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Sextuplet phenyl embrace in a metal–organic Kagomé lattice

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A novel Kagomé lattice that demonstrates the modular nature of metal–organic networks has been prepared and is to our knowledge the first example of a metal–organic coordination polymer that incorporates the sextuplet phenyl embrace as a supramolecular synthon.

Metal–organic coordination polymers exemplify the extent to which crystal engineering has emerged as a paradigm for the design and synthesis of novel supramolecular architectures exhibiting desired physical properties.[1] Within the realm of molecular magnetism[2] an appealing target is the so-called Kagomé lattice. The Kagomé lattice (Fig. 1(a)) is an example of a spin-frustrated topology in which the magnetic moments are positioned at the vertices of triangles, thereby disrupting antiferromagnetic coupling and facilitating weak ferromagnetic long-range order.[3] We recently reported[4] the synthesis, crystal structure, and magnetic studies of a nanoscale metal–organic Kagomé lattice[5] constructed *via* self-assembly of simple molecular components using the principles of crystal engineering. This synthesis utilizes a "bottom-up" approach in which the ubiquitous dimetal tetracarboxylate square-paddlewheel secondary building units (SBUs) $[M_2(O_2CR)_4L_2]$ (M = transition metal, L = axially coordinated ligand) are linked together at their vertices using angular bifunctional carboxylate ligands, such as benzene dicarboxylate (bdc), to generate triangular nanoscale SBUs (nSBUs).[6] These nanosized triangles in turn self-assemble at their vertices to generate the infinite, 2D open-framework Kagomé lattice. This synthetic approach brings with it the potential for modularity, and we have already reported the use of different metals in the SBU.[4,7] The possibility of substituting the bifunctional carboxylate ligand, changing the axially coordinated ligand, or incorporation of various guest molecules in the open channels also exists.

In this communication we address substitution of the bdc ligand and report the synthesis and X-ray crystal structure†‡ of a Kagomé lattice with a sterically demanding ligand, $[\{Cu_2(\text{pyridine})_2(\text{5-benzyloxy-1,3-bdc})_2\}_3]_n$, **I.** The 5-benzyloxy-1,3-bdc ligands (Fig. 2) sustain a 2D Kagomé lattice with a skeleton that is isostructural to that sustained by bdc in the prototypal Kagomé lattice. The benzyloxy moieties are accommodated because they extend into the large hexagonal cavities of adjacent Kagomé lattices, thereby precluding the presence of solvent or guest molecules (Fig. 1(b)). Pyridine molecules are coordinated to the copper atoms along the axial direction of the SBU and they extend into the triangular cavities. Layers of **I** pack along the *c*-axis in an eclipsed arrangement with an interlayer separation of 9.6305(9) Å. Remarkably, the prototypal Kagomé lattice was sustained by a less sterically demanding ligand but it exhibited an interlayer separation of 9.91 Å. This apparent anomaly appears to be related to the orientation of the benzyl ether side chains, which alternate around the hexagonal channel in such a manner that the phenyl rings are positioned to interact with two other phenyl rings from the third layer in each direction. The edge-to-face $CH\cdots\pi$ interactions between the phenyl rings is illustrated in Fig. 3.[8]

Within each hexagonal cavity and between every first and third layer, a total of six phenyl rings, three from above and three from below, interact through these $CH\cdots\pi$ interactions in a concerted manner and thereby exhibit the sextuplet phenyl embrace (SPE) (Fig. 4).[9] The centroid-to-centroid distances for these interactions are within the expected values and fall in the range of 5.186 to 5.194 Å. The sextuplet phenyl embrace is a subset of a more general supramolecular motif described as a multiple phenyl embrace by Dance and co-workers, and shown to be predominate in crystal structures containing PPh_4^+ cations or XPh_3 terminating ligands.[10] In addition to these discrete aggregates, a multiple phenyl embrace can also be used to direct the formation of infinite supramolecular (*i.e.* non-covalent) structures; 1D linear or zig-zag chains, 1D ladders, 2D sheets, and even 3D topologies based upon diamondoid and (10,3)a.[11] **I** does not fit into either of these two categories, discrete or supramolecular, as it involves SPE between two infinite metal–organic coordination polymers, and to the best of our knowledge no prior examples of any multiple phenyl embrace between two infinite covalently linked structures exist. The

