A novel metal–organic ternary topology constructed from triangular, square and tetrahedral molecular building blocks

Gregory J. McManus, Zhenqiang Wang, Derek A. Beauchamp and Michael J. Zaworotko*

Received (in Cambridge, UK) 21st August 2007, Accepted 3rd October 2007
First published as an Advance Article on the web 16th October 2007
DOI: 10.1039/b712905j

A novel metal–organic network [Cu$_4$(5-NH$_2$-1,3-bdc)$_4$-(pyridine)$_2$(H$_2$O)$_2$]$_n$, displaying an unprecedented topology has been constructed utilizing the different coordinating functional groups of 5-NH$_2$-1,3-bdc to generate a ternary network based upon vertex-linked triangular, square and tetrahedral molecular building blocks (MBBs).

Crystal engineering[1] offers a paradigm for the self-assembly of infinite and discrete nanoscale organic[2] and metal–organic/coordination[3] structures *via* a bottom-up "molecular building block (MBB) approach".[4] Structure–function relationships with properties such as magnetism,[5] luminescence,[6] and permanent porosity[7] have thereby been developed in a systematic manner. Wells catalogued network structures in crystals[8] and spawned the "node-and-spacer" methodology[9] which simplifies design since it reduces MBBs into topological points and lines. Interpretation and design of nets can also take into account the geometrical shape of the MBBs by representing nets as vertex-linked polygons or polyhedra (VLPP).[10]

Topologically the simplest nets are unitary nets comprised of only one type of MBB for which the topology of the net is directed by the geometry and arrangement of the MBBs: (10,3)-a (triangular MBBs), diamondoid (tetrahedral MBBs), NbO (square MBBs), and primitive cubic (octahedral MBBs) nets. The VLPP approach comes into its own for binary nets sustained by pairs of polygonal or polyhedral MBBs and even the simplest combinations of MBBs can result in structural diversity as exemplified by (3,4)-connected nets.[11] Nevertheless, the design of novel topologies remains challenging and is a dominant theme in crystal engineering since new topologies can serve as "blueprints" for the design of new classes of materials. We have proposed a design strategy based upon the VLPP approach for the synthesis of ternary nets sustained by a combination of three distinct polygons or polyhedra[12] utilizing zinc(II), which is known to offer structural diversity. In this communication we delineate how 3-connected triangular MBBs with different coordinating functional groups such as, 5-NH$_2$-1,3-bdc (5-amino-1,3-benzenedicarboxylate)[13] can promote the formation of two distinct metal centers and a ternary net (Fig. 1) with a new topology, USF-5: [Cu$_4$(5-NH$_2$-1,3-bdc)$_4$-(pyridine)$_2$(H$_2$O)$_2$]$_n$, **1**.†

The square MBB utilized in **1** is based upon the ubiquitous dicopper tetracarboxylate, Cu$_2$(RCO$_2$)$_4$L$_2$, or "paddlewheel" which is present in over 600 crystal structures in the Cambridge Structural Database (CSD).[14] The Cu(5-NH$_2$-1,3-bdc)$_{4/3}$(H$_2$O)]$_n$. building block in **1** is a pseudo-tetrahedral MBB. The five-coordinate Cu(RCO$_2$)$_2$(RNH$_2$)$_2$L chromophore is present in over 50 crystal structures in the CSD.

USF-5 is closely related to the previously reported USF-4[12] in that each triangular MBB is linked to one square MBB and two pseudo-tetrahedral MBBs which in turn are each linked to four triangular MBBs (Fig. 2). However, USF-5 is significantly different than USF-4 and previously reported (3,4)-connected networks, the long vertex symbols, $(4{\cdot}8_2{\cdot}8)_4(8{\cdot}8{\cdot}8_2{\cdot}8_2{\cdot}12_8{\cdot}12_8)$ $(4{\cdot}4{\cdot}8{\cdot}8{\cdot}8{\cdot}12_{13})_2$ being hitherto unprecedented.[15] Analysis of the physical properties observed in **1** and other ternary nets remains an ongoing study in our laboratory.

When the experimental conditions of **1** were altered to utilize 4-picoline instead of pyridine we obtained two products: green crystals isostructural to **1**;[16] and yellow crystals of [Cu(5-NH$_2$-1,3-bdc)(4-picoline)]$_n$, **2**. The 2-D honeycomb framework of **2** is composed of 3-connected 5-NH$_2$-1,3-bdc ligands and five-coordinate Cu(II) metal centers which also serve as 3-connected nodes. A series of Zn(II) analogues of this structure has recently been reported.[17]

In summary, we have demonstrated a second simple strategy for the design of ternary nets, *i.e.* triangular MBBs containing different coordinating functional groups (*i.e.* carboxylates and amines) which promote the formation of geometrically and chemically distinct metal centers. Further studies will investigate the design of ternary nets from a wider range of geometrical and chemical MBBs, including preformed MBBs.

