Framework Design with Molecular Blocks

Design of Frameworks with Mixed Triangular and Octahedral Building Blocks Exemplified by the Structure of [$Zn_4O(TCA)_2$] Having the Pyrite Topology **

*Hee K. Chae, Jaheon Kim, Olaf Delgado Friedrichs, Michael O'Keeffe, and Omar M. Yaghi**

A prerequisite to the design of crystalline materials is the knowledge of the possible structures that potentially may form by linking together specific molecular shapes. In this context, we recently argued that, from the large number of possible structures that could in principle be assembled from various molecular shapes, those with the highest symmetry are most likely to form in practice. Thus it is particularly important to identify these special structures since they represent the default structures for the assembly of shapes.[1]

This approach has been useful in the chemistry of extended metal–organic frameworks (MOFs) in which 3D structures assembled entirely from triangles,[2] squares,[3] tetrahedra,[4] or octahedra[5] usually form structures based on the $SrSi_2$, NbO, diamond and primitive cubic nets, respectively. Indeed, these have the highest possible symmetry for their respective building block shapes and have become as important to crystal designers as the Platonic solids are to molecular chemists. Herein we point out that the FeS_2 (pyrite) net found in [$Zn_4O(TCA)_2$]·$(DMF)_3(H_2O)_3$ (hereafter MOF-150; TCA = 4,4′,4″-Tricarboxytriphenylamine, DMF = *N*,*N*′-dimethylformamide), is the most regular net (and the most likely to form) for linking together triangles and octahedra and that it has some additional net properties that lead to its classification as a default net.

We use TCA and [$Zn_4O(CO_2)_6$] as secondary building units (SBUs) (Figure 1 a) to provide three- and six-coordinated vertices, respectively. The SBUs are produced by employing previously determined reaction parameters to effect their formation in situ.[5a,b] Thus, the reaction of zinc nitrate and TCA in DMF/EtOH/H_2O resulted in the formation of light brown truncated crystals, which were formulated by elemental microanalysis and single crystal X-ray diffraction studies.[6]

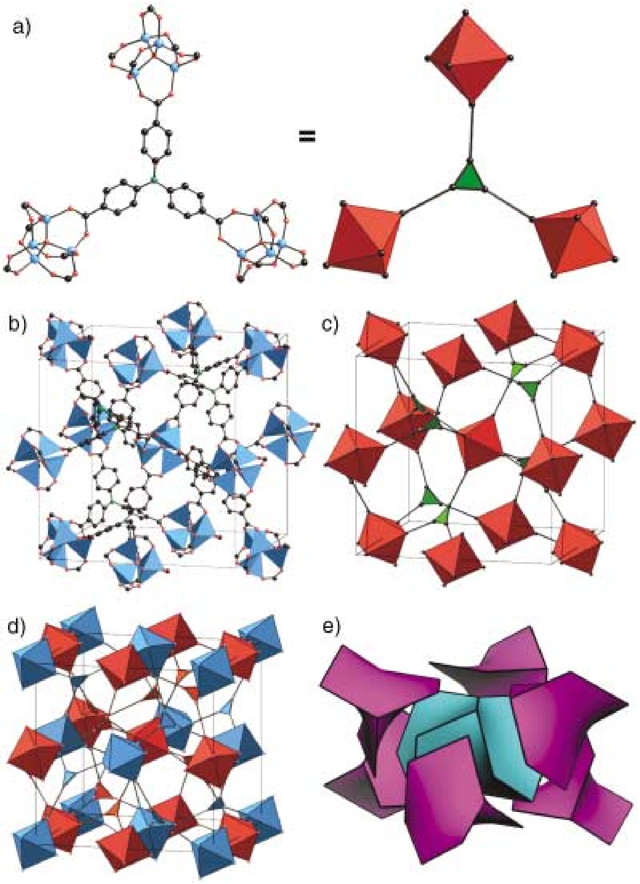

Figure 1. a) A TCA unit linked to three octahedral SBUs. Zn blue, O red, N green, C black. b) One net of MOF-150 with ZnO_4 tetrahedra (blue) filled in c) as (b) but stylized. d) Two intergrown nets as (c). e) Tiles of the pyrite net.