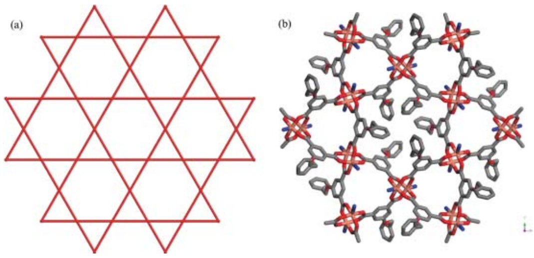

Fig. 1 (a) Schematic of Kagomé lattice. (b) Stick model of **I** viewed down the *c*-axis. One hexagonal channel is shown along with six trigonal cavities that form the sides of each hexagon. The pyridine rings have been removed for clarity, except for the nitrogen atoms (blue).

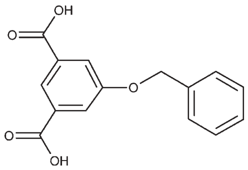

Fig. 2 5-Benzyloxy bdc.

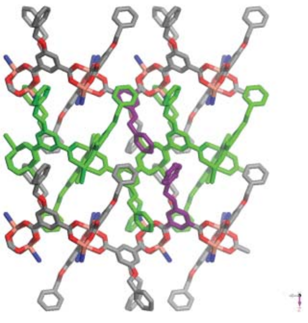

Fig. 3 Layers of **I** pack along the crystallographic *c*-axis. The first and third layers interact through $CH\cdots\pi$ interactions (purple ligands). The middle layer (green) is held in place by these ligands but forms no direct interactions (*i.e.* no hydrogen bonding, π–π stacking, or CH–π interactions) with the first and third layers.

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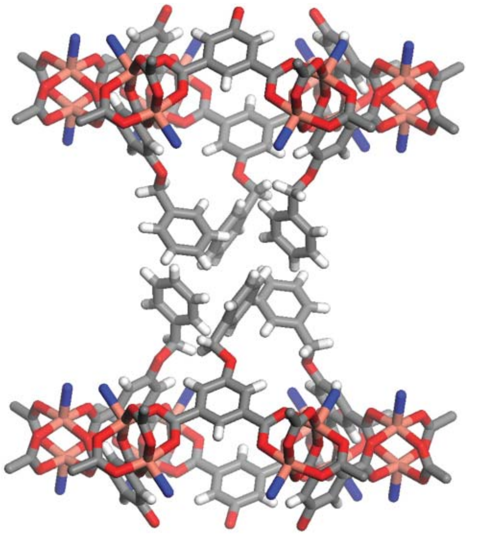

Fig. 4 Sextuplet phenyl embrace. The middle layer has been deleted.

structural consequences of this interaction are an interlayer separation shorter than that observed in the prototypal Kagomé lattice and eclipsing of adjacent layers.

In conclusion, a novel nanoscale Kagomé lattice has been synthesized *via* a "bottom-up" approach, and substitution of the bifunctional dicarboxylate clearly demonstrates the modular nature of this class of materials. Furthermore, the open framework nature of the Kagomé lattice facilitates accommodation of a relatively long substituent on the bdc ligand and precludes the presence of guest molecules. The manner in which the benzyloxy moieties thread through the large hexagonal channels suggests that even longer substituents could possibly be used. Further studies will therefore focus upon expanding the known range of metal–organic Kagomé lattices with a view to the incorporation of a wider range of bdc substituents, especially electron donating and/or withdrawing groups. A systematic evaluation of the effect of these groups upon crystal packing and magnetic properties of Kagomé lattices will thereby become feasible.

