COMMUNICATION

ChemComm
www.rsc.org/chemcomm

Designed layer assembly: a three-dimensional framework with 74% extra-framework volume by connection of infinite two-dimensional sheets†

T. J. Prior,[a] D. Bradshaw,[a] S. J. Teat[b] and M. J. Rosseinsky*[a]

[a] *Department of Chemistry, University of Liverpool, Liverpool, UK L69 7ZD*

[b] *Synchrotron Radiation Source, Daresbury Laboratory, Daresbury, Warrington, UK WA4 4AD*

Received (in Cambridge, UK) 11th November 2002, Accepted 20th January 2003
First published as an Advance Article on the web 28th January 2003

A coordination polymer with 74% extra-framework volume is prepared by predictable linking of the honeycomb network to generate a framework-structured solid designed with two distinct connecting ligands.

Design strategies for the prediction and preparation of metal–organic solids with appreciable extra-framework volume are a particular focus of attention in the search for new porous materials,[1–7] with the use of discrete molecular clusters of defined shape and connectivity as secondary building units yielding highly porous systems. While the assembly of *infinite* low-dimensional units previously identified in crystal structure analysis is a logical extension of this methodology,[8–10] there remain few examples of 3-D coordination polymers assembled wholly from covalent interactions using this approach.[11] There are many common one- and two-dimensional motifs already identified in coordination polymer chemistry through the connection of metal centres by multidentate ligands,[12] and selection of a suitable ternary bridging ligand should allow hierarchical assembly of these units into three-dimensional structures. In this paper the rational synthesis of a three-dimensional architecture with exceptional extra-framework volume by this route is described.

The 1,3,5-benzenetricarboxylate (btc) anion is a widely used three-connecting ligand in coordination polymer synthesis. The 120° angle between the carboxylate groups affords the (6,3) honeycomb or graphene sheet as a common structural feature of this chemistry.[13,14] The graphene sheets in the (6,3) btc phase $Ni_3(btc)_2(py)_6(BuOH)_6$·(guest) (py = pyridine)[15] are AAA stacked creating channels parallel to the stacking direction, with pyridine ligands projecting perpendicular to the infinite hexagonal layer (see ESI†). We have successfully employed 4,4′-bipyridine (bipy)—a linear connector with an extensive coordination polymer chemistry[16]—in place of py, to assemble the $Ni_3(btc)_2$ (6,3) sheets into the three-dimensional phase **1** (Fig. 1).‡ **1** is a pillared coordination polymer with channels running both within and between the layers with composition $[Ni_6(btc)_4(bipy)_6(CH_3OH)_3(H_2O)_9$·(guest)].§ The connectivity of the framework is exactly that forecast: the (6,3) $Ni_3(btc)_2$ nets have been joined into an AAA stacking sequence by the bridging 4,4′-bipyridine ligand connecting the Ni centres in adjacent layers. The closely related phase, $[Ni_3(btc)_2(bipy)_3(C_2H_6O_2)_3(H_2O)_3$·(guest)] **2**,¶ has also been prepared and its thermal stability to guest loss studied. TGA and XRD data for phase **2** suggest a pore filling of 6eg and $3\frac{1}{3}H_2O$ molecules per Ni centre, which, along with the metal-bound solvent molecules, can be removed by heating to 120 °C to render the material non-crystalline. (see ESI†) Given the very close structural similarity, it is proposed that phase **1** will exhibit similar characteristics upon guest loss.

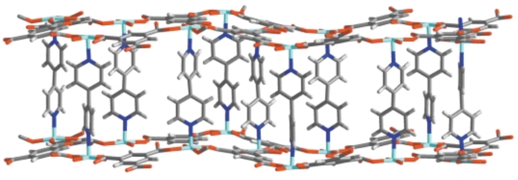

Fig. 1 The three-dimensional coordination polymer **1**, showing the pillaring of adjacent (6,3) $Ni_3(btc)_2$ sheets by 4,4′-bipy ligands (red – O, grey – C, blue – N, cyan – Ni).

