CHEMCOMM
Communication
www.rsc.org/chemcomm

A dense coordination polymer bearing an extensive and highly intricate hydrogen bonding array†

Timothy J. Prior and Matthew J. Rosseinsky*

Department of Chemistry, Robert Robinson Laboratories, University of Liverpool, UK L69 7ZD.
E-mail: m.j.rosseinsky@liv.ac.uk

Received (in Cambridge, UK) 27th March 2001, Accepted 21st May 2001
First published as an Advance Article on the web 14th June 2001

Linking of hydrogen bonded sheets by coordination polymer chains produces a three-dimensional solid derived from two distinct structural components.

Enhanced design strategies for the synthesis of extended molecular solids are of considerable current interest.[1] Existing methods focus on single supramolecular synthons and give rise to solids whose structures are dominated by one specific interaction. Here we describe the use of two molecular tectons, with both coordinative and hydrogen bonding[2] abilities, to construct a phase in which there are two distinct extended structural units.

There are two principal methods for the construction of extended molecular solids: hydrogen bonding or coordinative metal–ligand interactions. The construction of organic hosts from hydrogen bonding moieties has been widely studied.[3] This approach potentially offers excellent control over the construction of materials through the manipulation of the hydrogen bonding interactions. Although hydrogen bonding architectures containing metal ions exist, those exhibiting true coordination polymer units are rare,[4] being limited to frameworks in which the coordination polymer is the primary structural element, subsequently linked by hydrogen bonds. For example several 4,4′-bipyridyl frameworks display this formulation: metal–bipyridyl chains or layers are held together by secondary bipy$\cdots$water or bipy$\cdots$nitrate hydrogen bonds.[5]

The tectons selected in this work are trimesic acid (1,3,5-benzenetricarboxylic acid, H_3btc) and 1,4-diaminobenzene (1,4-DAB). Trimesic acid has attracted considerable interest as a host for inclusion compounds, co-crystallising with a wide variety of species.[6] 1,4-DAB is known to act as a rigid spacer between transition metal dimers,[7] although it has not previously been observed linking discrete metal cations. Reaction of these molecular components with Ni^{2+} under hydrothermal conditions‡ affords a dense metal–organic solid, N3DAB, with both coordination polymer and hydrogen bonded structural features.

Analysis of single crystal X-ray diffraction data§ collected using synchrotron radiation shows that N3DAB displays the first example of infinite hydrogen bonded sheets linked by coordination polymer chains (Fig. 1).

The structure is based on nickel centres octahedrally coordinated by three types of ligand, in an ‘*all trans*’ geometry (Fig. 2) allowing the formation of the two distinct sub-arrays: *trans* 1,4-DAB units form coordination polymer chains while *trans* btcH_2 units form hydrogen bonded sheets and are locked into the conformation allowing the formation of this infinite sheet by hydrogen bonding to water ligands (Fig. 3). In other systems where two *trans* btc units coordinate to the same metal centre, interligand hydrogen bonding of this type is very important in determining the geometry about the metal and hence the orientation of the btc units. In N3DAB this interaction is clearly also important as shown by the extreme rotation about the C7–C8 bond (ring-carboxylate): the torsion angle defined by C6, C7, C8 and O5 is 156.2°. In the absence of this hydrogen bond the angle would be expected to be very near 180°. The btcH_2 units joined to the Ni(1,4-DAB) chain display an unusual mode of coordination, being deprotonated at only one acid functionality. It is the dense and co-operative net of hydrogen bonding interactions which prevents the expected complete deprotonation of the H_3btc under the basic synthetic conditions used.