The structure consists of two identical interpenetrating nets, one of which is shown in Figure 1 b. In this structure, the basic zinc acetate octahedral SBUs, each composed of four ZnO_4 tetrahedra sharing a common corner, are linked by the tritopic TCA to form a 6,3-coordinated net shown in stylized form in Figure 1 c. The two interpenetrating frameworks are depicted in Figure 1 d. The underlying 6,3-coordinated framework has symmetry $Pa\bar{3}$, and the two interpenetrating frameworks have symmetry $Ia\bar{3}$ (as found in the crystal, Figure 1 d). The topology of each framework is related to the structure of the pyrite form of FeS_2; it has the same topology if the S–S bonding in pyrite is ignored, so we call it the pyrite net.[7] It has been observed, not interpenetrating, in a [$Hg(TPT)_3$]$^{3+}$ (TPT = 2,4,6-tri(4-pyridyl)-1,3,5-triazine) framework.[8] A cyanide with the pyrite topology (but now with the S–S link included) was also reported, again not interpenetrating.[9] We believe MOF-150 is the first example of a fully catenated structure (one in which all rings of one net are mechanically linked to rings of the other and vice versa) with mixed

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[*] Prof. Dr. O. M. Yaghi, Dr. J. Kim
Materials Design and Discovery Group
Department of Chemistry
University of Michigan
Ann Arbor, MI 48109-1055 (USA)
Fax: (+1) 734-615-9751
E-mail: oyaghi@umich.edu

Prof. Dr. H. K. Chae
Department of Chemistry
Hankuk University of Foreign Studies
Yongin, Kyungki-Do, 449-791 (S. Korea)

Dr. O. D. Friedrichs, Prof. Dr. M. O'Keeffe
Department of Chemistry and Biochemistry
Arizona State University
Tempe, AZ 85287-1604 (USA)

[**] The National Science Foundation support to MO'K (DMR-0103036) and OMY (DMR-9980469) is gratefully acknowledged. HKC is supported by the Korean Science and Engineering Foundation (KOSEF 2000-1-12200-002-3). TCA = 4,4′,4″-Tricarboxytriphenylamine.

DOI: 10.1002/anie.200351546

coordination. Interpenetration of nets of mixed coordination is well known,[3g,10] but they are never fully catenated.

Three DMF and three water molecules per formula unit fill the space remaining after interpenetration in the crystal. This space is calculated to be 52 % of the crystal volume and it is in the form of small capsules of 7–8 Å diameter that are interconnected by 4 Å openings. The solvent guests can be removed from the pores in air: A sample (18.526 mg) heated at 10 °C min^{-1} in air from 30 to 700 °C showed a weight loss (20.9 %) step at 240 °C corresponding to the loss of all guests (21.0 % calcd for three DMF and three H_2O molecules per unit formula).

MOF-150 is important both in its intrinsic net properties and in the fact that it led to the identification of the pyrite net as the default structure for the assembly of triangles and octahedra. It is instructive to discuss the topology of the net in terms of tilings of space.[11] Figure 1 e shows space-filling tiles (cages) that underlie the pyrite net. The tiling is composed of trihedral tiles (green) and hexahedral tiles (red) in the ratio 2:1 and the vertices and edges of the tiling are the vertices and edges of the pyrite net. The tiling is an example of a natural tiling in that all the rings of the net are faces of the tiles and vice versa.[12] Tilings are characterized by a transitivity *pqrs* which signifies that there are *p* kinds of vertex, *q* kinds of edge, *r* kinds of face (ring), and *s* kinds of tile.[13] The simple cubic network, which is derived from a tiling of space with congruent cubes, is an example of a net with transitivity 1111 (all vertices, edges, faces and tiles related by symmetry). The most regular net with two kinds of vertex is that of the fluorite (CaF_2) structure which has transitivity 2111; we believe that it is the only net in this class.[12]

The next most regular tilings with two kinds of vertex have transitivity 2112 and pyrite is a member of this very small class. The dual structure is obtained by placing new vertices inside the original tiles and allowing new edges to connect these new vertices in the interior of adjacent tiles. It should be clear that a net and its dual are fully catenated, and that for a net with transitivity *pqrs*, the dual has transitivity *srqp*. For a net to be self-dual the transitivity must be palindromic; and indeed the pyrite net is self-dual.

The pyrite net has other interesting properties that it shares only with the diamond net. All the rings are 6-rings and all are related by symmetry. There are two 6-rings per vertex and the average coordination number is four.

