

# A 3D metal-organic network, [Cu<sub>2</sub>(glutarate)<sub>2</sub>(4,4'-bipyridine)], that exhibits single-crystal to single-crystal dehydration and rehydration†

Beth Rather and Michael J. Zaworotko\*

Department of Chemistry, University of South Florida, 4202 E Fowler Ave (SCA400), Tampa, FL 33620, USA. E-mail: xtal@usf.edu

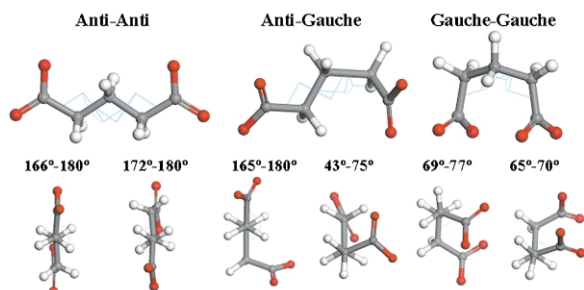
Received (in Columbia, MO, USA) 30th January 2003, Accepted 19th February 2003

First published as an Advance Article on the web 3rd March 2003

**The reaction of Cu(NO<sub>3</sub>)<sub>2</sub>, glutaric acid and 4,4'-bipyridine in water affords a novel 3D coordination polymer which exhibits reversible desorption and adsorption of water molecules with retention of single crystallinity.**

Crystal engineering of metal-organic networks *via* self-assembly of metal ions and multifunctional ligands has attracted considerable attention because of the structural diversity present in such compounds which in turn facilitates systematic evaluation of structure property relationships.<sup>1,2</sup> Rigid ligands afford multiple supramolecular isomers for a given set of molecular components and a range of reaction conditions. However, use of flexible ligands should in principle offer a greater degree of structural diversity and there has been interest in such ligands for magnetic<sup>3–5</sup> or porous<sup>6–8</sup> materials. The glutarate anion is a readily available bifunctional ligand which is a flexible analogue of benzene-1,3-dicarboxylate, a ligand which can sustain discrete<sup>9,10</sup> and infinite<sup>11,12</sup> structures with nanoscale features. As revealed by Figure 1, glutarate anions possess a three carbon aliphatic backbone and there exist three likely conformations: *anti-anti*, *anti-gauche* and *gauche-gauche*. A CSD survey‡ revealed that the *anti-anti* and *anti-gauche* conformations tend to be favoured in coordination compounds. Bimetallic building units are ubiquitous in coordination chemistry<sup>13,14</sup> and we report herein the use of glutarate anions to sustain 2D sheets which can be pillared to generate the modular 3D nets [Cu<sub>2</sub>(glutarate)<sub>2</sub>L·xH<sub>2</sub>O]<sub>n</sub>, L = 4,4'-bipyridine (bipy), **1** (*x* = 3, **1a**, *x* = 0, **1b**, *x* = 3, **1c**) and L = 1,2-bis(4-pyridyl)ethane (bipyethane), **2** (*x* = 5, **2a**, *x* = 2, **2b**, *x* = 5, **2c**).§

**1a** consists of corrugated sheets of metal-glutarate moieties parallel to [100] (Fig. 2a) that are pillared *via* axial coordination of canted bipy ligands (Fig. 2b).¶ The resulting 3D network contains channels with effective dimensions of *ca.* 2.9 Å × 4.0 Å occupied by 2 crystallographically independent water molecules that form hydrogen bonded chains (*d*(O···O) = 2.81 and 2.97 Å) which interact with the methylene groups of the glutarate ligands (*d*(C···O) = 3.66–3.88 Å), Fig. 2c. A similar