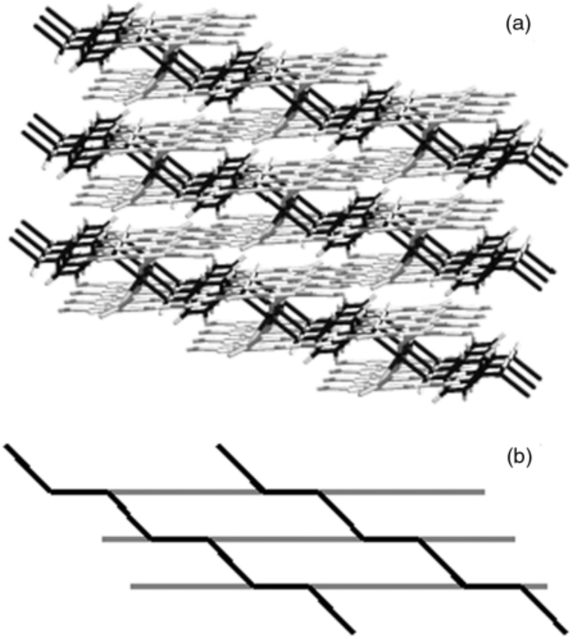

Fig. 1 (a) Infinite 2-D hydrogen bonded decks (grey) linked by 1-D coordination polymer chains (black). (b) Schematic illustration of the two infinite motifs in the structure of N3DAB.

The coordination polymer chains have stoichiometry Ni(1,4-DAB) and run parallel to the crystallographic *b* axis. The Ni–N–C angle is very close to 120° which gives the chain the zigzag arrangement shown in Fig. 2. These chains are decorated with pairs of btcH_2 at every nickel centre.

The hydrogen bonded sheets are composed of chains made up from Z-shaped links as shown in Fig. 4. These chains are knit

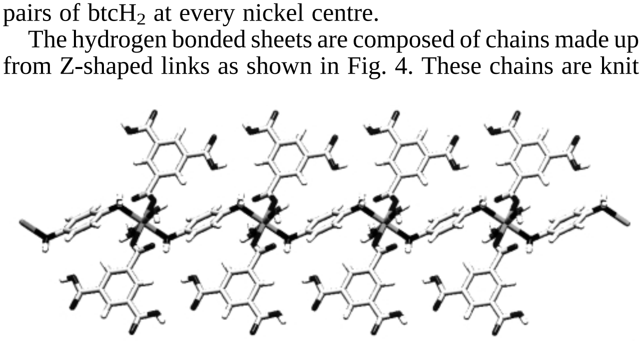

Fig. 2 A single Ni(1,4-DAB) zigzag coordination polymer chain decorated at every nickel with two btcH_2 units. Each btcH_2 forms part of an infinite hydrogen bonded layer (see Fig. 4).

---

† Electronic supplementary information (ESI) available: tables of crystallographic data. Full analysis of hydrogen bonding networks. Thermogravimetric data. See http://www.rsc.org/suppdata/cc/b1/b102809j/

DOI: 10.1039/b102809j

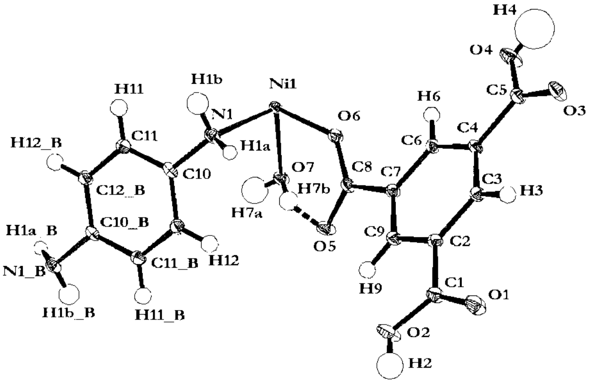

Fig. 3 ORTEP plot of the asymmetric unit of N3DAB. Atoms are shown as 50% thermal ellipsoids. Ni1 lies on the inversion centre. Note the hydrogen bond between O7 and O5 (2.70 Å). Symmetry equivalent atoms appended _B are generated by the symmetry operator $1 - x, - y, 1 - z$.

