Inorg. Chem. **2003**, *42*, 4792–4794

Ferromagnetic Ordering and Metamagnetism in Malonate Bridged 3D Diamond-like and Honeycomb-like Networks: $[Cu(mal)(DMF)]_n$ and $\{[Cu(mal)(0.5pyz)]\cdot H_2O\}_n$ (mal = Malonate Dianion, DMF = *N*,*N*-dimethylformamide, pyz = Pyrazine)

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Received March 31, 2003

Two three-dimensional (3D) malonate bridged networks, $[Cu(mal)(DMF)]_n$ (**1**) and $\{[Cu(mal)(0.5pyz)]\cdot H_2O\}_n$ (**2**), have been synthesized in H_2O–DMF solution. Compound **1** exhibits ferromagnetic ordering below 2.6 K (T_c), and **2** displays a metamagnetic behavior below 3.2 K (T_N).

The construction of multidimensional magnetic materials with magnetic ordering is one of the major challenges in magnetochemistry.[1] Malonate (dianion of malonic acid, hereafter noted mal), a flexible bridging ligand, is widely used for designing polynuclear metal complexes with interesting magnetic properties;[2−12] among them, mal bridged copper(II) complexes show a wide variety of molecular architectures.[7−12] However, no long-range magnetic ordering has been observed in any mal bridged coordination polymer, which may arise from the lack of strong three-dimensional magnetic coupling. Here we report two three-dimensional (3D) mal bridged copper(II) compounds, $[Cu(mal)(DMF)]_n$ (**1**) (DMF = *N*,*N*-dimethylformamide) and $\{[Cu(mal)(0.5pyz)]\cdot H_2O\}_n$ (**2**) (pyz = pyrazine); they represent the first two examples of magnetic ordering in mal-bridged complexes.

Compounds **1** and **2** were synthesized in H_2O-DMF solution (see Supporting Information). The X-ray single crystal structure analysis of **1** reveals a chiral 3D open framework.[13] As shown in Figure 1a, Cu1 exhibits a distorted CuO_5 square pyramidal geometry. The basal plane is well defined by O1, O3, O5, and O4b with Cu−O distances ranging from 1.927(3) to 1.972(3) Å; the apical position is occupied by O2a with Cu1−O2a = 2.243(3) Å. Cu1 is connected to Cu1b and Cu1d through carboxylate bridges in *syn*−*anti* configurations with Cu···Cu distances of 4.861 Å; the dihedral angle between the basal planes of adjacent copper atoms is 97.38°. Cu1 is also connected to other two Cu atoms (Cu1a and Cu1c) by carboxylate in *anti*−*anti* conformations with Cu···Cu separations of 6.099 Å; the dihedral angle between the basal planes of adjacent copper

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(13) Crystal data for **1**: [Cu(mal)(DMF)], $C_6H_9NO_5Cu$, $M_w = 238.69$, blue prism ($0.15 \times 0.12 \times 0.07$ mm^3), tetragonal, space group $P4_1$, $a = 8.40150(10)$ Å, $b = 8.40150(10)$ Å, $c = 12.0152(3)$ Å, $V = 848.10(3)$ Å^3, $Z = 2$, $D_c = 1.869$ g cm^{-3}, $\mu = 2.564$ cm^{-1}. A total of 1924 unique reflections were collected in the range $3.43° < \theta < 27.47°$, of which 1726 were considered observed [$I > 2\sigma(I)$] and used in the calculations. The refinement on F^2 converged to R1 = 0.0298 [$I > 2\sigma(I)$], wR2 = 0.0721 (all data). Crystal data for **2**: $[Cu(mal)(0.5pyz)]\cdot H_2O$, $C_5H_6NO_5Cu$, $M_w = 223.65$, blue block ($0.4 \times 0.3 \times 0.2$ mm^3), tetragonal, space group $P\bar{4}2_1c$, $a = 12.5982(18)$ Å, $b = 12.5982(18)$ Å, $c = 9.1950(18)$ Å, $V = 1459.4(4)$ Å^3, $Z = 8$, $D_c = 1.817$ g cm^{-3}, $\mu = 2.960$ cm^{-1}. A total of 963 unique reflections were collected in the range $2.29° < \theta < 27.48°$, of which 738 were considered observed [$I > 2\sigma(I)$] and used in the calculations. The refinement on F^2 converged to R1 = 0.0343 [$I > 2\sigma(I)$], wR2 = 0.0599 (all data). The data collections of **1** and **2** were made on a Nonius Kappa CCD with Mo Kα radiation ($\lambda = 0.71073$ Å) and a Rigaku R-Axis RIPID IP at 293 K. The structures were solved by direct methods and refined by a full-matrix least-squares technique based on F^2 using the SHELXL 97 program.