It is our thesis that unless specific information in the form of low-symmetry features of the SBU is provided, the default net will form for a given connectivity and indeed this is overwhelmingly the case.[1] Thus it might be expected that for 6,3-coordination the pyrite net would be the default net. However most framework materials with this connectivity reported to date have the rutile topology and in fact this was identified as the default structure,[1] but rutile is significantly less symmetric than pyrite having two kinds of edge and three kinds of ring (transitivity 2232). Most of the rutile-structured materials reported have been cyanides with interpenetrating, partly catenated, frameworks such as $\{M[C(CN)_3]_2\}$;[10,14] in some instances the three-coordinated vertex has more than one kind of link as in compounds with a $\{M[N(CN)_2]_2\}$ framework, so the appearance of a less-symmetrical network is less surprising in this instance.[15] The occurrence of the rutile net in bis(isonicotinate) Fe^{II} is understandable on the same grounds.[16] We also note that in the case of MOF-150, the "octahedral" SBU actually has tetrahedral (T_d) symmetry with the planes of opposite carboxylate groups at 90°. However, as can be seen from Figure 1 c, opposite triangular groups have to be coplanar. TCA is flexible enough to provide the twist angle of 45° needed between the carboxylates and triangles. With less-flexible linkers we might expect to find other, less-symmetrical nets; we are exploring this possibility.

Experimental Section

A mixture DMF/C_2H_5OH/H_2O (1.00/0.25/0.25 mL) containing the acid form of TCA (H_3TCA)[17] (0.005 g, 1.32×10^{-5} mol) and $Zn(NO_3)_2 \cdot 6H_2O$ (0.017 g, 5.71×10^{-5} mol) was sealed under vacuum in a quartz tube (10 mm external diameter, 15 cm length, 6 mL capacity) and heated (0.5 °C min^{-1}.) to 90 °C for 20 h, then cooled at 0.1 °C min^{-1} to room temperature. The light brown truncated octahedral crystals were washed with a DMF/ethanol mixture (3–4 mL) to give MOF-150 (0.01 g 55 % yield). Elemental analysis calcd (%) for $C_{51}H_{51}O_{19}N_5Zn_4 = [Zn_4O(TCA)_2]\cdot(DMF)_3\cdot(H_2O)_3$: C 47.14, H 3.96, N 5.39; found C 47.98, H 3.84, N 5.40.

Received: April 1, 2003 [Z51546]

Keywords: chelates · interpenetrating structures · metal–organic frameworks · solid-state structures · zinc

[1] M. O'Keeffe, M. Eddaoudi, H. Li, T. M. Reineke, O. M. Yaghi, *J. Solid State Chem.* **2000**, *152*, 3–20.

[2] a) O. M. Yaghi, C. E. Davis, G. Li, H. Li, *J. Am. Chem. Soc.* **1997**, *119*, 2861–2868; b) C. J. Kepert, M. J. Rosseinsky, *Chem. Commun.* **1999**, 375–376; c) S. V. Kolotuchin, P. A. Thiessen, E. E. Fenlon, S. R. Wilson, C. J. Loweth, S. C. Zimmerman, *Chem. Eur. J.* **1999**, *5*, 2537–2547; d) Y. H. Kiang, G. B. Gardner, S. Lee, Z. Xu, *J. Am. Chem. Soc.* **2000**, *122*, 6871–6883; e) J. S. Seo, D. Whang, H. Lee, S. I. Jun, J. Oh, Y. J. Jeon, K. Kim, *Nature* **2000**, *404*, 982–986; f) M. J. Horner, K. T. Holman, M. D. Ward, *Angew. Chem.* **2001**, *113*, 4169–4172; *Angew. Chem. Int. Ed.* **2001**, *40*, 4045–4048; g) S. Masaoka, S. Furukawa, H.-C. Chang, T. Mizutani, S. Kitagawa, *Angew. Chem.* **2001**, *113*, 3933–3935; *Angew. Chem. Int. Ed.* **2001**, *40*, 3817–3819; h) C. Inman, J. M. Knaust, S. W. Keller, *Chem. Commun.* **2002**, 156–157.

[3] a) H. Li, M. Eddaoudi, T. Groy, O. M. Yaghi, *J. Am. Chem. Soc.* **1998**, *120*, 8571–8572; b) M. Eddaoudi, J. Kim, M. O'Keeffe, O. M. Yaghi, *J. Am. Chem. Soc.* **2002**, *124*, 376–377; c) M. Eddaoudi, J. Kim, D. T. Vodak, A. Sudik, J. Wachter, M. O'Keeffe, O. M. Yaghi, *Proc. Natl. Acad. Sci. USA* **2002**, *99*, 4900–4904; d) J. Lu, A. Mondal, B. Moulton, M. Zaworotko, *Angew. Chem.* **2001**, *113*, 2171–2174; *Angew. Chem. Int. Ed.* **2001**, *40*, 2113–2116; e) F. A. Cotton, C. Lin, C. A. Murillo, *Acc. Chem. Res.* **2001**, *34*, 759–771; f) S. S. Y. Chu, S. M. F. Lo, J. P. H. Charmant, A. G. Orpen, I. D. Williams, *Science* **1999**, *283*, 1148–1150; g) B. Chen, M. Eddaoudi, S. T. Hyde, M. O'Keeffe, O. M. Yaghi, *Science* **2001**, *291*, 1021–1023; h) K. Biradha, Y. Hongo, M. Fujita, *Angew. Chem.* **2000**, *112*, 4001–4003; *Angew. Chem. Int. Ed.* **2000**, *39*, 3843–3845; i) M. E. Kosal, J.-H. Chou, S. R. Wilson, K. S. Suslick, *Nat. Mater.* **2002**, *1*, 118–121; j) C. Serre, F. Millange, C. Thouvenot, M. Nogues, G. Marsolier, D. Louer, G. Ferey, *J. Am. Chem. Soc.* **2002**, *124*, 13 519–13 526.