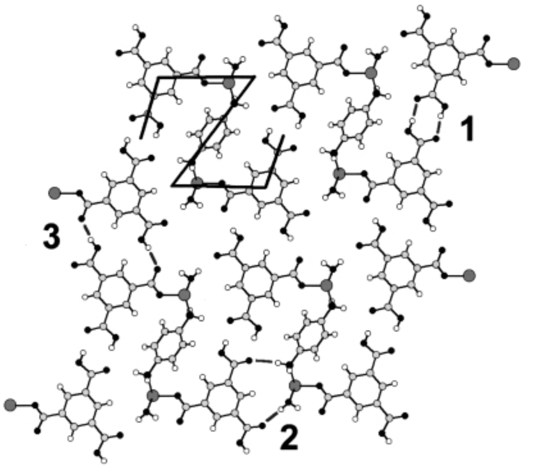

Fig. 4 Part of one of the infinite hydrogen bonded decks composed of Z-shaped links. One such link is highlighted. The three hydrogen bonds responsible for the formation of the infinite sheet are labelled 1, 2 and 3.

together into infinite sheets by further hydrogen bonds. However additional hydrogen bonding networks exist throughout the entire structure and are not constrained to run within the layers, reinforcing the remarkable extent of hydrogen bonding within the structure. Full analysis of the hydrogen bonding is given in the electronic supplementary information (ESI).† The highly electron-rich hydrogen bonded decks lie parallel to each other and their mean separation, 3.324(2) Å (a/2), is sufficiently close to suggest that the btcH$_2$ rings engage in π-stacking.

The unusual mode of coordination of 1,4-DAB offers potential for the formation of a wide range of coordination polymer networks. The coupling of the 1-D chains with different equatorial ligands offers the prospect of novel, potentially porous frameworks. The combination of coordination polymer chains with species known to form extended hydrogen bonded networks opens up a new avenue for synthesis of supramolecular hosts. This two-component approach to synthesis is attractive because of the control which may be exerted through the tectons present.

We thank Dr S. J. Teat for his expert assistance on DL Station 9.8 and the UK EPSRC for a studentship to T. J. P. and support through GR/N 08537.

Notes and references

‡ Very dark purple crystals of N3DAB were grown under hydrothermal conditions. Reagents were purchased from the Aldrich Chemical Company and used without further purification: 0.176 g (0.605 mmol) Ni(NO$_3$)$_2$·6H$_2$O, 0.2543 g (1.21 mmol) H$_3$btc, 0.1966 g (1.82 mmol) 1,4-diaminobenzene and 12 ml water were loaded into a 23 cm^3 Teflon-lined stainless-steel reactor which was then sealed. The reactor was heated in an autoclave for 16 h at 150 °C and then cooled to room temperature at a rate of 0.5 °C min^{-1}. Yield 74% (based on Ni). This synthesis affords phase pure N3DAB as demonstrated by the full indexing of powder diffraction patterns given in the ESI† (81 peaks) and chemical analysis (Calc.: C, 46.40; H, 3.58; N, 4.52; Ni, 9.45. Found: C, 46.41; H, 3.58; N, 4.55; Ni, 9.38%).

§ Single-crystal X-ray diffraction data were collected on a Bruker AXS SMART CCD area-detector diffractometer at Station 9.8 of the CLRC Daresbury Laboratory Synchrotron Radiation Source, UK. A dark purple platelet with dimensions 160 × 80 × 60 μm was covered in 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 0.6941 Å was employed (the wavelength is determined by measurement of unit cell parameters of a known structure). A sphere of data in reciprocal space was collected in three series of ω-rotation exposure frames each with different crystal orientation φ angles: each 1 s exposure employs a 0.15° rotation in ω. Reflection data were integrated using Bruker software.[8] Semiempirical corrections were applied to account for absorption and beam decay.[9] The structure was solved using direct methods in SHELXS-86.[10] Subsequent difference Fourier methods to locate all other atoms and full-matrix least-squares refinement on F^2 was carried out with SHELXL-97.[11] N3DAB, Ni(1,4-DAB)(btcH$_2$)$_2$(H$_2$O)$_2$, crystallises in the centrosymmetric space group $P\bar{1}$ (no. 2). The nickel atom lies in a pseudo-octahedral environment on the inversion centre.

