

## Periodic Tiling of Pentagons: The First Example of a Two-Dimensional $(5_{3,4})$ -net

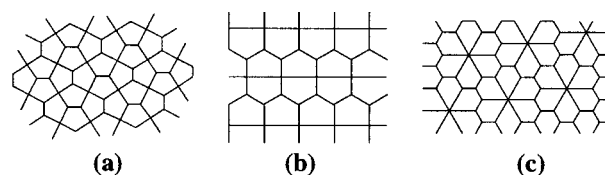
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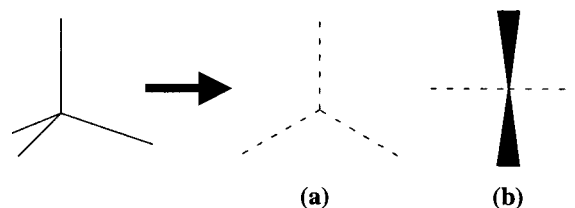
Received July 17, 2001  
Revised Manuscript Received August 3, 2001

Self-assembly of transition metals and multifunctional organic ligands represents a successful paradigm for the single-step synthesis of either infinite<sup>1</sup> or discrete<sup>2</sup> molecular structures, many of which exhibit nanoscale features such as pores or cavities. Of particular note has been the isolation and characterization of two-dimensional (2D) topologies that contain three-, four-, and six-sided polygons.<sup>1</sup> The incorporation of five-sided polyhedral assemblies into supramolecular polymers is, however, an area that remains undeveloped. When one considers that a regular pentagon has angles that are very close to the tetrahedral angle, it is surprising that even the synthesis of discrete molecular pentagons has, until recently, been unrealized.<sup>3</sup> It is, perhaps, less surprising that a 2D arrangement of pentagonal units has not been observed,<sup>4</sup> as it is widely held that pentagons cannot tile the plane. Although it is true that *regular* pentagons cannot tile the plane, there are in fact 14 different types of convex pentagons that tile the plane.<sup>5</sup> Indeed, three duals of the eight semi-regular nets<sup>6</sup> are pentagonal tilings (Figure 1). Herein we report what is to our knowledge the first example of a 2D network that exhibits one of these tiling patterns and possesses both three-connected and four-connected nodes. Specifically, we demonstrate that 3 equiv of hexamethylenetetramine, HMTA, can be complexed with 5 equiv of  $\text{Cu}_2(\mu\text{-O}_2\text{CCH}_2\text{CH}_3)_4$  to afford  $[(\text{HMTA})_3(\text{Cu}_2(\mu\text{-O}_2\text{CCH}_2\text{CH}_3)_4)_5]_n$ , **1**, the first example of a modular  $(5_{3,4})$ -network.

From a topological perspective, the 14 tilings that contain only pentagons can be divided into three groups on the basis of the connectivity of the vertices: five  $(5,3)$ -nets, eight  $(5_{3,4})$ -nets, and one  $(5_{3,6})$ -net. **1** has a topology similar to the  $(5_{3,4})$ -network illustrated in Figure 1a. In its most symmetric form, this network has four equidistant links per pentagon, and trigonal and square-planar nodes in the ratio of 2:1. Although these features are



**Figure 1.** The nets that are duals of three semi-regular nets, and which represent three of the 14 tilings that contain congruent pentagons.



**Figure 2.** A tetrahedral node projected down the three-fold axis (a), and two-fold axis (b) affording pseudotrigonal and pseudosquare geometries, respectively.

chemically accessible, crystal engineering has not yet demonstrated an ability to persistently control the self-assembly of this many components. We have, however, been able to synthesize this network using a modular two-component approach by linking the tetrahedrally disposed HMTA via the apical coordination sites of a dimetal tetracarboxylate cluster,  $\text{Cu}_2(\mu\text{-O}_2\text{CR})_4$ .<sup>7</sup>

Figure 2 illustrates how a tetrahedral node can be viewed as either a trigonal or a square-planar node when projected down the three-fold or two-fold axis, respectively. The exploitation of a tetrahedral node to generate this network imposes certain conditions: the network cannot be planar; the tetrahedral node must be able to adopt both a three-fold and four-fold coordination sphere; the individual pentagons must be nonplanar, that is, they are cyclopentanoic. In this context, HMTA is a suitable tetrahedral node, as it is known to adopt one-, two-, three-, and four-fold coordination.<sup>8</sup> It was our hope that by varying the stoichiometry of the reactants we would be able to direct the coordination of HMTA into the desired environments.

