NJC

Letter

A novel layered and pillared topology in a 3D open framework: synthesis, crystal structure and magnetic properties†

Saugata Sain,[a] Tapas Kumar Maji,[a] Golam Mostafa,[b] Tian-Huey Lu[b] and Nirmalendu Ray Chaudhuri*[a]

[a] *Department of Inorganic Chemistry, Indian Association for the Cultivation of Science, Jadavpur, Kolkata 700 032, India. E-mail: icnrc@mahendra.iacs.res.in; Fax: 91-33-473 2805*
[b] *Department of Physics, National Tsing Hua University, Hsinchu 300, R. O. C.*

Received (in Montpellier, France) 30th August 2002, Accepted 5th November 2002
First published as an Advance Article on the web 12th December 2002

A one pot reaction of $Cu(NO_3)_2$, malonate dianion (mal) and 1,2-bis(4-pyridyl)ethane (bpe) leads to a novel 3D open framework, $[\{Cu_3(mal)_2(bpe)_3(H_2O)_2\}(NO_3)_2(H_2O)_2]_n$ (1), composed of Cu–malonate layers pillared by bidentate bpe ligands encapsulating NO_3^- and water molecules in bidirectional intersecting channels; the framework's secondary building unit comprises unprecedented two hexa- and four penta-coordinate copper(II) nodes which are 6- and 4-connecting, respectively, and the magnetic properties of the complex show the highest overall ferromagnetic interaction ($J = 22$ cm^{-1}) of the previously reported *syn–anti* carboxylate bridged complexes.

The success of the strategy for the synthesis of porous and large channel with accessible metal sites containing materials with specific properties using "node and spacer" is rare in the literature.[1–3] However, the selectivity, especially in separation, catalysis and molecular recognition, for the reported materials is still poor, limiting their practical applications. One of the possible strategies to improve the selectivity and reactivity is to synthesize inorganic–organic hybrid frameworks with different metal coordination environments, as has been observed in some metalloenzymes.[4] In contrast to rigid organic spacers, a judicious use of flexible ligands may be useful in synthesizing such environments, and in mimicking the role of flexible amino acids (selectivity) in enzymes. Therefore, synthesis of this kind of material can provide us with not only the know-how about the formation of stable open frameworks purely based on flexible ligands with different nodal geometry, but also the properties that result in reversible guest exchange and, possibly, higher selective catalytic activity. Though there are several interesting reports of molecular architectures based on mixed rigid and flexible ligands,[5] reports on the above-mentioned type of frameworks have been absent largely, apparently because these polymeric structures are difficult to control. Herein, we report the synthesis, structure and magnetic properties of $[\{Cu_3(mal)_2(bpe)_3(H_2O)_2\}(NO_3)_2(H_2O)_2]_n$ (**1**) [mal = malonate dianion and bpe = 1,2-bis(4-pyridyl)-ethane] and the versatility and the flexibility of malonate and bpe ligands towards Cu(II).

The structure determination reveals that the 3D open-framework of **1** consists of $[\{Cu_3(malonate)_2(H_2O)_2\}]_n$ layers and bpe pillars. In the layers, each mal dianion chelates a Cu2 centre, with the remaining two oxygen atoms bridging to two adjacent Cu1 atoms, thus forming an infinite covalently bonded cationic layer perpendicular to [100]. The coordinated water oxygen lies in the plane of this layer. It should be noted that most M–(mal) form layered structures.[6] The layer structure features a brick-wall network as shown in Fig. 1, in which every six metal centres are interconnected to form a rhombic ring in the ***bc***-plane. Finally, adjacent layers are linked by the bpe ligand as molecular pillars to furnish a 3D-open framework with the shortest 6-gon circuit consisting of four 4-connecting Cu1 centres and two 6-connecting Cu2 centres. The most prominent feature of complex **1** is the presence of a bi-directional system of intersecting channels with dimensions of 4.1×8.5 Å and 4.5×6.5 Å (atom to atom) along [100] (Fig. 2) and [010] (Fig. 3) respectively. The nitrate anions compensate for the cationic charge of the layers and reside together with the water molecules in the interlayer space. Both of them occupy the channels in the [100] direction but nitrate ions are eclipsed by pyridines of the bpe ligand in the [001] direction. The guest moieties establish O–H···O hydrogen bonds [$O\cdots O_{av} = 2.817$ Å] among themselves but not with the framework. There are two crystallographically independent Cu(II) atoms. Cu1 is coordinated by two oxygens from two malonate groups, one oxygen from a water molecule in the layer and two pyridyl nitrogen atoms from two μ-bpe ligands in a distorted