The asymmetric unit of **1** contains three independent Ni(II) centres which are bound, in a monodentate fashion, by two fully deprotonated btc ligands. (see ESI†) At each Ni, water and/or methanol complete the coordination in the equatorial plane. These metal-bound water molecules form two hydrogen bonds to the *trans* bound carboxylates to stabilise the approximately coplanar arrangement of the btc units, which is a prerequisite for layer formation.[15] The orientation of the btc rings serves to maximise these hydrogen bonding interactions at each Ni centre giving rise to a rippled (6,3) sheet throughout the structure. The sheets themselves are made up of edge-sharing 48-membered rings of six Ni cations and six btc anions. At every Ni centre, bipy occupies the axial positions perpendicular to adjacent sheets, forming a cross link between them. The pillaring of this layered compound with bipy leads to a considerable extra-framework volume of 74%.‖

The centroids of the hexagons in adjacent $Ni_3(btc)_2$ layers are aligned to generate hexagonal-shaped channels which run parallel to the stacking direction, *c* (Fig. 2a). The channel diameter defined by the separation between the van der Waals surfaces in **1** is dependent on the metal bound solvent which protrudes into the void, describing channels of 12.3 and 11.0 Å, respectively, in the water- and methanol-bound cases. The bipy pillars generate further channels parallel to the layers extending throughout the *xy* plane. Along the *a* and *b* axes in **1** the channel windows are fully eclipsed by face-on oriented bipy molecules. However, normal to [1 0 0] and [0 1 0] the windows are much more open (Fig. 2b). The windows offering access to these channels are defined by the van der Waals surfaces of the bipy molecules, and are 8 Å in height and 4.4 Å in width at their closest edge to edge contact.

The combination of channels running parallel and perpendicular to the (6,3) layer stacking direction gives rise to large pockets of extra-framework space. Three cavities are located at the channel intersections centred on the Wyckoff 1a (0, 0, 0.4260), 1b (1/3, 2/3, 0.3784) and 1c (2/3, 1/3, 0.3934) positions. The largest of these are the 1b and 1c sites, which can accommodate spheres of diameter 15.3 and 15.6 Å, respectively, when van der Waals surfaces are considered. In both cases only metal-bound water molecules extend into the voids. The cavity centred on the 1a position is, however, much smaller (diameter 13.5 Å) due to metal-bound methanol extending into the channels. These spheres give approximate cavity volumes of 1300, 1900 and 2000 Å³ for the Wyckoff positions 1a, 1b and 1c respectively (Fig. 3).

We have demonstrated the predictable assembly of a pre-identified infinite structural unit (which exists in other crystalline solids) using a suitable bridging ligand and solvent system. This cross-linking of common extended, rather than molecular, structural motifs may be a promising technique in coordination

---

† Electronic supplementary information (ESI) available: structure of the AAA stacked pyridine phase, asymmetric unit of **1**, structure of phase **2**, thermal stability of phase **2**. See http://www.rsc.org/suppdata/cc/b2/b211124c/

DOI: 10.1039/b211124c

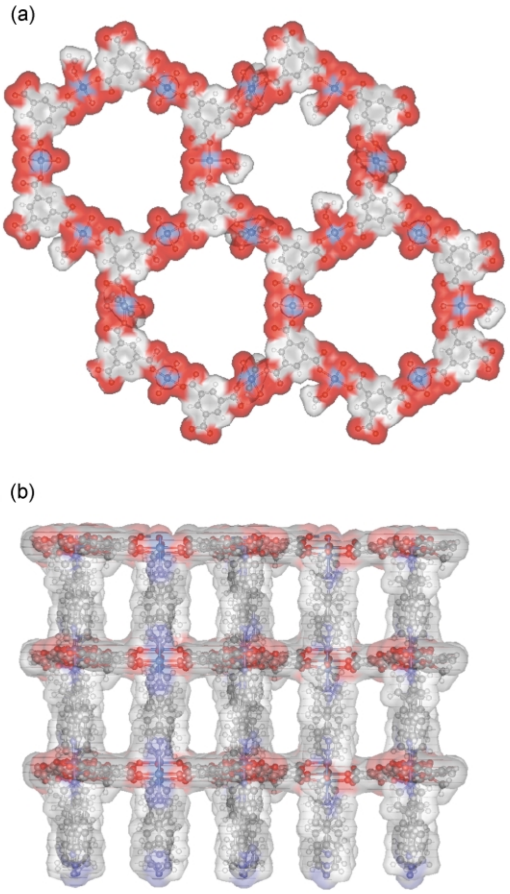

Fig. 2 The channels formed by the AAA stacking in **1** viewed (a) parallel to the stacking direction and (b) along the (1 0 0) plane. The framework is represented by its van der Waals surfaces (red – O, grey – C, blue – N, cyan – Ni).