**1** was prepared by slow diffusion of a solution of HMTA in MeOH into a solution of  $\text{Cu}_2(\mu\text{-O}_2\text{CCH}_2\text{CH}_3)_4(\text{MeOH})_2$  that was prepared in situ, large blue crystals forming within days. Figure 3 presents overhead and perspective views of the crystal structure<sup>9</sup> of **1**, which is sustained by five-membered rings. This is a consequence of the HMTA nodes assuming an undistorted tetrahedral geometry and coordinating to either three or four spacers in a 2:1 ratio. The dinuclear copper carboxylate spacers are typical:<sup>7</sup> square-pyramidal coordination to four basal oxygens (ca. 1.9 Å) and one apical nitrogen (ca. 2.2 Å) having Cu–Cu separations of 2.58 and 2.59 Å for two crystallographically independent spacers. As expected, the sheets of **1** are curved, and the packing of adjacent sheets appears to be the consequence of shape considerations. The ethyl groups efficiently fill the pentagonal cavities, which have sides of 1.00 nm and diagonals of 1.54 nm, and mitigate against the inclusion of solvent molecules. The overhead view (Figure 3a) is a projection down [001] and

(7) For references related to dinuclear tetracarboxylate clusters see: Cotton, F. A.; Walton, R. A. *Multiple Bonds between Metal Atoms*, 2nd ed.; Oxford University Press: Oxford, UK, 1993.

(8) Examples of all modes of coordination for HMTA can be found in the April 2001 release of the Cambridge Structural Database: Allen, F. H.; Kennard, O. *Chem. Des. Autom. News* **1993**, 8(1), 31–37.

(9) Crystallographic details for **1** at 200 K:  $\text{Cu}_{12.5}\text{C}_{20.5}\text{H}_{16}\text{N}_3\text{O}_{10}$ , 623.21 g mol<sup>-1</sup>, tetragonal, *P*-42<sub>1</sub>*m*,  $a = b = 22.1967(15)$  Å,  $c = 10.7915(10)$  Å,  $V = 5667.4(7)$  Å<sup>3</sup>. Final values of  $R_1 = 0.0465$  and  $wR_2 = 0.1017$  were obtained for 4240 independent reflections. A good match between simulated XPD and observed XPD of the bulk sample was seen. **1** is thermally stable to 295 °C, at which point it undergoes a 69.8% weight loss.

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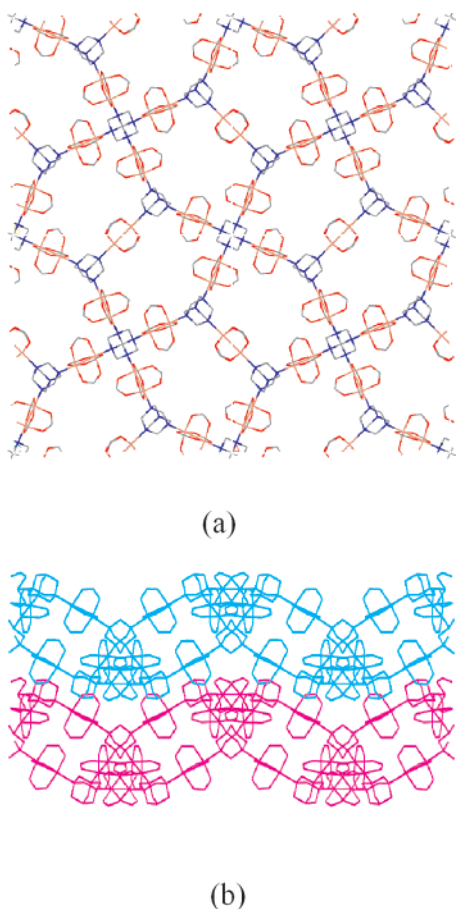
(2) For examples of discrete nanoscale structures that are based upon Platonic or Archimedean solids, see the following: (a) MacGillivray, L. R.; Atwood, J. L. *Angew. Chem., Int. Ed.* **1999**, *38*, 1019–1034. (b) Johnson, D. W.; Xu, J. D.; Saalfrank, R. W.; Raymond, K. N. *Angew. Chem., Int. Ed.* **1999**, *38*, 2882–2885. (c) Fujita, M.; Umemoto, K.; Yoshizawa, M.; Fujita, N.; Kusakawa, T.; Biradha, K. *Chem. Commun.* **2001**, 509–518. (d) Leininger, S.; Olenyuk, B.; Stang, P. J. *Chem. Rev.* **2000**, *100*, 853–908. (e) Moulton, B.; Lu, J. J.; Mondal, A.; Zaworotko, M. J. *Chem. Commun.* **2001**, 863–864.

(3) (a) Campos-Fernandez, C. S.; Clerac, R.; Koomen, J. M.; Russell, D. H.; Dunbar, K. R. *J. Am. Chem. Soc.* **2001**, *123*, 773–774. (b) Hasenknopf, B.; Lehn, J. M.; Boumediene, N.; Dupontgervais, A.; Vandorsselaer, A.; Kneisel, B.; Fenske, D. *J. Am. Chem. Soc.* **1997**, *119*, 10956–10962.

(4) For an example of a supramolecular network that is topologically congruent with the [001] projection of Bikitaite, having a mix of octagons and pentagons, see: Keller, S. W.; Lopez, S. J. *J. Am. Chem. Soc.* **1999**, *121*, 6306–6307.