10.1021/ic034346x CCC: $25.00
Published on Web 06/25/2003

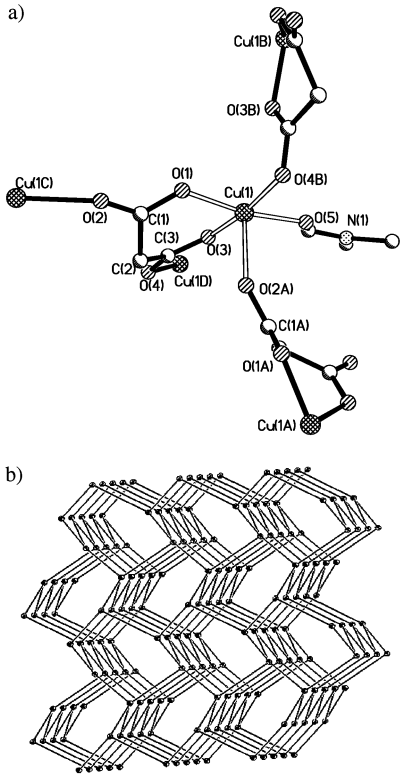
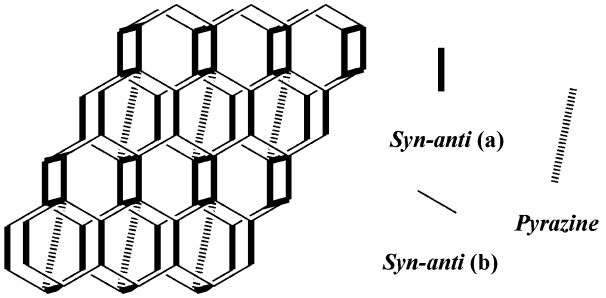


Figure 1. (a) ORTEP drawing of **1** (a = $-1 + y$, $1 - x$, $-0.25 + z$; b = $1 - y$, x, $0.25 + z$; c = $1 - y$, $1 + x$, $0.25 + z$; d = y, $1 - x$, $-0.25 + z$); hydrogen atoms are omitted for clarity. (b) Projection of **1** showing the diamond-like structure based on the topology of Cu−Cu connections.

Chart 1



atoms is 97.38°. Thus, each Cu atom is bridged to four other Cu atoms by mal, forming a 3D diamond-like network as shown in Figure 1b.

The crystal structure of **2** is the same as the one that was very recently reported while we were preparing this paper[13,14] (Figure S1). Nevertheless, its unique 3D topological architecture, shown in Chart 1, is worth mentioning. Each Cu atom is five-connected with four mal bridged Cu atoms and one pyz bridged Cu atom. If the pyz bridges are omitted, the four-connected network can be viewed as a metal-apex 3D honeycomb-like structure from *a* or *b* axis, which is quite rare compared with other 3D four-connected diamond or NbO coordination polymers,[15] and is reminiscent of the five-connected Cu net in ref 16. In each nonplanar honeycomb

