Crystal engineering of a 3-D coordination polymer from 2-D building blocks†

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Linking of 'all chair' two-dimensional honeycomb networks, structurally analogous to CF_x, with the 4-aminopyridine ligand leads to a three-dimensional molecular framework.

The construction of porous hosts[1] through crystal engineering[2] is currently attracting a great deal of interest in pursuit of novel materials which may act as catalysts or selective sorbents. Approaches include construction of hydrogen bonded architectures,[3] pillared clay mimics,[4] zeolite analogues[5] such as the AlPOs and GaPOs, and coordination polymer chemistry.[6] A considerable challenge in the field is to achieve predictable combination of structural features, which we have effected by linking the two-dimensional honeycomb motif in three dimensions with a bidentate amine ligand, identified by simple chemical reasoning.

1,3,5-Benzenetricarboxylic acid, H_3btc, has received considerable interest as a tridentate ligand capable of forming coordination polymers.[7] The structures are controlled by the extent of deprotonation of the H_3btc and the nature of the auxiliary ligands coordinated to the metal centre. The graphene-like (6,3) net[8] is well matched to the molecular geometry of btc, and thus two-dimensional honeycomb sheets,[9] some with pyridine projecting perpendicular to the sheets,[10] are a common feature of this chemistry. This opens up the opportunity of linking together these honeycomb layers, thereby predictably generating a three-dimensional architecture, using a suitable bidentate auxiliary ligand.

A wide variety of potential linking ligands to combine these infinite two-dimensional building blocks may be envisaged. We reasoned that a bidentate linker chemically resembling pyridine but without the marked framework forming tendency of, for example, 4,4′-bipyridine, was required. These considerations led to the choice of 4-aminopyridine (4AP). The Cambridge Crystallographic Database‡ currently contains twelve examples where 4AP binds to metal cations through the pyridine function, but there are no examples in the current literature where it, or its *N*-methylated derivatives, act as bidentate ligands. Reaction of tridentate layer-forming and bidentate layer-linking components yields a phase with the desired structural features.

Controlled diffusion§ of 4AP into a butan-1-ol solution of nickel nitrate and H_3btc yields pure UOL-1, $Ni_3(btc)_2(\mu\text{-}4AP)_2(4AP)_4 \cdot 6C_4H_9OH \cdot 2H_2O$. Analysis of single-crystal X-ray diffraction data collected using synchrotron radiation§ reveals that the structure consists of concertina sheets, shown in Fig. 1, composed of hexagonal 48-membered rings, linked by 4AP. Each ring is made up of six btc units joining six Ni^{II} cations and each sheet may be described topographically as a (6,3) net. In the present case the (6,3) net is not the ubiquitous flat graphene sheet but a topologically equivalent (6,3) net of chair conformation six-rings, which form a coordination polymer analogue of the puckered layers in graphite monofluoride, CF_x.[11]

Every btc is fully deprotonated and binds to three nickel cations: one carboxylate arm of the btc is monodentate to nickel, while the other two arms are bidentate with bite angles of 62.6(1) and 62.3(1)°. Two nickel cations (Ni2) act as linear connectors in the side of the concertina layer and these display
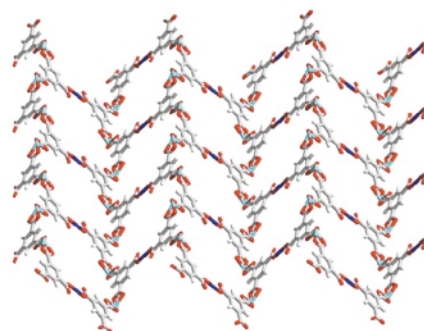
Fig. 1 A single concertina sheet composed of Ni^{2+} and 1,3,5-benzene-tricarboxylate. The 'all chair' conformation of the six-membered rings generates a corrugated sheet which is structurally analogous to the layers in CF_x. 4-Aminopyridine ligands and encapsulated solvent have been omitted (colour scheme: Ni1, light blue; Ni2, dark blue; C, grey; O, red; H, light grey).