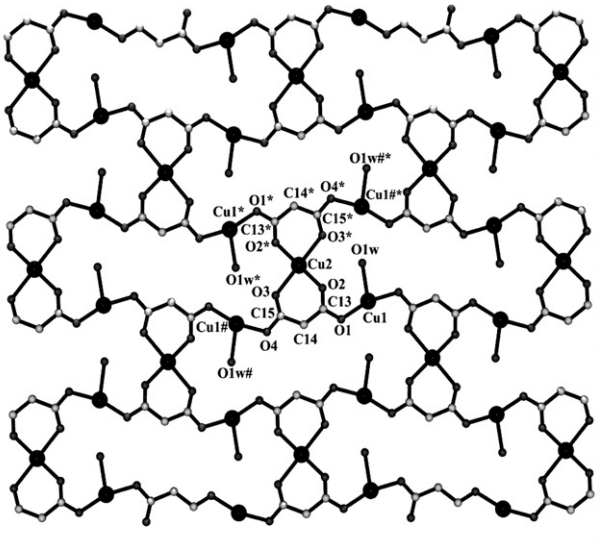

Fig. 1 Brick-walled shaped view of the $[\{Cu_3(malonate)_2(H_2O)_2\}]_n$ layer (symmetry code: * = $1-x$, $1-y$, $2-z$; # = $1-x$, $1/2+y$, $1.5-z$; #* = x, $1/2-y$, $1/2+z$).

† Electronic supplementary information (ESI) available: Fig. S1: showing the brick-walled shaped view of the $[\{Cu_3(malonate)_2(H_2O)_2\}]_n$ layer; Fig. S2: space-filled diagram showing channels viewed down *x*-axis. See http://www.rsc.org/suppdata/nj/b2/b208650f/

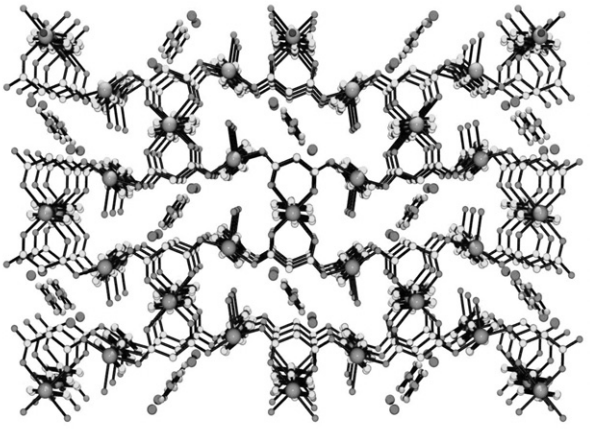

Fig. 2 View of complex **1** showing the bi-directional intersecting channels with dimensions of 4.1×8.5 Å and 4.5×6.5 Å along the [100] direction.

square pyramidal environment. Cu2 is located at an inversion centre and octahedrally coordinated by four oxygen atoms from two chelated malonate ligands and two nitrogens from two μ-bpe ligands. The Cu–O(mal) and Cu–N(bpe) bond lengths are in the ranges 1.951(2)–2.265(2) Å and 1.869–2.325 Å respectively and the Cu1–O1w bond length is 2.251(2) Å. The bond angles between the *cis* ligands and the Cu1 centres range from 83.86(9)–112.70(9)°, while the corresponding angles for Cu2 range from 87.11(10)–92.89(10)°. The malonate ligand adopts a planar conformation. The two carboxylate bridges (Cu1–O1–C13–O2–Cu2 and Cu2–O3–C15–O4–Cu1$^{\#}$) exhibit *syn–anti* conformations and the dihedral angle between these two planes is 2.3°. The two intralayer copper–copper distances are 4.755(1) (Cu1···Cu2) and 5.154(1) Å (Cu1$^{\#}$···Cu2), whereas the Cu–bpe–Cu distance is 13.389(1) Å.