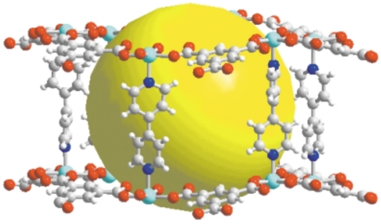

Fig. 3 The channels parallel and perpendicular to the layers intersect to form a large cavity of 15.6 Å centred on the 1c position.

polymer chemistry to afford materials with large cavities and channels. In the present case, extended bipy[17] and btc[18] ligands to enhance further the pore volumes demonstrated here in **1** are readily available.

We thank the EPSRC for support under GR/N08537, J. F. Bickley and A. Steiner for assistance with crystallographic data collection and analysis, and J. B. Claridge for useful and extensive discussion. T. J. P. also thanks S. Malhotra for valuable discussions concerning topology.

Notes and references

‡ The key to the synthesis is to identify a solvent system which disfavours the formation of discrete metal-bipy coordination polymer frameworks, yet allows the formation of the ternary metal–bipy–btc network. In the Ni–bipy–NO_3 system, ethylene glycol (eg) does not afford a simple binary network, and was therefore selected to grow the ternary networks.

§ Pillared layered phase **1**: a stock solution of nickel nitrate hexahydrate (29 mg, 0.1 mmol) and H_3btc (13.8 mg, 0.07 mmol) was prepared in 20 mL of eg. This solution was split into four 5 mL portions which were placed into straight glass test tubes (height 150 mm, diameter 18 mm). On to each portion is layered pure eg (5 mL). 4,4′-bipyridine (33.6 mg, 0.22 mmol) was dissolved in 2 mL of MeOH and 0.5 mL portions of this solution were layered carefully onto the pure eg layer in each tube. The test tubes were sealed with parafilm and left to stand at room temperature. After ~ 12 weeks small hexagonal shaped blue single crystals suitable for X-ray analysis were produced. Crystal data for **1**: $C_{49}H_{33}N_6O_{18}Ni_3$, M = 1169.94, hexagonal plate 0.14 × 0.11 × 0.08 mm, trigonal, space group $P3$ (no. 143), a = 33.5211(10), c = 11.3015(5) Å, γ = 120°, V = 10997.7(7) Å^3, Z = 3, ρ_{calc} = 0.530 g cm^{-3}, λ = 0.6867 Å, $F(000)$ = 1791, μ = 0.41 mm^{-1}, T = 150 K, $2\theta_{max}$ = 50.92°, 87340 reflections were measured of which 30013 were independent (R_{int} = 0.0534). Solvent within the voids was not crystallographically well defined and this extra-framework electron density was removed from the structure and the data treated with the SQUEEZE routine within PLATON.[19] This gave a void electron population of 679, corresponding to 4 eg and 5 MeOH molecules per Ni centre. Data/restraints/parameters = 30013/161/299, R_1 = 0.1469, wR_2 = 0.3414 for 22377 data with ($I > 2\sigma I$). Single crystal data were collected at 150 K at station 9.8 of the SRS at Daresbury Laboratories using an AXS Smart CCD area diffractometer equipped with an Oxford Cryostream low temperature system. The structure was solved by direct methods within SHELXS[20] in the acentric space group $P3$ (Laue class $\bar{3}$) and refined with full-matrix least-squares on F^2. Data were corrected for both beam decay and absorption using a semi-empirical method based on equivalents.[21] CCDC 191255. See http://www.rsc.org/suppdata/cc/b2/b211124c/ for crystallographic data in CIF or other electronic format.