slightly distorted octahedral coordination. The other four Ni cations (Ni1) are each six-coordinate with an environment that may be described as an extremely distorted octahedron. Two btc units are linked together at Ni1 and the angle subtended between their mean planes is 81.7(9)°. This is reflected in the extreme puckering of the layers: adjacent corrugations subtend an angle of 76.4° to each other (Fig. 2). The coordination about the two crystallographically different nickel atoms is completed entirely by the btc described above and 4AP. Both monodentate (through the pyridine function) and bidentate 4AP are observed. Nickel cations (Ni1) at the peaks and troughs of each corrugated layer are linked by two bidentate 4AP molecules to nickel (Ni2) at the midpoints of the hexagons in adjacent layers, as shown in Fig. 2. To our knowledge this is the first crystallographic report of bidentate 4-aminopyridine.

While it might be possible to link plane (6,3) graphene nets using a bridging ligand with *linear* coordination geometry (such as pyrazine), this is not the case for 4AP. Unlike the pyridine function, which can bind a metal in the plane of the aromatic
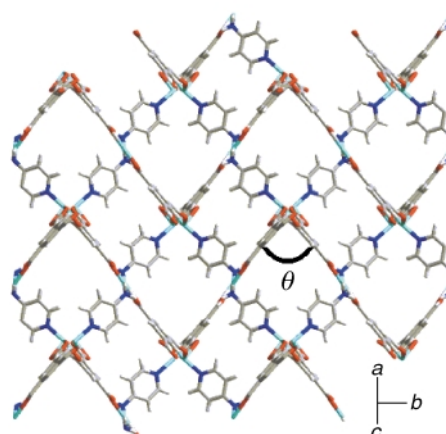
Fig. 2 Linking of ABAB stacked concertina sheets by bidentate 4-aminopyridine (4AP). The angle denoted θ is 76.4°. Monodentate 4AP and solvent are omitted (colour scheme: Ni, light blue; N, dark blue; C, grey; O, red; H, light grey).
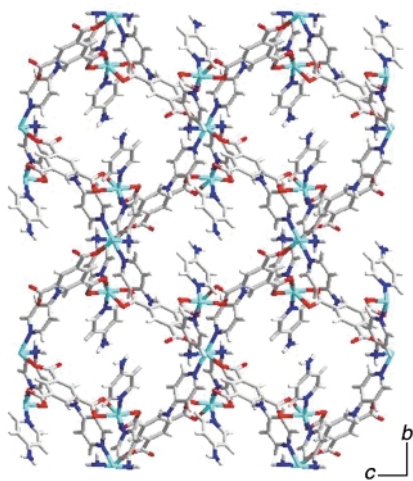
Fig. 3 View down *a* showing protrusion of monodentate 4AP into rectangular pores 15.4 × 7.7 Å in size. Pore solvent is omitted (colour scheme: Ni, light blue; N, dark blue; C, grey; O, red; H, light grey).

ring, the amino function can only bind a cation lying out of the plane of the ring because of the directionality of its coordination. Adoption of the graphite monofluoride layer allows the pyridine function of 4AP to bind in a linear mode, while the amino function can bind forming a C–N–Ni angle of 119.0(1)°. Thus the different geometric requirements of the two ends of the linker enforce the CF_x geometry on to the sheets: puckering must occur if the 4AP is to link the octahedral cations in adjacent layers.

The concertina sheets are stacked in an ABAB manner producing a three-dimensional architecture with pores running parallel to *a* (15.4 × 7.7 Å shortest van der Waals contacts) and *c* (15.1 × 6.0 Å). Monodentate 4AP protrudes into these pores forming necks where the pore is narrowed to *ca.* 3.4 Å, while providing an extremely hydrophilic lining to the cavities (Fig. 3). The program PLATON[12] reveals that the total solvent accessible volume within the crystal, summing voxels more than 1.2 Å away from the framework, is 42.2%. In the pristine material this pore volume is filled with butan-1-ol and water molecules, all engaged in hydrogen bonding with the framework. The hydroxyl groups of two of the three independent butan-1-ol molecules act as donors to btc carboxylates in the framework (O⋯O distances are 2.68(1) and 2.83(1) Å). The remaining butan-1-ol forms a hydrogen bond to water [2.70(1) Å] which in turn binds to a framework carboxylate [2.73(1) Å]. Removal of this solvent from within the pores may be effected thermally and leads to framework collapse.