[4] a) J. Kim, B. Chen, T. M. Reineke, H. Li, M. Eddaoudi, D. B. Moler, M. O'Keeffe, O. M. Yaghi, *J. Am. Chem. Soc.* **2001**, *123*, 8239–8247; b) K. Barthelet, D. Riou, G. Férey, *Solid State Sci.*

2002, *4*, 841–844; c) O. R. Evans, Z. Wang, R.-G. Xiong, B. M. Foxman, W. Lin, *Inorg. Chem.* **1999**, *38*, 2969–2973; d) L. Carlucci, G. Ciani, D. M. Proserpio, S. Rizzato, *CrystEngComm* **2002**, *4*, 1–13; e) K. Barthelet, D. Riou, G. Ferey, *Chem. Commun.* **2002**, 1492–1493; f) L. C. Tabares, J. A. R. Navarro, J. M. Salas, *J. Am. Chem. Soc.* **2001**, *123*, 383–387; g) C. Klein, E. Graf, M. W. Hosseini, A. D. Cian, *New J. Chem.* **2001**, *25*, 207–209; h) D. S. Reddy, T. Dewa, K. Endo, Y. Aoyama, *Angew. Chem.* **2000**, *112*, 4436–4438; *Angew. Chem. Int. Ed.* **2000**, *39*, 4266–4268.

[5] a) H. Li, M. Eddaoudi, M. O'Keeffe, O. M. Yaghi, *Nature* **1999**, *402*, 276–279; b) M. Eddaoudi, J. Kim, N. L. Rosi, D. T. Vodak, J. Wachter, M. O'Keeffe, O. M. Yaghi, *Science* **2002**, *295*, 469–472; c) H. K. Chae, M. Eddaoudi, J. Kim, S. I. Hauck, J. F. Hartwig, M. O'Keeffe, O. M. Yaghi, *J. Am. Chem. Soc.* **2001**, *123*, 11482–11483; d) T. M. Reineke, M. Eddaoudi, D. B. Moler, M. O'Keeffe, O. M. Yaghi, *J. Am. Chem. Soc.* **2000**, *122*, 4843–4844; e) S. Y. Yang, L. S. Long, Y. B. Jiang, R. B. Huang, L. S. Zheng, *Chem. Mater.* **2002**, *14*, 3229–3231; f) L. G. Beauvais, M. P. Shores, J. R. Long, *J. Am. Chem. Soc.* **2000**, *122*, 2763–2772.