(5) (a) Wells, D. *The Penguin Dictionary of Curious and Interesting Geometry*; Penguin: London, 1991. (b) Grünbaum, B.; Shephard, G. C. *Tilings and Patterns*; W. H. Freeman: New York, 1987. (c) Gardner, M.; Klamer, D. A. *Mathematical Recreations: A Collection in Honor of Martin Gardner*; Prindle, Weber, and Schmidt: Boston, 1981.

(6) Wells, A. F. *Three-Dimensional Nets and Polyhedra*; Wiley: New York, 1977.



**Figure 3.** Overhead and perspective views of the  $(5_4^3)$ -network (H atoms omitted for clarity) seen in the crystal structure of  $[\text{HMTA}]_3[\text{Cu}_2(\mu\text{-O}_2\text{CEt})_4]_5$ , **1**.

illustrates how the network projects on to the plane to give the  $(5_4^3)$ -net illustrated in Figure 1a.

There are two crucial design elements that direct the formation of the  $(5_4^3)$ -net and mitigate against the formation of alternate supramolecular isomers,<sup>10</sup> in particular those based upon cyclohexanoid rings: the nature of the acid functionality, R, in the  $\text{Cu}_2(\mu\text{-O}_2\text{CR})_4$  linker, and the ratio, X, between HMTA and linker. For the conditions R = ethyl and X = 3:5, **1** is obtained. Other networks can be obtained by varying these conditions: a 1D zigzag structure<sup>11</sup> is observed when HMTA coordinates to 2  $\text{Cu}_2(\mu\text{-O}_2\text{CR})_4$  linkers (R = Me or *t*-Bu, X = 1:1) and a diamondoid structure<sup>12</sup> results from the coordination of four linkers to HMTA (X = 1:2). Indeed, there are numerous supramolecular isomers that can be formed by systematically modifying R and X. Particularly, coordination of HMTA to three spacers is expected to yield both 2D three-connected topologies (i.e., a (6,3)-net) and also 3D topologies (i.e., the (10,3)-nets) depending on the nature of R.<sup>13</sup> Three-dimensional nets having the same (3,4)-connectivity as **1** are also expected to result by varying X.<sup>6</sup>

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(13) For a review of three-connected topologies see: Batten, S. R.; Robson, R. *Angew. Chem., Int. Ed.* **1998**, *37*, 7(11), 1461–1494.

In our opinion these structures illustrate several salient structural features. First, in the majority of modular structures, the role of the organic ligand is to serve as a spacer that links nodes that are defined by metal geometry. Only a few multidimensional structures have been reported where a metal, or metal cluster, acts as a linear spacer, thereby linking organic moieties with a defined geometry. The ubiquitous dimetal tetracarboxylate cluster,  $\text{M}_2(\text{O}_2\text{CR})_4$ , has accessible apical coordination sites and is ideally suited to serve as a metal-based linear spacer.<sup>14</sup> Although the majority of structures using these clusters have been 1D chains (linear and zigzag), there have been reports of 2D (square grid and hexagonal) and 3D (diamondoid) structures. Similar topologies have been reported using mononuclear silver(I) as a metal spacer.<sup>15</sup>

Second, the modular nature of the structures afforded by coordination of dimetal carboxylates to HMTA implies that there is a wide range of permutations that should be readily available from a synthetic perspective. In particular, there are numerous carboxylates and numerous transition metals that are available for incorporation into such structures. These compounds might therefore represent suitable prototypes for structure/function studies, especially in the area of molecular magnetism since  $\text{Cu}_2(\mu\text{-O}_2\text{CR})_4$ -based structures have been shown to be magnetically active.<sup>16</sup>

In summary, **1** illustrates how subtle supramolecular effects can control not only the superstructure but also the fundamental building blocks that result in the superstructure. We consider the generation of nanoscale cyclopentanoid rings from tetrahedral nodes to be potentially relevant since, when such rings are fused, they necessarily exhibit curvature. They therefore represent a possible entry into neutral spheroid structures that would be related to the discrete molecular dodecahedra recently reported by Stang et al.<sup>17</sup> Alternatively, with a change in stoichiometry, infinite frameworks based upon fused distorted dodecahedra (pyritohedra) might be formed, as well as other 2D network structures such as the  $(5_4^3)$ -net illustrated in Figure 1b.

**Acknowledgment.** We gratefully acknowledge the generous financial support of the National Science Foundation (DMR 0101641) Crystallographic data (excluding structure factors) for **1** have been deposited with the Cambridge Crystallographic Data Centre as supplementary publication no. CCDC 165884. Copies of the data can be obtained, free of charge, on application to CCDC, 12 Union Road, Cambridge CB2 1EZ, UK (fax: +44 1223 336033 or e-mail: deposit@ccdc.cam.ac.uk).

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