Magnetic studies of the title complex were performed using a SQUID magnetometer on a crystalline sample in the temperature range 300–2 K in an applied field of 0.5 T. The experimental magnetic data indicate global ferromagnetic coupling

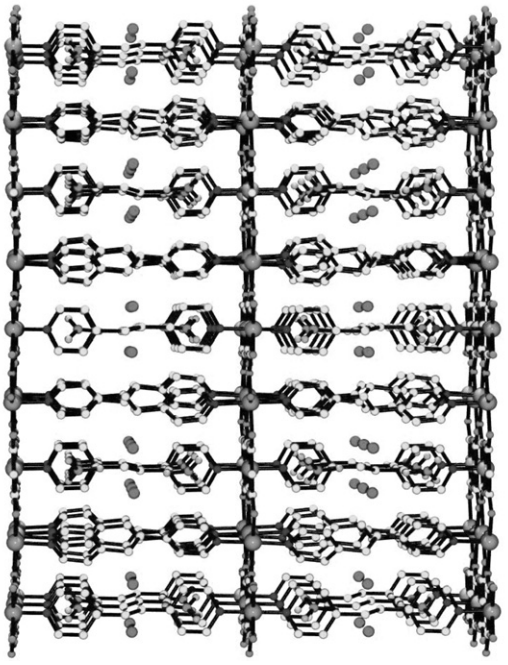

Fig. 3 View of complex **1** along the [010] direction showing π–π interactions.

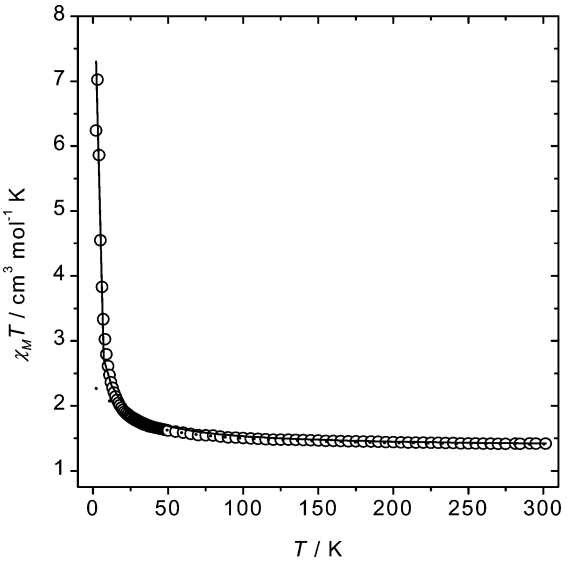

Fig. 4 $\chi_M T$ *vs.* T plot for complex **1**. The solid line corresponds to the best fit obtained (the dotted line corresponds to a simulation with $J = 22$ cm^{-1} and $g = 2.2$).

(Fig. 4). Two kinds of magnetic pathways can be considered, *i.e.* intralayer and interlayer. The magnetic coupling between layers may be considered nil, owing to the large distance between Cu(II) ions (13.4 Å) through the bridging ligand, without any important magnetic pathway. Thus the coupling is considered only within each layer. In each layer there is only one important magnetic pathway, *i.e.* Cu1–O1–C13–O2–Cu2–O2*–C13*–O1*–Cu1* (Fig. 1). This pathway is through carboxylate in *syn–anti* configuration and this configuration gives a small ferromagnetic coupling.[6–8] On the other hand, the possible Cu1–O1–C13–C14–C15–O4–Cu1$^{\#}$ pathway (Fig. 1) is very weak as it is a coupling through three carbon atoms, and thus almost nil. The Cu2–O3 distance is the long distance (Jahn–Teller distortion in Cu2 = 2.265 Å) and the possible coupling Cu1$^{\#}$–O4–C15–O3–Cu2 (Fig. 1) is small and, likely, ferromagnetic, owing to the orthogonality of the orbitals ($d_{x^2-y^2}$ of Cu1 and d_{z^2} of Cu2). Thus, the "quasi-isolated" magnetic entity is a Cu(II) trinuclear complex (Cu1–Cu2–Cu1). The fit was made choosing all experimental points and cutting the $\chi_M T$ points at 15, 20, 30 and 40 K, because at low temperatures the curve seems to indicate cooperative phenomena. Effectively, the $\chi_M T$ value for three unpaired electrons (ferromagnetic coupling) would be close to 2 cm^3 mol^{-1} K (assuming $g > 2.00$, typical for Cu(II) ions). The experimental datum is 7 cm^3 mol^{-1} K, higher than that expected. For the fit, the formula given by Kahn[9] was selected, considering only a g value (to avoid over-parametrization with two g values very similar to each other). This formula was modified according to the molecular-field approximation (to interpret the intermolecular interactions), by adding a J' term.[9] Cutting at 40 K the best fit gives: $J = 21.3$ cm^{-1}, $g = 2.2$ and $R = 1.0 \times 10^{-5}$; for $T = 30$ K, $J = 21.1$ cm^{-1}, $g = 2.21$ and $R = 1.0 \times 10^{-5}$; for $T = 20$ K, $J = 22.3$ cm^{-1}, $g = 2.20$ and $R = 1.0 \times 10^{-4}$; for $T = 15$ K, $J = 23.9$ cm^{-1}, $g = 2.2$ and $R = 7.3 \times 10^{-4}$. Considering all points and introducing in the formula the J' parameter, the best fit gives: $J = 25.3$ cm^{-1}; $J' = 0.77$ cm^{-1}; $g = 2.2$ and $R = 1.9 \times 10^{-3}$. Thus, the consideration of all points gives a similar ferromagnetic J value, small "intermolecular" ferromagnetic interactions (J') but a worse R factor. In fact, the best R factor is obtained when the $\chi_M T$ points are cut at 40 or 30 K. All these features clearly indicate that the hypothesis of only a trinuclear system for the fit is not perfectly valid. The omission of the other possible interactions (mentioned above) affects the fit at lower temperatures. A curve with the average J value 22 cm^{-1} and $g = 2.2$ was simulated