Crystal data: a = 6.6480(18), b = 8.550(2), c = 11.124(3) Å, α = 70.280(6), β = 79.594(6), γ = 76.093(6)°, V = 574.43 Å^3, Z = 2, μ = 0.932 mm^{-1}. Using a single detector position, 5650 intensities were recorded, producing 2987 unique data ($\theta_{\max}$ 29.38°). R_{int} = 0.0103. Conventional R [$I > 2\sigma(I)$, all data] 0.0462 (0.0526), $wR2$ 0.1256 (0.1279). GOF on F^2 1.135 (1.136). CCDC 162906. See http://www.rsc.org/suppdata/cc/b1/b102809j/ for crystallographic data in CIF or other electronic format.

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; G. F. Swiegers and T. J. Malefetse, *Chem. Rev.*, 2000, **100**, 3483; A. K. Cheetham, G. Ferey and T. Loiseau, *Angew. Chem., Int. Ed.*, 1999, **38**, 3269.

2 C. B. Aakeröy, A. M. Beatty and K. R. Lorimer, *J. Chem. Soc., Dalton Trans.*, 2000, 3869.

3 G. R. Desiraju, *Chem. Commun.*, 1997, 1475; A. Anthony, G. R. Desiraju, R. K. R. Jetti, S. S. Kuduva, N. N. L. Madhavi, A. Nangia, R. Thaimattam and V. R. Thalladi, *Mater. Res. Bull.*, 1998, 1; A. J. Blake, N. R. Champness, P. Hubberstey, W. S. Li, M. A. Withersby and M. Schröder, *Coord. Chem. Rev.*, 1999, **183**, 117; C. B. Aakeröy and A. S. Borovik, *Coord. Chem. Rev.*, 1999, **183**, 1.

4 A. D. Burrows, D. M. P. Mingos, A. J. P. White and D. J. Williams, *Chem. Commun.*, 1996, 97; S. R. Breeze and S. N. Wang, *Inorg. Chem.*, 1993, **32**, 5981.

5 L. Carlucci, G. Ciani, D. M. Proserpio and A. Sironi, *J. Chem. Soc., Dalton Trans.*, 1997, 1801; C. J. Kepert and M. J. Rosseinsky, *Chem. Commun.*, 1999, 375; M. X. Li, G. Y. Xie, Y. D. Gu, J. Chen and P. J. Zheng, *Polyhedron*, 1995, **14**, 1235; M. Kondo, T. Yoshitomi, K. Seki, H. Matsuzaka and S. Kitagawa, *Angew. Chem., Int. Ed. Engl.*, 1997, **36**, 1725; Y. B. Dong, M. D. Smith, R. C. Layland and H. C. zur Loye, *J. Chem. Soc., Dalton Trans.*, 2000, 775.

6 F. H. Herbstein, *Top. Curr. Chem.*, 1987, **140**, 107; K. Biradha, D. Dennis, V. A. MacKinnon, C. V. K. Sharma and M. J. Zaworotko, *J. Am. Chem. Soc.*, 1998, **120**, 11 894; R. E. Melendez and M. J. Zaworotko, *Supramol. Chem.*, 1997, **8**, 157; G. Ferguson, C. Glidewell, G. D. McManus and P. R. Meehan, *Acta Crystallogr., Sect. C*, 1998, **54**, 418.

7 I. M. Müller, T. Röttgers and W. S. Sheldrick, *Chem. Commun.*, 1998, 823.

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

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

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

11 G. M. Sheldrick, SHELXL-97: program for the refinement of crystal structures, Universität Göttingen, 1997.