[6] X-ray structure data: Siemens SMART CCD diffractometer, ω scans, graphite-monochromated $Mo_{K\alpha}$ radiation, SAINT for data integration, SADABS for absorption correction, XPREP for correction of Lorentz and polarization effects, and structure solution with direct methods and subsequent difference Fourier techniques by using SHELX-TL. Data collection for MOF-150: a) A brown octahedron crystal was analyzed: approximate dimensions: $0.16 \times 0.16 \times 0.14$ mm at $-115\,°C$, cubic, space group $Ia\bar{3}$ No. 206) with $a = 22.328(4)$ Å, $V = 11132(4)$ Å^3, $Z = 8$, $d_{calc} = 1.551\ \mathrm{g\,cm^{-3}}$, and $\mu(Mo_{K\alpha}) = 17.80\ \mathrm{cm^{-1}}$, $F(000) = 5312$, 985 unique reflections within $2\theta_{max} = 41.70°$, $T_{max} = 0.93$, $T_{min} = 0.59$. The Zn_4O cluster in the SBU consisted of two independent disordered Zn atoms (Zn(1) and Zn(2)) in the asymmetric unit, which generated eight Zn sites in the cluster. While Zn(1) atom with half occupancy was present in a general position, Zn(2) atom with half occupancy sit on a threefold crystallographic axis. The carboxylic oxygen atoms of the TCA link were also disordered over two sites with the same occupancies. A threefold axis penetrated through the center of the TCA link, the N(1) atom. Both guest molecules, the water and DMF molecules were disordered over two sites around a twofold crystallographic axis, which penetrated into the nitrogen atom, N(1S) in the DMF molecule. All non-hydrogen atoms were refined anisotropically. The hydrogen atoms of the TCA link were generated with idealized geometries. The final cycle of full-matrix least-squares refinement was based on 704 observed reflections ($I > 2.00\sigma(I)$) and 153 variable parameters and refined to convergence $R_1 = 0.0837$ and $R_w = 0.2266$. The maximum and minimum peaks on the final difference Fourier map corresponded to 0.769 and $-0.732\ \mathrm{e^-\,Å^{-3}}$, respectively; b) All crystal structures in this report may be viewed and manipulated on the web: http://www.umich.edu/~yaghigrp/structures.html. CCDC-201056 (MOF-150) contains the supplementary crystallographic data for this paper. These data can be obtained free of charge via www.ccdc.cam.ac.uk/conts/retrieving.html (or from the Cambridge Crystallographic Data Centre, 12, Union Road, Cambridge CB21EZ, UK; fax: (+44) 1223-336-033; or deposit@ccdc.cam.ac.uk).

[7] The high-pressure form of PdF_2 has the structure without anion–anion bonds. A. Tressaud, J. L. Soubreyroux, H. Touhara, G. Demazeau, F. Langlais, *Mater. Res. Bull.* **1981**, *16*, 207–214.

[8] S. R. Batten, B. F. Hoskins, R. Robson, *Angew. Chem.* **1995**, *107*, 884–886; *Angew. Chem. Int. Ed. Engl.* **1995**, *34*, 820–822.

[9] S. Nishikiori, T. Iwamoto, *J. Chem. Soc. Chem. Commun.* **1993**, 1555–1556.

[10] a) S. R. Batten, R. Robson, *Angew. Chem.* **1998**, *110*, 1558–1595; *Angew. Chem. Int. Ed.* **1998**, *37*, 1460–1494; b) P. Kroll, R. Riedel, R. Hoffmann, *Phys. Rev. B* **1999**, *60*, 3126–3139; c) J. S. Miller, *Adv. Mater.* **2001**, *13*, 525–527.

[11] a) O. Delgado Friedrichs, A. W. M. Dress, D. H. Huson, J. Klinowski, A. L. Mackay, *Nature* **1999**, *400*, 644–647; b) M. O'Keeffe, *Nature* **1999**, *400*, 617–618.

[12] O. Delgado Friedrichs, M. O'Keeffe, O. M. Yaghi, *Acta Crystallogr. Sect. A* **2003**, *59*, 22–27.

[13] O. Delgado Friedrichs, D. H. Huson, *Discrete Comput. Geom.* **2000**, *24*, 279–292.

[14] S. R. Batten, B. F. Hoskins, B. Moubaraki, K. S. Murray, R. Robson, *J. Chem. Soc. Dalton Trans.* **1999**, 2977–2986.

[15] S. R. Batten, B. F. Hoskins, B. Moubaraki, K. S. Murray, R. Robson, *J. Chem. Soc. Dalton Trans.* **1999**, 2977–2986.

[16] R. G. Xiong, S. R. Wilson, W. Lin, *J. Chem. Soc. Dalton Trans.* **1998**, 4089–4090.

[17] The synthesis of H_3TCA was accomplished by using literature procedures. H. Schrage, F. Vogtle, E. Steckhan, *J. Inclusion Phenom.* **1988**, *6*, 157–165. Characterization data: ^{1}H NMR (400 MHz, [D$_6$]DMSO): $\delta = 7.904$ ($J = 8.8$ Hz), 7.137 ppm ($J = 8.8$ Hz). ^{13}C NMR (400 MHz, [D$_6$]DMSO): $\delta = 123.7$, 125.9, 131.2, 149.8, 166.7 ppm. Elemental analysis calcd (%) for $C_{21}H_{15}O_6N = H_3TCA$: C 66.83, H 4.01, N 3.71; found: C 66.37; H 4.30, N 3.40. FTIR (KBr, 3500–400): $\tilde{\nu} = 3071$ (br), 1687(s), 1597(vs), 1511(m), 1417(m), 1327(s), 1272(s), 1177 (m), 1107 (w), 1017 (w), 852 (w), 767 (m), 707 (w), 652 (w), 552 cm^{-1} (w)