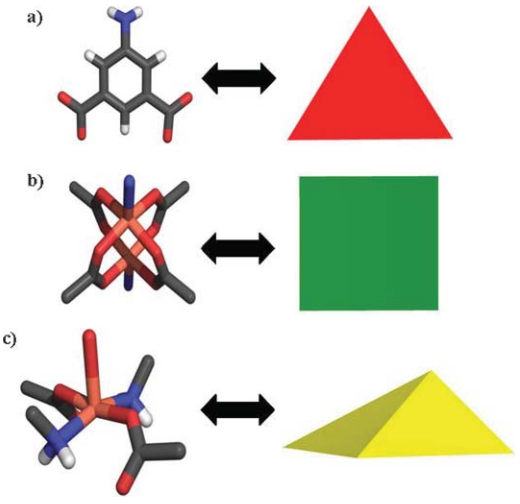

Fig. 1 Molecular building blocks (MBBs) employed in the ternary net USF-5: (a) 5-NH$_2$-1,3-bdc – triangular MBB; (b) Cu$_2$(RCO$_2$)$_4$L$_2$ – square MBB; (c) Cu(RCO$_2$)$_2$(RNH$_2$)$_2$L – pseudo-tetrahedral MBB.

Department of Chemistry, University of South Florida, 4202 E. Fowler Ave., CHE 205, Tampa, Florida, 33620, USA. E-mail: xtal@usf.edu; Fax: 1 813 974 3203; Tel: 1 813 974 4129

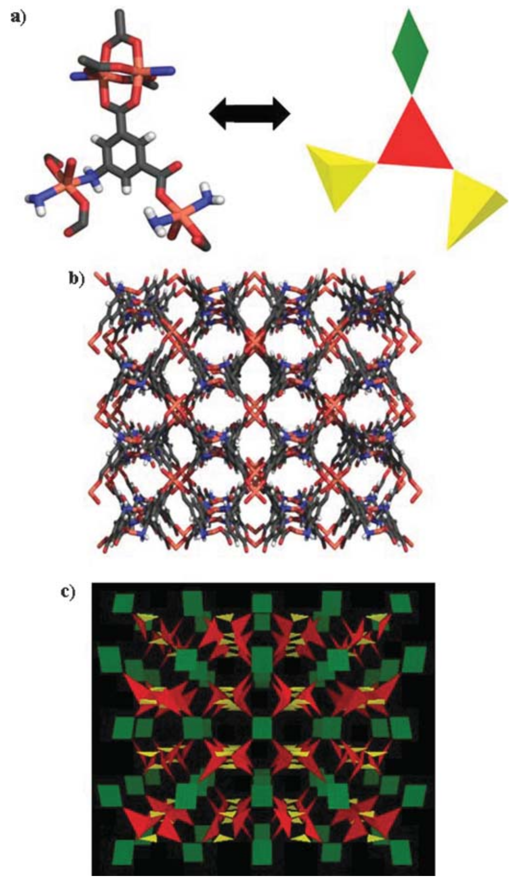

Fig. 2 (a) Triangular 5-NH_2-1,3-bdc units linked to one square MBB and two pseudo-tetrahedral MBBs. (b) Crystal structure of **1** viewed down the [100] axis in stick representation (pyridine and H_2O ligands have been deleted for clarity). (c) Schematic representation of **1** in VLPP format viewed down the [100] axis.

The authors gratefully acknowledge the financial support of the National Science Foundation (DMR-0101641).

Notes and references

† *Experimental data* for **1**: Green crystals form in 38% yield within one day of layering a 10.0 mL methanolic solution of $Cu(NO_3)_2{\cdot}2.5H_2O$ (116 mg, 0.499 mmol) through a 10.0 mL methanol buffer layer onto a 10.0 mL methanolic solution containing 5-amino-1,3-benzenedicarboxylic acid (91 mg, 0.50 mmol) and pyridine (0.12 mL, 1.5 mmol). Experimental data for **2**: Green (compound **1**) and yellow (compound **2**) crystals form within one day of layering a 10.0 mL methanolic solution of $Cu(NO_3)_2{\cdot}2.5H_2O$ (116 mg, 0.499 mmol) through a 10.0 mL methanol buffer layer onto a 10.0 mL methanolic solution containing 5-amino-1,3-benzenedicarboxylic acid (91 mg, 0.50 mmol) and 4-picoline (0.15 mL, 1.5 mmol).

