

Channel-containing 1D coordination polymers based on a linear dimetallic spacer

Warwick J. Belcher, Christopher A. Longstaff, Marcus R. Neckenig and Jonathan W. Steed*

Department of Chemistry, King's College London, Strand, London, UK WC2R 2LS.

E-mail: jon.steed@kcl.ac.uk

Received (in Columbia, MO, USA) 19th March 2002, Accepted 29th May 2002

First published as an Advance Article on the web 19th June 2002

A new channel-containing 1D coordination polymer has been prepared by the combination of a linear dimetallic spacer, $\text{Cu}_2(\text{O}_2\text{CMe})_4$, and a linear didentate ligand, 1,3-di-4-pyridylpropane; the new material includes methanol, acetic acid and diethylene glycol.

The quest to rationally design and synthesise synthetic channel-containing materials based on metal coordination polymers ('organic zeolites') is highly topical.^{1–5} While many materials have been prepared, some exhibiting robust porous frameworks and even reversible guest complexation/decomplexation,^{6,7} products are still often difficult to predict given the vast array of possible nets that may be generated by combination of metals with multiple available coordination sites and di-, tri- or multidentate ligands. Recent work has shown that one key to the generation of porous networks is the incorporation of long spacer moieties. Thus ligands such as 1,2-di-4-pyridylethane, 1,4-di-4-pyridylbenzene and 1,4-di-4-pyridyldiphenyl¹ have been successfully used to generate porous coordination frameworks exhibiting varying degrees of guest inclusion.^{8–10} However, the use of such ligands is complicated by competition between framework interpenetration^{11,12} and guest binding, although recently Atwood *et al.* have shown that intra-cavity space may be controlled by specific hydrogen bonding interactions.¹³

While ligands with long spacer groups have been studied extensively, however, there are few reports of the use of multinuclear metal-containing fragments to increase host channel width and hence bring about guest inclusion. Work by Yaghi and coworkers has shown that such multimetallic fragments, in combination with long spacer ligands, can reduce the degree of interpenetration observed in framework structures, allowing the formation of large pores.^{4,14–17} As part of an ongoing programme aimed at formation and control of coordination polymer architecture^{3,18} we now report the combined use of a long, linear ligand with a dimetallic fragment possessing linearly arranged binding sites to produce a neutral, porous, channel-containing coordination polymer framework capable of including a variety of guest species. Neutral coordination polymer frameworks obviate the need for counter-anions which otherwise fill up channels or pores within the structure rendering them unavailable for guest inclusion.

Copper(II) acetate dihydrate adopts a classic 'lantern' structure with a metal–metal bond bridged by four μ_2 -acetato ligands. The acetato ligands themselves may be replaced by bidentate dicarboxylates to yield 3D polymer frameworks,^{4,19} however, tighter control over the resulting polymer architecture may be obtained achieved *via* the two axial aqua ligands, situated 180° apart, one on each metal. These ligands are highly labile and are readily displaced under mild conditions by a range of Lewis bases.²⁰ Zaworotko and coworkers have used this approach recently with copper(II) propanoate and hexamethylene tetramine to generate a non-porous 2D pentagonal grid.²¹ In our hands reaction of $[\{\text{Cu}(\text{O}_2\text{CMe})_2(\text{H}_2\text{O})\}_2]$ with the extended 1,3-di-4-pyridylpropane ligand (dpp)² in refluxing methanol followed by slow cooling, predictably results in the formation of a zigzag, non-interpenetrated 1D coordination polymer network, $[\{\text{Cu}(\text{O}_2\text{CMe})_2\}_2(\mu\text{-dpp})]_n$ **1** characterised

by X-ray crystallography, (Fig. 1).[†] The compound is formed in essentially quantitative yield and the crystals were shown to be representative of the bulk by elemental analysis. The zigzag shape of each polymer chain is a direct consequence of the preference for *anti* torsion angles along the propyl chain of the ligand.² The individual chains line up in layers with each layer crossing the layer beneath at an angle of 49.1° (Fig. 2(a)) This results in the formation of infinite channels running perpendicular to each layer which arise from the small size of the acetate methyl groups which point into the channel compared to the channel radius as defined by the length of the dpp ligand and dinuclear copper(II) building blocks. Each channel has an average van der Waals area of 60 Å² and occupies 522 Å³ per *c* axis repeat (*i.e.* 1044 Å³ per unit cell or 32.8%) In the as-synthesised material each channel is occupied by methanol arranged in an irregular but ordered pair of four-fold helices.