¶ Phase **2** [$Ni_3(btc)_2(bipy)_3(C_2H_6O_2)_3(H_2O)_3$·(guest)] was prepared by the diffusion of an eg solution of $Ni(NO_3)_2·6H_2O$ and H_3btc into an eg solution of 4,4′-bipyridine in an H-cell of approximate volume 20 mL. Although the structures of both phases are based on the pillared honeycomb motif, the structure of **1**, determined using synchrotron radiation, involves a $\sqrt{3} \times \sqrt{3}$ expansion in the xy plane of the unit cell of **2** corresponding to a group → subgroup transformation of type IIc, ($2a + b$, $-a + b$, c). The weakness of the superstructure reflections prevents their measurement with a laboratory source for **2** but it is highly probable that the true cell of **2** is the supercell found for **1**. Therefore only the structure of the supercell phase **1** is described herein.

‖ The total solvent accessible volume was determined by summing voxels more than 1.2 Å from the framework using the program PLATON.[19] This extra-framework volume is similar to those reported by Yaghi and co-workers for MOF-5[2], $Zn_4O(BDC)_3$·guest, with an extra-framework volume calculated by PLATON of 77.0%, and MOF-14[18] which has composition $Cu_3(BTB)_2(H_2O)$·guest (where BTB is the trianion of 4,4′,4″-benzene-1,3,5-triyl-tribenzoic acid) has 64% void volume. Crystalline solids with void volumes in the range 80–91% have recently been reported.[22]

1 A. Stein, S. W. Keller and T. E. Mallouk, *Science*, 1993, **259**, 1558.
2 H. L. Li, M. Eddaoudi, M. O′Keeffe and O. M. Yaghi, *Nature*, 1999, **402**, 276.
3 M. Eddauodi, H. L. Li and O. M. Yaghi, *J. Am. Chem. Soc.*, 2000, **122**, 1391.
4 J. Kim, B. Chen, T. M. Reineke, H. Li, M. Eddaouddi, D. B. Moler, M. O′Keeffe and O. M. Yaghi, *J. Am. Chem. Soc.*, 2001, **123**, 8339.
5 S. Noro, S. Kitagawa, M. Kondo and K. Seki, *Angew. Chem., Int. Ed.*, 2000, **39**, 2082.
6 S. Noro, R. Kitaura, M. Kondo, S. Kitagawa, T. Ishii, H. Matsuzaka and M. Yamashita, *J. Am. Chem. Soc.*, 2002, **124**, 2568.
7 K. Seki, *Chem. Commun.*, 2001, 1496.
8 K. T. Holman, A. D. Pivovar, J. A. Swift and M. D. Ward, *Acc. Chem. Res.*, 2001, **34**, 107.
9 A. J. Blake, N. R. Brooks, N. R. Champness, P. A. Cooke, M. Crew, A. M. Deveson, L. R. Hanton, P. Hubberstey, D. Fenske and M. Schröder, *Cryst. Eng.*, 1999, **2**, 181.
10 C. B. Aakeröy, A. M. Beatty, D. S. Leinen and K. R. Lorimer, *Chem. Commun.*, 2000, 935.
11 S. R. Batten, B. F. Hoskins and R. Robson, *New J. Chem.*, 1998, **22**, 173.
12 S. R. Batten and R. Robson, *Angew Chem., Int. Ed.*, 1998, **37**, 1460.
13 O. M. Yaghi, G. M. Li and H. L. Li, *Nature*, 1995, **378**, 703.
14 H. J. Choi and M. P. Suh, *J. Am. Chem. Soc.*, 1998, **120**, 10622.
15 C. J. Kepert, T. J. Prior and M. J. Rosseinsky, *J. Solid State Chem.*, 2000, **152**, 261.
16 B. Moulton and M. J. Zaworotko, *Chem. Rev.*, 2001, **101**, 1629.
17 K. Biradha, Y. Hongo and M. Fujita, *Angew. Chem., Int. Ed.*, 2000, **39**, 3843.
18 B. Chen, M. Eddaoudi, S. T. Hyde, M. O′Keeffe and O. M. Yaghi, *Science*, 2001, **291**, 1021.
19 A. L. Spek, *Acta Crystallogr., Sect. A: Fundam. Crystallogr.*, 1990, **46**, C34.
20 G. M. Sheldrick, SHELXS-97, Universität Gottingen, Germany, 1997.
21 G. M. Sheldrick, SADABS, Universität Gottingen, Germany, 1997.
22 M. Eddaoudi, J. Kim, N. Rosi, D. Vodak, J. Wachter, M. O′Keeffe and O. M. Yaghi, *Science*, 2002, **295**, 469.