Crystallographic data for **1**: $C_{21}H_{30}Cu_2N_3O_{15.50}$, $M_r = 699.56$, orthorhombic, space group *Ibam*, $a = 14.669(7)$, $b = 16.833(8)$, $c = 24.743(11)$ Å, $V = 6109(5)$ Å^3, $Z = 8$, $D_c = 1.521$ g cm^{-3}, $\mu = 1.464$ mm^{-1}, $F(000) = 2872$, $2\theta_{max} = 50.22°$ ($-17 \leqslant h \leqslant 16$, $-8 \leqslant k \leqslant 20$, $-29 \leqslant l \leqslant 29$), $T = 298(2)$ K, 14695 measured reflections, $R1 = 0.0671$ for 1283 reflections ($I > 2\sigma(I)$), $wR2 = 0.1883$ for 2787 independent reflections (all data) and 201 parameters, GOF = 0.882. *Crystallographic data* for **2**: $C_{14}H_{12}CuN_2O_4$, $M_r = 335.80$, monoclinic, space group $P2_1/n$, $a = 12.7210(18)$, $b = 7.7387(11)$, $c = 14.005(2)$ Å, $\beta = 108.106(2)°$, $V = 1310.4(3)$ Å^3, $Z = 4$, $D_c = 1.702$ g cm^{-3}, $\mu = 1.684$ mm^{-1}, $F(000) = 684$, $2\theta_{max} = 50.28°$ ($-13 \leqslant h \leqslant 15$, $-9 \leqslant k \leqslant 9$, $-16 \leqslant l \leqslant 16$), $T = 298(2)$ K, 6452 measured reflections, $R1 = 0.0447$ for 1776 reflections ($I > 2\sigma(I)$), $wR2 = 0.1139$ for 2316 independent reflections (all data) and 191 parameters, GOF = 1.041.

Data were collected on a Bruker SMART-APEX CCD diffractometer using Mo-Kα radiation ($\lambda = 0.71073$ Å). Crystal data were corrected for Lorentz and polarization effects, and the SADABS program was used for absorption correction. The structures were solved by direct methods and the structure solution and refinement was based on $|F^2|$. All non-hydrogen atoms were refined with anisotropic displacement parameters, whereas hydrogen atoms were placed in calculated positions and given isotropic *U* values 20% higher than the atom to which they are bonded. All crystallographic calculations were conducted with the SHELXTL software suite.

CCDC 658210 and 658211. For crystallographic data in CIF or other electronic format see DOI: 10.1039/b712905j

1 (*a*) G. M. J. Schmidt, *Pure Appl. Chem.*, 1971, **27**, 647; (*b*) R. Pepinsky, *Phys. Rev.*, 1955, **100**, 971; (*c*) B. Moulton and M. J. Zaworotko, *Chem. Rev.*, 2001, **101**, 1629; (*d*) D. Braga, *Chem. Commun.*, 2003, 2751.

2 (*a*) L. R. MacGillivray and J. L. Atwood, *Nature*, 1997, **389**, 469; (*b*) O. Ugono and K. T. Holman, *Chem. Commun.*, 2006, 2144; (*c*) H. M. El-Kaderi, J. R. Hunt, J. L. Mendoza-Cortes, A. P. Côté, R. E. Taylor, M. O'Keeffe and O. M. Yaghi, *Science*, 2007, **316**, 268; (*d*) P. K. Thallapally, G. O. Lloyd, T. B. Wirsig, M. W. Bredenkamp, J. L. Atwood and L. J. Barbour, *Chem. Commun.*, 2005, 5272.

3 (*a*) S. Kitagawa, R. Kitaura and S. Noro, *Angew. Chem., Int. Ed.*, 2004, **116**, 2388; (*b*) M. Fujita, K. Umemoto, M. Yoshizawa, N. Fujita, T. Kusukawa and K. Biradha, *Chem. Commun.*, 2001, 509; (*c*) C. Janiak, *Dalton Trans.*, 2003, 2781; (*d*) A. Y. Robin and K. M. Fromm, *Coord. Chem. Rev.*, 2006, **250**, 2127; (*e*) S. L. James, *Chem. Soc. Rev.*, 2003, **32**, 276.

4 (*a*) Y. Liu, V. Ch. Kravtsov, R. Larsen and M. Eddaoudi, *Chem. Commun.*, 2006, 1488; (*b*) J. J. Perry, V. Ch. Kravstov, G. J. McManus and M. J. Zaworotko, *J. Am. Chem. Soc.*, 2007, **129**, 10076.