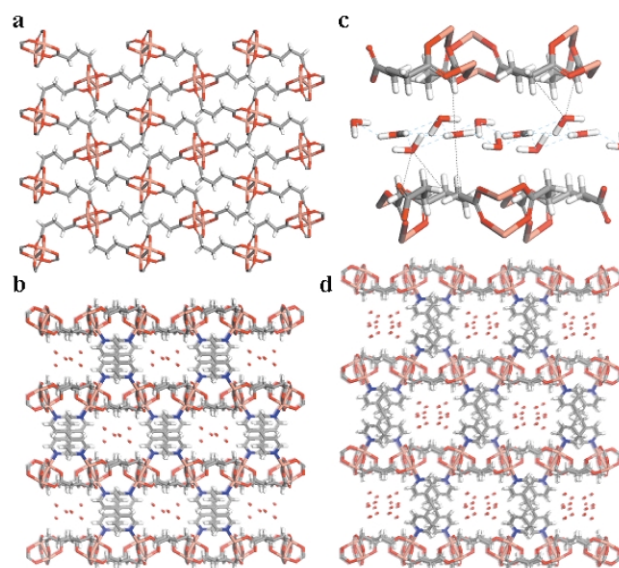


**Fig. 1** The three possible conformations of glutarate alkyl chains and the corresponding projections down the Csp<sup>3</sup>–Csp<sup>3</sup> bonds with the range of torsion angles observed in the structures deposited in the CSD.

† Electronic supplementary information (ESI) available: experimental details, IR, TGA and XRPD of all compounds. See <http://www.rsc.org/suppdata/cc/b3/b301219k/>.

1D polymer of ordered water molecules was observed in a 3D hydrogen bonded ionic network that contains channels with the requisite size and environment. However, this structure does not survive desorption of the guest water molecules.<sup>15</sup> The glutarate ligands adopt the *anti-gauche* mode with torsion angles of 175° and 57° and the orientation of the carboxylate moiety with respect to the backbone generates dihedral angles of *ca.* 43° and 37° (Fig. 2a). The bridging bipy ligands connect the sheets in a criss-cross pattern that facilitates π–π face-to-face interactions (*d*(C···C) = 3.38 to 3.58 Å). Such a criss-crossed network possesses a topology related to the α-polonium net, a topology that has also been generated *via* M(CN)<sub>2</sub> sheets linked by pyrazine ligands.<sup>16</sup>

Thermogravimetric analysis of **1a** revealed that it is stable up to 300 °C with loss of *ca.* 8.5% mass between 60 and 120 °C, consistent with desorption of water molecules (calculated 9%). Interestingly, when heated at 150 °C for 3 days, crystals of **1a** were observed to remain crystalline and the crystal structure of the apohost, **1b**, confirmed that removal of guest molecules does not influence the 3D network. IR and thermal analysis were used to confirm that **1b** can adsorb water molecules under various conditions. For example, under an atmosphere of *ca.* 60% water vapour, a powdered sample of **1b** adsorbs water and reaches saturation after *ca.* 1 hour whereas single crystals of **1b** take *ca.* 15 hours to reach saturation. The X-ray crystal structure of such a sample, **1c**, revealed it to be unchanged with respect to **1a**. Attempts to incorporate other guest molecules during crystallization of **1** were unsuccessful (methanol, hexanes, mixtures of water: methanol (1:1, 1:5 and 1:10), benzene, nitrobenzene or anisole) and resulted in the formation of **1a**. Attempts to adsorb other guests by direct contact with **1b** were also unsuccessful (gas chromatographic experiments and infra-



**Fig. 2** Detailed view of the Cu<sub>2</sub>(glutarate)<sub>2</sub> sheets down [100] in **1** and **2** (a), crystal structures of the 3D nets of **1a** (b) and **2a** (d) down [001] and view of a channel of water molecules in **1a** (c).

red spectra indicated that methanol, ethanol, acetonitrile or n-hexane are not adsorbed under anhydrous conditions).†