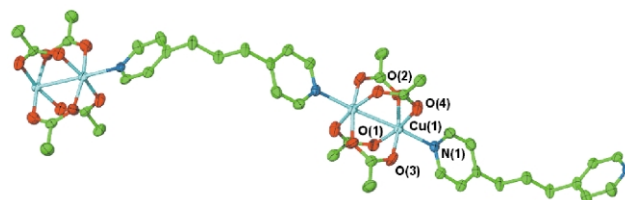


Fig. 1 Four repeat units of the infinite coordination polymer $[\{\text{Cu}(\text{O}_2\text{CMe})_2(\mu\text{-dpp})\}_n]$ **1**. Bond lengths and angles about the Cu(II) centres are normal with Cu–Cu 2.6294(11), Cu–O(av.) 1.971(4) Å and Cu–N 2.176(4) Å.

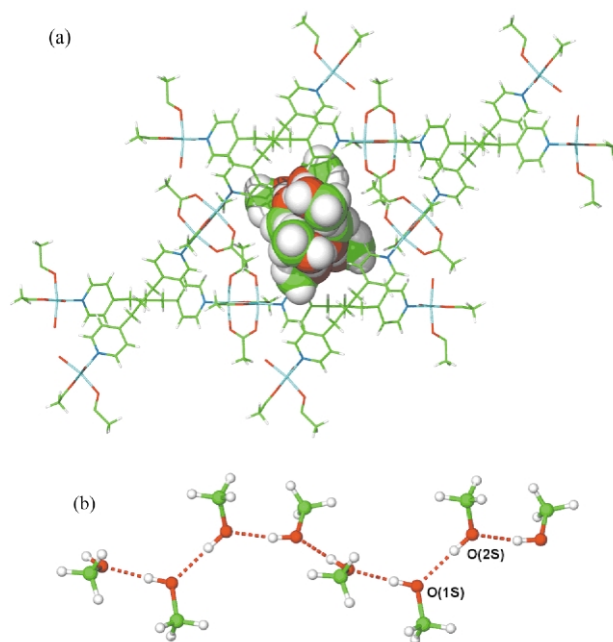


Fig. 2 (a) Space-filling plot of the infinite channels in **1** viewed along the channel axis showing the included pair of ordered four-fold helices of methanol, (b) side view of one of the guest helices. Hydrogen bonded O...O distances: O(1S)...O(2S) 2.574(13), O(2S)...O(1S) 2.674(11) Å.

The two helices are of opposite handedness and are related by a centre of symmetry. The methyl substituents of the methanol molecules are directed towards the channel walls indicating the hydrophobic nature of the cavity, while the OH groups hold the helix together *via* an infinite chain of OH...O hydrogen bonds, Fig. 2.

Interestingly coordination polymer **1** could also be prepared mechanochemically^{22,23} by simple grinding of solid copper(II) acetate dihydrate with dpp in a pestle and mortar. The formation of the product is apparent by a colour change‡ from blue to blue–green over the course of *ca.* 15 min. MAS ¹³C NMR spectra of **1**·4MeOH compared to the sample of **1** generated by grinding are closely similar with the exception of a pronounced peak at δ 50.3 assigned to methanol, suggesting that, in the solid phase synthesis product, the channels are filled by water.

The thermal stability of **1**·4MeOH was probed by TGA analysis that indicated that guest loss was facile. Elemental analysis suggests that even at room temperature samples gradually lost methanol and absorbed atmospheric moisture, apparently retaining some crystallinity. Warming samples of **1**·4MeOH to 80 °C in air resulted in guest loss. DSC analysis of freshly prepared samples of **1**·4MeOH showed up to three minor endotherms all under 80 °C attributed to guest desorption. Decomposition of the host framework by loss of the dpp ligand to give anhydrous copper(II) acetate occurred at 210 °C.