together with the experimental points, showing the clear separation in the low temperature region (Fig. 4). The value of J (*ca.* 20 cm^{-1}) is greater than those reported in the literature for similar *syn–anti* carboxylate bridges.[6,7] The short Cu–O(1,2) distances (1.960 and 1.975 Å) may be the origin of this ferromagnetic J value.

Thermogravimetric analysis of **1**, under a nitrogen flux, show that both the solvated and the coordinated water molecules are lost stepwise at ~50 and ~90 °C respectively and the dehydrated framework remains stable up to ~180 °C without any further weight loss. The dehydrated compound gets rehydrated on keeping it in water overnight. It is observed that the single crystallinity does not remain intact on elimination of channel water at ~50 °C. Since the catenation of polymeric frameworks can allow a certain flexibility of the architecture, it can potentially favour a solvent exchange process, investigation of this is in progress.

Experimental

An aqueous solution (5 mL) of disodium malonate (1 mmol, 0.148 g) was added dropwise to a methanolic solution (10 mL) of $Cu(NO_3)_3{\cdot}3H_2O$ (1 mmol, 0.241 g) producing a sky blue solution which was allowed to stir for 30 min; to this a methanolic solution (10 mL) of ligand bpe (1 mmol, 0.184 g) was added slowly. The resulting deep blue solution was refluxed for 4 h, cooled and filtered. The filtrate was kept in a $CaCl_2$ desiccator and after a week suitable deep blue single crystals for X-ray structure determination were obtained. These were collected, washed with isopropanol and dried (yield 80%). Anal. Found (calcd): C, 46.35 (46.38); H, 3.83 (3.86); N, 10.26 (10.30); Cu, 17.48 (17.53%).

Crystal data

$C_{42}H_{48}Cu_3N_8O_{18}$, $M = 1143.53$, monoclinic, space group $P21/c$ (No. 14), $a = 13.3890(14)$, $b = 16.3111(16)$, $c = 10.9990(11)$ Å, $\beta = 91.352(2)°$, $V = 2401.4(4)$ $Å^3$, $Z = 2$, $D_c = 1.582$ g cm^{-3}, μ(Mo-Kα) = 1.399 mm^{-1}, $T = 293$ K, λ(Mo-Kα) = 0.71073 Å, θ min–max = 1.5–28.3°, total data = 14 940, unique data 5727, $R_{int} = 0.060$, observed data [$I > 2\sigma(I)$] = 3109, $R = 0.0479$, $wR = 0.1110$. The bpe ligand on Cu2 is disordered over nearly perpendicular orientations with 65:35 occupancy ratio.

CCDC reference number 183452. See http://www.rsc.org/suppdata/nj/b2/b208650f/ for crystallographic data in CIF or other electronic format.