The crystal structure of **2** is similar to that of **1** with differences due to the presence of the additional ethylene moieties (Fig. 2d).¶ **2a** contains channels with effective dimensions of *ca.* 3.5 Å × 4.4 Å occupied by 5 independent water molecules. The glutarate backbone possesses an *anti-gauche* conformation with torsion angles of 173° and 60° and a relative orientation of the carboxylate moieties with respect to the backbone of *ca.* 39° and 33°. The bipyethane ligands are canted and criss-cross between the dicopper tetraglutarate sheets. They engage in edge-to-face aromatic stacking interactions ( $d(\text{C}\cdots\text{C}) = 3.54$  to  $4.11$  Å) reinforced by  $\text{CH}_2\cdots\text{CH}_2$  interactions ( $d(\text{C}\cdots\text{C}) = 3.76$  Å) and  $\text{CH}\cdots\pi$  interactions ( $d(\text{C}\cdots\text{C}) = 3.85$  to  $3.89$  Å). **2a** was observed to desorb its guest water molecules following exposure to the atmosphere for *ca.* 1 hour.† The resulting apohost **2b** retained single crystallinity and was observed to adsorb water molecules *via* immersion in water. The resulting crystals, **2c**, were confirmed to be isostructural to **2a**. The slightly larger channels in **2a** would therefore appear to result in lower affinity for water molecules when compared to **1a**, which readily adsorbs from gas as well as liquid contact.

In conclusion, compound **1** represents a novel porous network that was generated in water and acts as a highly selective adsorbent for water molecules. That **1** retains single crystallinity might be attributed to the stability of the 2D sheets and the ability of the cross-linking ligands to engage in stacking interactions. Compounds **1** and **2** are new members of a relatively small group of molecular materials that reversibly desorb guest molecules with retention of single crystallinity.<sup>6,17–27</sup> In the context of porosity, it has been suggested that the generation of porous materials that retain crystallinity during reversible desorption and exhibit high selectivity towards guest molecules might be relevant as adsorbents for separations and sensing devices.<sup>28</sup>

We gratefully acknowledge the financial support of NSF (DMR 0101641) and we thank A. Kabir for his help with the GC experiments.

## Notes and references

† A conformational analysis of crystal structures containing the glutarate fragment and metals was conducted using the CSD (CCDC 2002 Conquest Version 1.5) and revealed that out of 30 non-equivalent glutarate ligands, 12 exhibit the *anti-anti* mode, 13 the *anti-gauche* mode and 5 the *gauche-gauche* conformation.

§ **1** and **2** form *via* reaction of  $\text{Cu}(\text{NO}_3)_2 \cdot 2.5\text{H}_2\text{O}$  (1.165 g, 5.009 mmol), glutaric acid (1.982 g, 15.00 mmol) and bipy (0.390 g, 2.50 mmol) or bipyethane (0.460 g, 2.52 mmol) in water. The initial precipitates so formed were characterized by single crystal unit cell determination (dark blue crystals obtained during the synthesis of **2**) and X-ray powder diffraction (crystals obtained during the synthesis of **1** and **2**) were found to be the known  $\text{M}(4,4'\text{-bipyridine})_{1.5}$  ladder<sup>29</sup> and bilayer<sup>30</sup> compounds, respectively. These initial products converted to green crystals of **1** and **2** by heating the reaction mixtures at *ca.* 80 °C for several hours. Yields of 1.392 g (2.353 mmol) and 1.615 g (2.479 mmol) for **1** and **2**, respectively, were obtained; excess glutaric acid was recycled by filtration of the supernatant solution and recrystallisation.

¶ *Crystallographic data:* Intensity data for **1a**, **1b**, **1c** and **2a**, **2b**, **2c** were collected at 100 K on a Bruker SMART-APEX diffractometer using  $\text{Mo}_{\text{K}\alpha}$  radiation ( $\lambda = 0.7107$  Å). Lorentz and polarization corrections were applied and diffracted data were also corrected for absorption using the SADABS program. Structures were solved by direct methods and Fourier techniques. Structure solution and refinement were based on  $|F|^2$ . All non-hydrogen atoms were refined with anisotropic displacement parameters except for the oxygen atoms of solvent in **2c**. The H atoms of the C–H groups were fixed in calculated positions. The two molecules of water in the asymmetric unit of **1a** lie at general and special positions, thereby affording the reported 1:3 stoichiometry. The water molecules of **1c** were disordered over several positions and were refined with fixed site occupation factors (sof). In **2**, the oxygen atoms of the solvent were disordered over several general positions (8 for **2a**, 5 for **2b** and 9 for **2c**) and refined with fixed sof for total occupancies of 2.5, 1 and 2.5 respectively. These correspond to 1:5, 1:2

and 1:5 stoichiometries since the tetracarboxylate moieties lie around special positions. All crystallographic calculations were conducted with SHELXTL 6.10.