Notes and references

† *Synthesis and initial characterization:* 5-*o*-benzyl bdc was prepared from commercially available dimethyl 5-hydroxyisophthalate by known procedures for the alkylation of phenols.[12] **I** was synthesized under ambient conditions *via* a slow diffusion/layering method. In a typical synthesis, 84.1 mg (0.310 mmol) of 5-*o*-benzyl bdc was dissolved in 10 mL of MeOH and mixed with 2 mL of 1,2-dichlorobenzene and 0.08 mL (1.00 mmol) of pyridine. Layered on top of this mixture was a solution of 69.7 mg (0.299 mmol) of $Cu(NO_3)_2 \cdot 2.5H_2O$ dissolved in 7 mL MeOH, using 5 mL of pure MeOH as a "blank" middle layer between the two solutions. The layered reaction was left undisturbed to allow for slow diffusion, and after two weeks green hexagons suitable for single crystal X-ray diffraction were collected.

‡ *Single crystal structure determination:* single crystal data were collected on a Bruker-AXS SMART APEX/CCD diffractometer [graphite-monochromated MoKα radiation, $\lambda = 0.71073$ Å ($T = 100(2)$ K)]. The data were corrected for Lorentz and polarization effects and for adsorption using the SADABS program.[13] The structures were solved by direct methods using SHELXS-97[14] and difference Fourier synthesis. Full-matrix least-squares structure refinement against $|F^2|$ was carried out using SHELX-97. The non-hydrogen atoms were refined anisotropically and hydrogen atoms were placed in geometrically calculated positions and refined with temperature factors 1.2 times those of their bonded atoms. *Crystal data:* $[Cu_2(C_5H_5N)_2(C_{15}H_{10}O_5)_2]$, **I**, $M_r = 825.74$, trigonal, space group $= P\bar{3}$ (no. 147), $a = b = 18.4013(8)$ Å, $c = 9.6305(9)$ Å, $V = 2824.1(3)$ Å^3, $Z = 3$, $\mu = 1.190$ mm^{-1}, $\rho_{calcd} = 1.457$ Mg m^{-3}. A total of 18160 reflections were collected in the θ range 1.28–28.30° and merged to give 4496 unique data ($R_{int} = 0.0411$) of which 3755 with $I > 2\sigma(I)$ were considered to be observed. Final $R = 0.0421$, $wR = 0.0970$, GOF = 1.136 were obtained for 256 parameters. CCDC 242573. See http://www.rsc.org/suppdata/cc/b4/b408973a/ for crystallographic data in .cif or other electronic format.

1 B. Moulton and M. J. Zaworotko, *Chem. Rev.*, 2001, **101**, 1629–1658; G. M. J. Schmidt, *Pure Appl. Chem.*, 1971, **27**, 647–678; R. Robson, B. F. Abrahams, S. R. Batten, R. W. Gable, B. F. Hoskins and J. P. Liu, *ACS Symp. Ser.*, 1992, **499**, 256–273; M. Eddaoudi, D. B. Moler, H. Li, B. Chen, T. M. Reineke, M. O'Keeffe and O. M. Yaghi, *Acc. Chem. Res.*, 2001, **34**, 319–330; C. Y. Su, A. M. Goforth, M. D. Smith, P. J. Pellechia and H. C. zur Loye, *J. Am. Chem. Soc.*, 2004, **126**, 3576–3586; A. J. Blake, N. R. Champness, P. Hubberstey, W. S. Li, M. A. Withersby and M. Schroder, *Coord. Chem. Rev.*, 1999, **183**, 117–138; C. Janiak, *Dalton Trans.*, 2003, 2781–2804.

2 O. Kahn, *Molecular Magnetism*, VCH, Weinheim, Germany, 1993; M. Melnik, *Coord. Chem. Rev.*, 1982, **42**, 259–293; A. J. Tasiopoulos, A. Vinslava, W. Werndorfer, K. A. Abboud and G. Christou, *Angew. Chem., Int. Ed.*, 2004, **43**, 2117–2121.

3 A. P. Ramirez, *Annu. Rev. Mater. Sci.*, 1994, **24**, 453; J. Frunzke, T. Hansen, A. Harrison, J. S. Lord, G. S. Oakley, D. Visser and A. S. Wills, *J. Mater. Chem.*, 2001, **11**, 179–185.