Acknowledgements

The authors wish to thank the Council of Scientific and Industrial Research, New Delhi, for financial support (granted to N. R. C.) and the National Science Council, ROC for financial support to T. H. L. and G. M. (grant no. NSC 90-2112-M-007-063 and NSC 90-2811-M-007-007).

References

1 (*a*) R. Robson, *J. Chem. Soc., Dalton Trans.*, 2000, 3735; (*b*) B. Moulton and M. Zaworotko, *Chem. Rev.*, 2001, **101**, 1629 and references therein; (*c*) a web site has been set up by S. R. Batten containing known examples of interpenetrating nets: http://web.chem.monash.edu.au/Department/Staff/Batten/intptn.htm.
2 (*a*) O. M. Yaghi, C. E. Davis, G. Li and H. Li, *J. Am. Chem. Soc.*, 1997, **119**, 2861; (*b*) T. K. Maji, P. S. Mukherjee, G. Mostafa, E. Zangrando and N. Ray Chaudhuri, *Chem. Commun.*, 2001, 1368; (*c*) H. Li, M. Eddaoudi, M. Okeeffe and O. M. Yaghi, *Nature*, 1999, **402**, 276.
3 (*a*) P. J. Hagrman, D. Hagrman and J. Zubieta, *Angew. Chem., Int. Ed.*, 1999, **38**, 2638; (*b*) F. M. Tabellion, S. R. Seidel, A. M. Arif and P. J. Stang, *J. Am. Chem. Soc.*, 2001, **123**, 11 982; (*c*) L. Carlucci, G. Ciani, D. M. Prosperpio and S. Rizzato, *Chem. Commun.*, 2000, 1319.
4 (*a*) D. E. Vos, F. Thibault-Starzyk and P. A. Jacobs, *Angew. Chem., Int. Ed.*, 1994, **33**, 431; (*b*) A. L. Balch, M. Mazzanti, T. M. St. Claire and M. M. Olmstead, *Inorg. Chem.*, 1995, **34**, 2194; (*c*) A. L. Balch, M. Mazzanti and M. M. Olmstead, *J. Chem. Soc., Chem. Commun.*, 1994, 269.
5 (*a*) P. S. Mukherjee, S. Dalai, G. Mostafa, E. Zangrando, T. H. Lu, G. Rogez, T. Mallah and N. Ray Chaudhuri, *Chem. Commun.*, 2001, 1346; (*b*) Z. Shi, L. Zhang, S. Gao, G. Yang, J. Hua, L. Gao and S. Feng, *Inorg. Chem.*, 2000, **39**, 1990; (*c*) P. Lightfoot and A. Snedden, *J. Chem. Soc., Dalton Trans.*, 1999, 3549; (*d*) J. Li, H. Zeng, J. Chen, Q. Wang and X. Wu, *Chem. Commun.*, 1997, 1213; (*e*) J. Y. Lu, M. A. Lawandy and J. Li, *Inorg. Chem.*, 1999, **38**, 2695; (*f*) C. S. Hong and Y. Do, *Inorg. Chem.*, 1998, **37**, 4470; (*g*) C. S. Hong, S.-K. Son, Y. S. Lee, M.-J. Jun and Y. Do, *Inorg. Chem.*, 1999, **38**, 5602.
6 (*a*) C. Ruiz-Pérez, J. Sanchiz, M. Hernández-Molina, F. Lloret and M. Julve, *Inorg. Chem.*, 2000, **39**, 1363 and references therein; (*b*) C. Ruiz-Pérez, M. Hernández-Molina, P. Lorenzo-Luis, F. Lloret, J. Cano and M. Julve, *Inorg. Chem.*, 2000, **39**, 3845.
7 (*a*) E. Colacio, M. Ghazi, R. Kivekäs and J. M. Romero, *Inorg. Chem.*, 2000, **39**, 2882 and references therein; (*b*) Y. Rodríguez-Martín, C. Ruiz-Pérez, J. Sanchiz, F. Lloret and M. Julve, *Inorg. Chim. Acta*, 2001, **318**, 159.
8 A. Rodríguez-Fortea, P. Alemany, S. Alvarez and E. Ruiz, *Chem. Eur. J.*, 2001, **7**, 627.
9 O. Kahn, *Molecular Magnetism*, VCH Publishers, Weinheim, 1993.