*Crystal data for 1a:* Monoclinic,  $C2/c$ ,  $a = 21.191(2)$ ,  $b = 13.190(2)$ ,  $c = 8.521(2)$  Å,  $\beta = 100.314(2)^\circ$ , volume =  $2343.3(4)$  Å<sup>3</sup>,  $Z = 4$ ,  $D_c = 1.694$  g cm<sup>-3</sup>,  $\mu = 1.878$  mm<sup>-1</sup>,  $F(000) = 1224$ ,  $2\theta_{\text{max}} = 54.96^\circ$  ( $-19 \leq h \leq 27$ ,  $-17 \leq k \leq 14$ ,  $-11 \leq l \leq 10$ ). Final residuals (for 159 parameters) were  $R1 = 0.0376$  for 2670 reflections with  $I > 2\sigma(I)$ , and  $R1 = 0.0452$ ,  $wR2 = 0.0963$ ,  $\text{Goof} = 1.046$  for all 7149 data. Residual electron density was 0.946 and  $-0.575$  e.Å<sup>-3</sup>. **1b** and **1c** exhibit similar structural data as **1a** except for the absence of water (sof 0.03–0.07 for residues, residual electron density = 0.533 and  $-0.416$  e.Å<sup>-3</sup>) in **1b** and the presence of disordered oxygen atoms of the solvent **1c**.

*Crystal data for 2a:* Monoclinic,  $C2/c$ ,  $a = 24.238(2)$ ,  $b = 13.053(2)$ ,  $c = 8.631(2)$  Å,  $\beta = 91.473(2)^\circ$ , volume =  $2729.8(5)$  Å<sup>3</sup>,  $Z = 4$ ,  $D_c = 1.585$  g cm<sup>-3</sup>,  $\mu = 1.625$  mm<sup>-1</sup>,  $F(000) = 1328$ ,  $2\theta_{\text{max}} = 54.96^\circ$  ( $-30 \leq h \leq 30$ ,  $-16 \leq k \leq 11$ ,  $-10 \leq l \leq 11$ ). Final residuals (for 222 parameters) were  $R1 = 0.0410$  for 3082 reflections with  $I > 2\sigma(I)$ , and  $R1 = 0.0484$ ,  $wR2 = 0.0972$ ,  $\text{Goof} = 1.049$  for all 8295 data. Residual electron density was 0.594 and  $-0.417$  e.Å<sup>-3</sup>. **2b** and **2c** exhibit similar crystal data as **2a** except for the presence of 2 disordered oxygen atoms in **2b**.

CCDC reference numbers 203221–203226. See <http://www.rsc.org/suppdata/cc/b3/b301219k/> for crystallographic data in CIF format.