The bidentate 4-aminopyridine ligand therefore allows the construction of molecular frameworks in which the infinite two-dimensional honeycomb building blocks characteristic of btc are linked to form a three-dimensional pore network. The (6,3) net unusually adopts the corrugated conformation of CF_x to allow connection of the layers, driven by the geometry of the connecting 4AP ligand. This systematic construction of a framework using linking units to join identifiable structural features may have wider application in coordination polymer chemistry.

Notes and references

‡ Cambridge Structural Database, Version 5.20 (October 2000) with 224 400 entries. www.ccdc.cam.ac.uk

§ 4-Aminopyridine (80 mg, 0.85 mmol) was allowed to mix with $Ni(NO_3)\cdot6H_2O$ (17.4 mg, 60 μmol) and H_3btc (8.4 mg, 40 μmol) by diffusion through butan-1-ol in an H-cell (height 60 mm, crossbar 90 mm, circular cross-section diameter 15 mm). Extremely small single crystals were obtained after *ca.* 4 weeks. Single-crystal X-ray diffraction was carried out on a Bruker AXS SMART CCD area detector diffractometer at Station

9.8 of the CLRC Daresbury Laboratory Synchrotron Radiation Source, UK. A light green rod-shaped crystal of dimensions 15 × 15 × 40 μm was removed from the mother liquor and covered with a thin film of perfluoropolyether oil and mounted on the tip of a two-stage glass fibre. The crystal was cooled to 123 K in an Oxford Instruments nitrogen gas cryostream. Synchrotron radiation of wavelength 0.6923 Å was employed (determined by measurement of a known crystal). A sphere of data was collected in three series of ω-rotation exposure frames each with different crystal orientation φ angles: each 3 s exposure employs a 0.15° rotation in ω. Data were integrated using Bruker software[13] and semi-empirical corrections[14] were applied to account for beam decay and absorption. The structure was solved using direct methods within SHELXS-86.[15] Full-matrix least-squares refinement on F^2 was carried out with SHELXL-93.[16] Hydrogen atoms were located from the difference Fourier and fitted with a riding model.

UOL-1 crystallises in the centrosymmetric monoclinic space group $P2_1/n$ (no. 14): $a = 13.1698(9)$, $b = 19.1965(12)$, $c = 16.6969(11)$ Å, $\beta = 108.9670(11)°$, $V = 3992$ Å^3. Using a single detector position, 14 214 intensities were recorded, producing 9505 unique data (θ_{max} 30.24 °), $R_{int} = 0.0749$, conventional R [$I > 2\sigma(I)$, all data] 0.0866 (0.1069), $wR2$ 0.2068 (0.2222). GOF on F^2 1.083 (1.083). CCDC 154064. See http://www.rsc.org/suppdata/cc/b0/b009455m/ for crystallographic data in .cif or other electronic format.

The diffusion synthesis affords phase-pure UOL-1 as demonstrated by the fully indexed powder diffraction patterns given as ESI.†

1 T. J. Barton, L. M. Bull, W. G. Klemperer, D. A. Loy, B. McEnaney, M. Misono, P. A. Monson, G. Pez, G. W. Scherer, J. C. Vartuli and O. M. Yaghi, *Chem. Mater.*, 1999, **11**, 2633.

2 C. B. Aakeröy and A. S. Borovik, *Coord. Chem. Rev.*, 1999, **183**, 1; A. J. Blake, N. R. Champness, P. Hubberstey, W. S. Li, M. A. Withersby and M. Schröder, *Coord. Chem. Rev.*, 1999, **183**, 117; D. Braga and F. Grepioni, *Coord. Chem. Rev.*, 1999, **183**, 19; M. O'Keeffe, M. Eddaoudi, H. L. Li, T. Reineke and O. M. Yaghi, *J. Solid State Chem.*, 2000, **152**, 3.

