decomposes.

In an attempt to explore the generalizability of this synthesis, the analogous compound has been synthesized with (*R*)- β -phenylalaninehydroxamic acid, and analysis of the single-crystal X-ray data reveal that this material forms a 2-dimensional network which is the mirror image of that found for **1**. The same network has also been synthesized with *p*-methylbenzoate in place of benzoate with only minor changes in the powder XRD data.

Analogous synthesis in the absence of nitrate or any other anion except benzoate yields a very similar structure in which the same $[-\text{MC}-\text{Cu}_{\text{dimer}}-]_n$ chains exist, but there is no anion bridging in a second dimension (Figure 2). The only significant difference in the solid-state structure of this nitrate-free synthesis lies in the fact that the chains are able to pack more closely without the nitrate bridge present. In this respect, the 2-dimensional network represented by **1** can be thought of as simply this 1-dimensional chain structure which has expanded to accommodate a nitrate guest. The size and orientation of the channels is maintained in this structure even in the absence of the nitrate bridges; therefore, it can be inferred that the formation of these channels is driven by the orientation and packing of the phenyl substituents in the $[-\text{MC}-\text{Cu}_{\text{dimer}}-]_n$ framework (Figure 3).

In summary, we report a versatile approach for the synthesis of chiral 2D networks that has the potential for broad compositional variation. The properties of the network might be altered by the metals placed in the metallacrown, the chiral ligand used

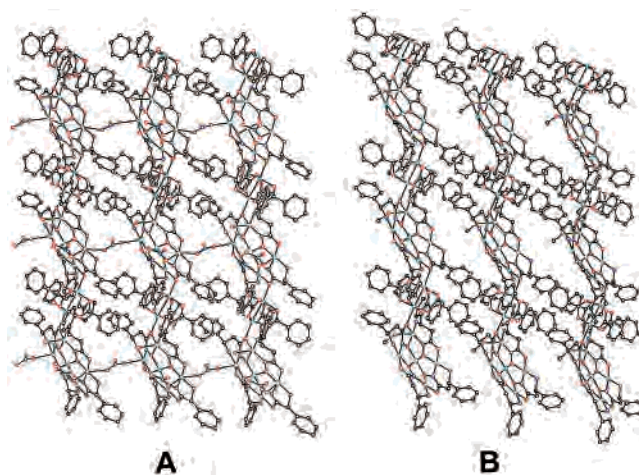


Figure 2. (A) 2-Dimensional network generated by **1**. (B) Packing of chains in the nitrate-free version of **1**. Both are derived from crystallographic data. Absence of the nitrate guest in B leads to closer packed chains.

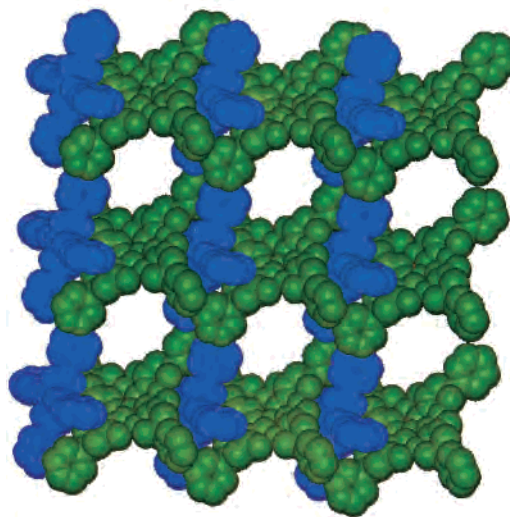


Figure 3. Packing of **1** parallel to the 2-dimensional sheet. The metallacrowns are shown in green, and the copper benzoate paddlewheel dimers are shown in blue; bridging nitrates are not visible in this view, and all solvents and benzoic acid guests have been removed.

to support the metallacrown, the bridging anion used to link the faces of the metallacrown, and the choice of bridging dimer used to form the metal chain. By these modifications, one can envision tuning magnetic and optical properties of the solid as well as altering thermal stability and substrate recognition properties. Probably most important, we have shown that metallacrown building blocks guarantee a predefined solid-state chirality that can be prepared inexpensively and easily in bulk quantities.

Acknowledgment. The authors thank Professor O. M. Yaghi for valuable discussions and Dr. Jeff Kampf for collecting the X-ray data.

Supporting Information Available: A summary of crystal data and tables of atomic coordinates, bond lengths, and bond angles for **1** (Tables S1–S4); a thermal ellipsoid plot of **1** with numbering scheme (Figure S1); a TGA trace of **1** (Figure S2); and powder XRD data for all compounds (Figure S3). The crystallographic parameters for **1** have been deposited as a CIF file. This material is available free of charge via the Internet at <http://pubs.acs.org>.

(9) UV–visible (methanol solution): 618 nm ($503 \text{ M}^{-1} \text{ cm}^{-1}$), 322 nm ($2250 \text{ M}^{-1} \text{ cm}^{-1}$). CD (methanol solution): 740 nm (+), 550 nm (+), 380 nm (–). FAB-MS (3-nitrobenzyl alcohol matrix): 1029 ($\text{Cu}_5(\beta\text{-pheHA})_4$), 1091 ($\text{Cu}_5(\beta\text{-pheHA})_4 + \text{NO}_3$).