4 B. Moulton, J. Lu, R. Hajndl, H. Srikanth and M. J. Zaworotko, *Angew. Chem., Int. Ed.*, 2002, **41**, 2821–2824; H. Srikanth, R. Hajndl, B. Moulton and M. J. Zaworotko, *J. Appl. Phys.*, 2003, **93**, 7089–7091; J. L. Atwood, *Nat. Mater.*, 2002, **1**, 91–92.

5 See the following references related to examples of metal–organic Kagomé lattices: M. Eddaoudi, J. Kim, D. Vodak, A. Sudik, J. Wachter, M. O'Keeffe and O. M. Yaghi, *Proc. Natl. Acad. Sci. USA*, 2002, **99**, 4900–4904; E. B. Rusanov, V. V. Ponomarova, V. V. Komarchuk, H. Stoeckli-Evans, E. Fernandez-Ibanez, F. Stoeckli, J. Sieler and K. V. Domasevitch, *Angew. Chem., Int. Ed.*, 2003, **42**, 2499–2501; D. M. Shin, I. S. Lee, Y. K. Chung and M. S. Lah, *Inorg. Chem.*, 2003, **42**, 5459–5461; M. Murugesu, R. Clerac, C. E. Anson and A. K. Powell, *J. Phys. Chem. Solids*, 2004, **65**, 667–676.

6 S. A. Bourne, J. Lu, A. Mondal, B. Moulton and M. J. Zaworotko, *Angew. Chem., Int. Ed.*, 2001, **40**, 2111–2113; B. Chen, M. Eddaoudi, T. M. Reineke, J. W. Kampf, M. O'Keeffe and O. M. Yaghi, *J. Am. Chem. Soc.*, 2000, **122**, 11559–11561.

7 H. Abourahma, G. J. McManus, B. Moulton, R. D. Bailey-Walsh and M. J. Zaworotko, *Macromol. Symp.*, 2003, **196**, 213–227.

8 W. B. Jennings, B. M. Farrell and J. F. Malone, *Acc. Chem. Res.*, 2001, **34**, 885–894; T. Steiner, *Angew. Chem., Int. Ed.*, 2002, **41**, 48–76; M. Nishio, M. Hirota and Y. Umezawa, *The CH/π interaction: Evidence, Nature, and Consequences*, Wiley-VCH, New York, 1998.

9 I. G. Dance and M. L. Scudder, *J. Chem. Soc., Chem. Commun.*, 1995, 1039–1040; I. G. Dance and M. L. Scudder, *J. Chem. Soc., Dalton Trans.*, 1998, 1341–1350; T. Steiner, *J. Chem. Crystallogr.*, 1999, **29**, 1235–1237.

10 G. R. Lewis and I. G. Dance, *Inorg. Chim. Acta*, 2000, **306**, 160–167; I. G. Dance and M. L. Scudder, *New J. Chem.*, 1998, **22**, 481; M. L. Scudder and I. G. Dance, *Chem.–Eur. J.*, 2002, **8**, 5456–5468.

11 P. M. van der Werff, S. R. Batten, P. Jensen, B. Moubaraki, K. S. Murray and E. H.-K. Tan, *Polyhedron*, 2001, **20**, 1129–1138; M. L. Scudder and I. G. Dance, *J. Chem. Soc., Dalton Trans.*, 1998, 3167–3175; T. Steiner, *Acta Crystallogr., Sect. C: Cryst. Struct. Commun.*, 2000, **56**, 1033–1034; M. L. Scudder and I. G. Dance, *J. Chem. Soc., Dalton Trans.*, 1998, 3155–3165; M. L. Scudder and I. G. Dance, *CrystEngComm*, 2001, **12**, 1–4.

12 S. Valiyaveettil, V. Enkelmann and K. Mullen, *Chem. Commun.*, 1994, 2097–2098.

13 G. M. Sheldrick, *SADABS: Area-Detector Absorption Correction*, Siemens Industrial Automation, Inc., Madison, WI, 1996.

14 G. M. Sheldrick, *SHELX-97 program for crystal structure determination*, University of Gottingen, Germany, 1998.