Attempts were made to replace the included methanol with a wide range of other potential guests by slow cooling of methanol solutions of **1** containing stoichiometric amounts or small excesses of guest. In each case **1**·4MeOH was the only product isolated. Complexes of **1** with other guests could be generated, however, either by avoidance of methanol, or by prolonged evaporation of methanolic solutions of **1** in the presence of relatively involatile guests. Thus crystallisation of **1** from acetic acid–dioxane 1 : 1 v/v gave **1**·2MeCO₂H while slow evaporation of a methanolic solution of **1** in the presence of a stoichiometric amount of diethyleneglycol gave **1**·MeOH·H(O–C₂H₄)₂OH, Table 1. In contrast to **1**·4MeOH, the diethyleneglycol complex **1**·MeOH·H(OC₂H₄)₂OH, exhibited significantly enhanced stability showing sequential loss of methanol (99 °C) followed by diethylene glycol (161 °C) in both TGA and DSC scans.

Interestingly, crystallisation from glacial acetic acid repeatedly gave a new material, $\{[\text{Cu}(\text{O}_2\text{CCMe})_2]_2(\mu\text{-NC}_5\text{H}_4\text{C}(\text{O})\text{CH}_2\text{CH}_2\text{C}_5\text{H}_4\text{N})\}_n \cdot 2\text{MeCO}_2\text{H}$, having apparently undergone oxidation of the dpp ligand. Details of this surprising result will be reported separately.

Both **1**·2MeCO₂H and **1**·MeOH·H(OC₂H₄)₂OH were characterised by X-ray crystallography. In each case the host framework proved to be essentially identical to that found for **1**·4MeOH with the channel pore running parallel to the crystallographic *c* axis. Unlike **1**·4MeOH, however, the guest molecules in both complexes proved to be disordered, consistent with the situation often encountered with urea clathrates in which $c_{\text{host}} \neq c_{\text{guest}}$.²⁴ In the present case, each structure exhibits two strands of disordered electron density in a fashion analogous to the parent material. In the disorder model adopted interatomic contacts suggest hydrogen bonding between acid

and alcohol functionalities while hydrophobic portions point outwards.

In conclusion we outline a predictable route to neutral coordination polymer framework **1** and, by implication, other related frameworks in which the dimensions of the spacer dipyriddy type ligand are modified. Framework **1** contains a large channel capable of including a variety of guest species. The stability of the inclusion complex increases with increasing guest chain length. The host framework is stable up to 210 °C.

We thank Dr A. Aliev of the ULIRS SS NMR service for recording the MAS ¹³C NMR spectra and Dr M. Odlyha of the ULIRS thermal analysis service for the TGA and DSC data. We are grateful to King's College for funding and Dr L. J. Barbour, University of Missouri–Columbia, for the program XSeed.

Notes and references

† Crystal data for **1**·4MeOH: C₂₄H₃₈Cu₂N₂O₁₁, *M* = 657.64 g mol⁻¹, orthorhombic, space group *Pccn*, *a* = 12.9409(5), *b* = 28.2648(5), *c* = 8.7103(13) Å. *U* = 3186.0(5) Å³, *Z* = 4, μ = 1.388 mm⁻¹, *T* = 100 K, Reflections measured: 13 795, unique data: 3113, parameters: 191, *R*₁ [*F*² > 2 σ (*F*²)] 0.0578, *wR*₂ (all data) 0.1624. CCDC reference number 182082. See <http://www.rsc.org/suppdata/cc/b2/b202652j/> for crystallographic data in CIF or other electronic format.

‡ Single crystals of **1**·4MeOH exhibit anisotropic visible absorption, appearing either blue or green depending on the direction from which they are viewed.