- 1 B. Moulton and M. J. Zaworotko, *Chem. Rev.*, 2001, **101**, 1629.
- 2 O. M. Yaghi, H. L. Li, C. Davis, D. Richardson and T. L. Groy, *Acc. Chem. Res.*, 1998, **31**, 474.
- 3 E. G. Bakalbassis, M. Korabik, A. Michailides, J. Mrozinski, C. Raptopoulou, S. Skoulika, A. Terzis and D. Tsaousis, *Dalton Trans.*, 2001, 850.
- 4 C. Hornick, P. Rabu and M. Drillon, *Polyhedron*, 2000, **19**, 259.
- 5 Y. Kim and D. P. Jung, *Inorg. Chem.*, 2000, **39**, 1470.
- 6 M. P. Suh, J. W. Ko and H. J. Choi, *J. Am. Chem. Soc.*, 2002, **124**, 10976.
- 7 P. M. Forster and A. K. Cheetham, *Angew. Chem., Int. Ed.*, 2002, **41**, 457.
- 8 R. Kitaura, K. Fujimoto, S. Noro, M. Kondo and S. Kitagawa, *Angew. Chem., Int. Ed.*, 2002, **41**, 133.
- 9 B. Moulton, J. Lu, A. Mondal and M. J. Zaworotko, *Chem. Commun.*, 2001, 863.
- 10 M. Eddaoudi, J. Kim, J. B. Wachter, H. K. Chae, M. O'keeffe and O. M. Yaghi, *J. Am. Chem. Soc.*, 2001, **123**, 4368.
- 11 B. Moulton, J. J. Lu, R. Hajndl, S. Hariharan and M. J. Zaworotko, *Angew. Chem., Int. Ed.*, 2002, **41**, 2821.
- 12 S. S. Y. Chui, S. M. F. Lo, J. P. H. Charmant, A. G. Orpen and I. D. Williams, *Science*, 1999, **283**, 1148.
- 13 F. A. Cotton, C. Lin and C. A. Murillo, *Acc. Chem. Res.*, 2001, **34**, 759.
- 14 M. Eddaoudi, D. B. Moler, H. L. Li, B. L. Chen, T. M. Reineke, M. O'keeffe and O. M. Yaghi, *Acc. Chem. Res.*, 2001, **34**, 319.
- 15 S. Subramanian and M. J. Zaworotko, *Chem. Commun.*, 1993, 952.
- 16 B. F. Abrahams, M. J. Hardie, B. F. Hoskins, R. Robson and E. E. Sutherland, *Chem. Commun.*, 1994, 1049.
- 17 G. J. Halder, C. J. Kepert, B. Moubaraki, K. S. Murray and J. D. Cashion, *Science*, 2002, **298**, 1762.
- 18 E. J. Cussen, J. B. Claridge, M. J. Rosseinsky and C. J. Kepert, *J. Am. Chem. Soc.*, 2002, **124**, 9574.
- 19 S. Noro, R. Kitaura, M. Kondo, S. Kitagawa, T. Ishii, H. Matsuzaka and M. Yamashita, *J. Am. Chem. Soc.*, 2002, **124**, 2568.
- 20 K. Biradha and M. Fujita, *Angew. Chem., Int. Ed.*, 2002, **41**, 3392.
- 21 J. Y. Lu and A. M. Babb, *Chem. Commun.*, 2002, 1340.
- 22 D. V. Soldatov, E. V. Grachev and J. A. Ripmeester, *Crystal Growth & Design*, 2002, **2**, 401.
- 23 T. K. Maji, P. S. Mukherjee, G. Mostafa, E. Zangrando and N. R. Chaudhuri, *Chem. Commun.*, 2001, 1368.
- 24 Y. H. Liu, H. L. Tsai, Y. L. Lu, Y. S. Wen, J. C. Wang and K. L. Li, *Inorg. Chem.*, 2001, **40**, 6426.
- 25 H. Li, M. Eddaoudi, M. O'keeffe and O. M. Yaghi, *Nature*, 1999, **402**, 276.
- 26 C. J. Kepert and M. J. Rosseinsky, *Chem. Commun.*, 1999, 375.
- 27 C. J. Kepert, D. Heseck, P. D. Beer and M. J. Rosseinsky, *Angew. Chem., Int. Ed.*, 1998, **37**, 3158.
- 28 S. M. Kuznicki, V. A. Bell, S. Nair, H. W. Hillhouse, R. M. Jacobinas, C. M. Braunbarth, B. H. Toby and M. Tsapatsis, *Nature*, 2001, **412**, 720.
- 29 P. Losier and M. J. Zaworotko, *Angew. Chem., Int. Ed. Engl.*, 1996, **35**, 2779.
- 30 T. L. Hennigar, D. C. Macquarrie, P. Losier, R. D. Rogers and M. J. Zaworotko, *Angew. Chem., Int. Ed. Engl.*, 1997, **36**, 972.