5 (*a*) S. R. Batten, B. F. Hoskins, B. Moubaraki, K. S. Murray and R. Robson, *J. Chem. Soc., Dalton Trans.*, 1999, 2977; (*b*) C. S. Campos-Fernandez, R. Clerac and K. R. Dunbar, *Angew. Chem., Int. Ed.*, 1999, **38**, 3477; (*c*) M. Kurmoo and C. J. Kepert, *New J. Chem.*, 1998, **22**, 1515.

6 (*a*) G. J. McManus, J. J. Perry, M. Perry, B. D. Wagner and M. J. Zaworotko, *J. Am. Chem. Soc.*, 2007, **129**, 9094; (*b*) W. J. Rieter, K. M. Taylor and W. Lin, *J. Am. Chem. Soc.*, 2007, **129**, 9852.

7 (*a*) M. Eddaoudi, J. Kim, N. Rosi, D. Vodak, J. Wachter, M. O'Keeffe and O. M. Yaghi, *Science*, 2002, **295**, 469; (*b*) S. Hasegawa, S. Horike, R. Matsuda, S. Furukawa, K. Mochizuki, Y. Kinoshita and S. Kitagawa, *J. Am. Chem. Soc.*, 2007, **129**, 2607; (*c*) X. Zhao, B. Xiao, A. J. Fletcher, K. M. Thomas, D. Bradshaw and M. J. Rosseinsky, *Science*, 2004, **306**, 1012; (*d*) K. L. Mulfort and J. T. Hupp, *J. Am. Chem. Soc.*, 2007, **129**, 9604.

8 A. F. Wells, *Three-Dimensional Nets and Polyhedra*, Wiley, New York, 1977.

9 S. R. Batten and R. Robson, *Angew. Chem., Int. Ed.*, 1998, **37**, 1460.

10 (*a*) J. Lu, A. Mondal, B. Moulton and M. J. Zaworotko, *Angew. Chem., Int. Ed.*, 2001, **40**, 2113; (*b*) G. J. McManus, Z. Wang and M. J. Zaworotko, *Cryst. Growth Des.*, 2004, **4**, 11; (*c*) H. Chun, D. Kim, D. N. Dybtsev and K. Kim, *Angew. Chem., Int. Ed.*, 2004, **116**, 989.

11 (*a*) B. Chen, M. Eddaoudi, S. T. Hyde, M. O'Keeffe and O. M. Yaghi, *Science*, 2001, **291**, 1021; (*b*) S. S. Y. Chui, S. M. F. Lo, J. P. H. Charmant, A. G. Orpen and I. D. Williams, *Science*, 1999, **283**, 1148; (*c*) B. F. Abrahams, S. R. Batten, H. Hamit, B. F. Hoskins and R. Robson, *Angew. Chem., Int. Ed. Engl.*, 1996, **35**, 1690; (*d*) D. N. Dybtsev, H. Chun and K. Kim, *Chem. Commun.*, 2004, 1594; (*e*) S. Hong, Y. Zou, D. Moon and M. S. Lah, *Chem. Commun.*, 2007, 1707; (*f*) Y. H. Liu and M. T. Ding, *Acta. Crystallogr., Sect. E.*, 2007, **63**, m1828.

12 Z. Wang, V. Ch. Kravtsov and M. J. Zaworotko, *Angew. Chem., Int. Ed.*, 2005, **44**, 2877.

13 There are 23 crystal structures containing 5-amino-1,3-benzenedicarboxylate coordinated to metal centers deposited in the CSD V5.28 (Nov. 2006 + 2 updates)—none of which can be interpreted as a ternary net.

14 F. H. Allen, *Acta Crystallogr., Sect. B*, 2002, **58**, 380.

15 (*a*) O. V. Dolomanov, A. J. Blake, N. R. Champness and M. Schröder, *J. Appl. Crystallogr.*, 2003, **36**, 1283; (*b*) M. O'Keeffe, M. Eddaoudi, H. Li, T. Reineke and O. M. Yaghi, *J. Solid State Chem.*, 2000, **152**, 3; (*c*) M. O'Keeffe and S. T. Hyde, *Zeolites*, 1993, **13**, 592.

16 Unit cell parameters: $a = 14.526(2)$, $b = 17.382(3)$, $c = 24.444(4)$ Å, $V = 6171.9(17)$ Å^3.

17 K. O. Kongshaug and H. Fjellvåg, *Inorg. Chem.*, 2006, **45**, 2424.