Table 1 Unit cell parameters for inclusion compounds of **1**; space group *Pccn*

Unit cell/Å	Guest		
	MeOH	MeCO ₂ H	MeOH–H(OC ₂ H ₄) ₂ OH
<i>a</i>	12.9409(5)	12.7595(6)	13.0748(7)
<i>b</i>	28.2648(5)	28.2350(18)	28.4081(10)
<i>c</i>	8.7103(13)	8.7376(4)	8.7086(6)

- 1 K. Biradha, Y. Hongo and M. Fujita, *Angew. Chem., Int. Ed.*, 2000, **39**, 3843.
- 2 L. Pan, B. Woodlock, X. Wang, K.-C. Lam and A. L. Rheingold, *Chem. Commun.*, 2001, 1762.
- 3 G. Guliera and J. W. Steed, *Chem. Commun.*, 1999, 1563.
- 4 M. Eddaoudi, D. B. Moler, H. Li, B. Chen, T. M. Reineke, M. O'Keefe and O. M. Yaghi, *Acc. Chem. Res.*, 2001, **34**, 319.
- 5 O. M. Yaghi, H. Li, C. Davis, D. Richardson and T. L. Groy, *Acc. Chem. Res.*, 1998, **31**, 474.
- 6 O. M. Yaghi, G. Li and H. Li, *Nature*, 1995, **378**, 703.
- 7 H. Li, M. Eddaoudi, M. O'Keefe and O. M. Yaghi, *Nature*, 1999, **402**, 276.
- 8 M. A. Withersby, A. J. Blake, N. R. Champness, P. A. Cooke, P. Hubberstey, A. L. Realf, S. J. Teat and M. Schröder, *J. Chem. Soc., Dalton Trans.*, 2000, 3261.
- 9 M. Maekawa, H. Konaka, Y. Suenaga, T. Kuroda-Sowa and M. Munakata, *J. Chem. Soc., Dalton Trans.*, 2000, 4160.
- 10 K. N. Power, T. L. Hennigar and M. J. Zaworotko, *Chem. Commun.*, 1998, 595.
- 11 S. R. Batten, B. F. Hoskins, B. Moubaraki, K. S. Murray and R. Robson, *Chem. Commun.*, 2000, 1095.
- 12 J. W. Steed and J. L. Atwood, *Supramolecular Chemistry*, Wiley, Chichester, 2000.
- 13 J. L. Atwood, L. J. Barbour and A. Jerga, *Proc. Natl. Acad. Sci. USA*, 2002, **99**, 4837.
- 14 S. Ferlay, S. Koenig, M. W. Hosseini, J. Pansanel, A. De Cian and N. Kyritsakas, *Chem. Commun.*, 2002, 218.
- 15 M. J. Zaworotko, *Chem. Soc. Rev.*, 1994, **23**, 283.
- 16 B. Moulton, E. B. Rather and M. J. Zaworotko, *Cryst. Eng.*, 2001, **4**, 309.
- 17 J. C. Dai, X. T. Wu, Z. Y. Fu, S. M. Hu, W. X. Du, C. P. Cui, L. M. Wu, H. H. Zhang and R. Q. Sun, *Chem. Commun.*, 2002, 12.
- 18 G. Guilera and J. W. Steed, *J. Supramol. Chem.*, 2001, **1**, 31.
- 19 K. Seki, *Chem. Commun.*, 2001, 1496.
- 20 G. A. Barclay and C. H. L. Kennard, *J. Chem. Soc.*, 1961, 5244.
- 21 B. Moulton, J. Lu and M. J. Zaworotko, *J. Am. Chem. Soc.*, 2001, **123**, 9224.
- 22 P. J. Nichols, C. L. Raston and J. W. Steed, *Chem. Commun.*, 2001, 1062.
- 23 J. F. Fernandez-Bertran, *Pure Appl. Chem.*, 1999, **71**, 581.
- 24 M. D. Hollingsworth and K. D. M. Harris, in *Comprehensive Supramolecular Chemistry*, ed. J. L. Atwood, J. E. D. Davies, D. D. MacNicol and F. Vögtle, Pergamon, Oxford, 1996, vol. 6, pp. 177–237.