3 F. H. Herbstein, *Top. Curr. Chem.*, 1987, **140**, 107; R. E. Melendez and M. J. Zaworotko, *Supramol. Chem.*, 1997, **8**, 157; R. E. Melendez and A. D. Hamilton, *Top. Curr. Chem.*, 1998, **198**, 97.

4 M. L. Kantam, P. L. Santhi, K. V. R. Prasad and F. Figueras, *J. Mol. Catal. A: Chem.*, 2000, **156**, 289; A. Rujiwatra, C. J. Kepert and M. J. Rosseinsky, *Chem. Commun.*, 1999, 2307; K. Biradha, D. Dennis, V. A. MacKinnon, C. V. K. Sharma and M. J. Zaworotko, *J. Am. Chem. Soc.*, 1998, **120**, 11 894; K. Bahranowski, R. Grabowski, B. Grzybowska, A. Kielski, E. M. Serwicka, K. Wcislo, E. Wisla-Walsh and K. Wodnicka, *Top. Catal.*, 2000, **11**, 255.

5 A. K. Cheetham, G. Ferey and T. Loiseau, *Angew. Chem., Int. Ed.*, 1999, **38**, 3269; P. A. Wright, M. J. Maple, A. M. Z. Slawin, V. Patinec, R. A. Aitken, S. Welsh and P. A. Cox, *J. Chem. Soc., Dalton Trans.*, 2000, **8**, 1243.

6 B. F. Abrahams, S. R. Batten, M. J. Grannas, H. Hamit, B. F. Hoskins and R. Robson, *Angew. Chem., Int. Ed.*, 1999, **38**, 1475; K. Biradha, C. Seward and M. J. Zaworotko, *Angew. Chem., Int. Ed.*, 1999, **38**, 492; M. Eddaoudi, H. L. Li and O. M. Yaghi, *J. Am. Chem. Soc.*, 2000, **122**, 1391; H. Gudbjartson, K. Biradha, K. M. Poirier and M. J. Zaworotko, *J. Am. Chem. Soc.*, 1999, **121**, 2599; T. M. Reineke, M. Eddaoudi, D. Moler, M. O'Keeffe and O. M. Yaghi, *J. Am. Chem. Soc.*, 2000, **122**, 4843; P. Lightfoot and A. Snedden, *J. Chem. Soc., Dalton Trans.*, 1999, 3549.

7 M. J. Plater, M. R. S. Foreman, E. Coronado, C. J. Gomez-Garcia and A. M. Z. Slawin, *J. Chem. Soc., Dalton Trans.*, 1999, 4209; O. M. Yaghi, G. M. Li and H. L. Li, *Nature*, 1995, **378**, 703; C. J. Kepert, T. J. Prior and M. J. Rosseinsky, *J. Am. Chem. Soc.*, 2000, **122**, 5158; S. S. Y. Chui, S. M. F. Lo, J. P. H. Charmant, A. G. Orpen and I. D. Williams, *Science*, 1999, **283**, 1148.

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

9 H. J. Choi and M. P. Suh, *J. Am. Chem. Soc.*, 1998, **120**, 10 622; H. J. Choi, T. S. Lee and M. P. Suh, *Angew. Chem., Int. Ed. Engl.*, 1999, **38**, 1405.

10 C. J. Kepert, T. J. Prior and M. J. Rosseinsky, *J. Solid State Chem.*, 2000, **152**, 261.

11 N. N. Greenwood and A. Earnshaw, *Chemistry of the Elements*, Butterworth-Heinemann, London, 2nd edn., 1997, p. 290.

12 A. L. Spek, *Acta Crystallogr., Sect. A*, 1990, **46**, C34.

13 Bruker AXS Inc., Madison, WI, SMART (control) and SAINT (integration) software, version 4, 1994.

14 G. M. Sheldrick, SADABS, Universität Göttingen, 1997.

15 G. M. Sheldrick, SHELXS-86, Universität Göttingen, 1986.

16 G. M. Sheldrick, SHELXL-93: Program for the refinement of crystal structures, Universität Göttingen, 1993.