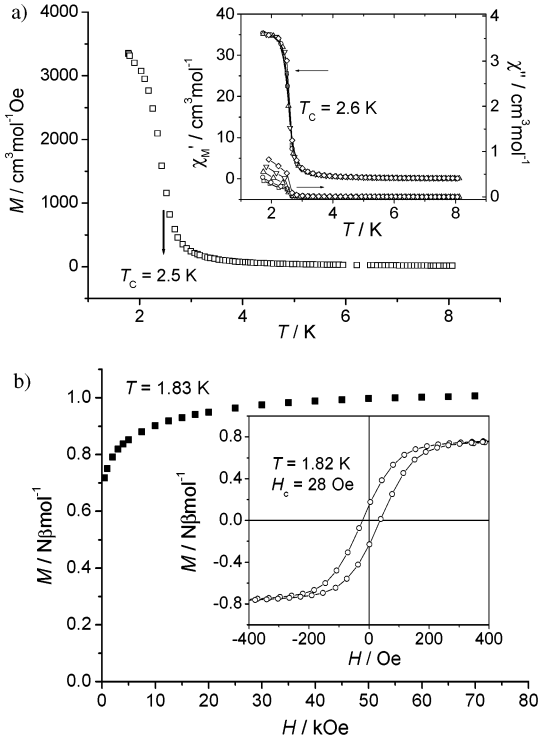


Figure 2. (a) Temperature dependence of magnetization of **1** measured at 200 Oe. Inset: real (χ_M') and imaginary (χ_M'') ac magnetic susceptibilities in zero applied dc field and an ac field of 2 Oe at different frequencies (199, 355, 633, 1111 Hz) for **1**. (b) Field dependence of magnetization for **1** at 1.83 K (inset: magnetic hysteresis loop at 1.82 K for **1**).

layer, each Cu atom is connected with one Cu in a *syn−anti* mode (a), and to two other Cu atoms in a *syn−anti* mode (b), with Cu···Cu distances of 4.847 and 5.279 Å, respectively. Half Cu atoms of adjacent two honeycomb layers are connected by mal in *syn−anti* mode (a), forming nonplanar quadrangles with each edge of 4.847 Å. The dihedral angles between the basal planes of adjacent copper atoms are 100.27° and 110.78°, for *syn-anti* mode (a) and *syn-anti* mode (b) connections, respectively. The Cu···Cu separation spaced by pyrazine bridge between the layers is 6.846 Å.

Temperature dependence of the magnetic susceptibility χ_M of **1** was measured in a magnetic field of 10 kOe (Figure S2). The $\chi_M T$ value at room temperature is 0.407 $cm^3\ mol^{-1}$ K, which increases smoothly upon cooling to ca. 20 K and then sharply reaches a maximum value of 1.2 $cm^3\ mol^{-1}$ K at ca. 2.4 K. The magnetic susceptibility in the range 20−300 K obeys the Curie−Weiss law with Curie constant C = 0.389(7) $cm^3\ mol^{-1}$ K, and a positive Weiss constant θ of 7.9(1) K, which indicates the presence of ferromagnetic coupling between Cu ions. The temperature dependence of the magnetization measured in a low field of 200 Oe shows an abrupt increase in M at ca. 2.4 K (Figure 2a), suggesting an onset of long-range ferromagnetic ordering. The ac magnetic susceptibility (inset of Figure 2a) confirms the appearance of magnetic ordering, and the critical temperature

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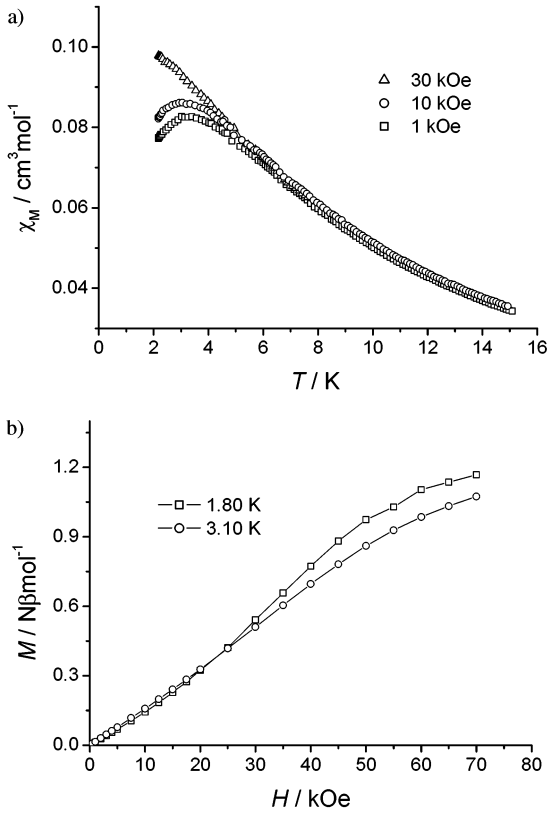

Figure 3. (a) Temperature dependence of χ measured in applied field at 1 kOe (□), 10 kOe (○) and 30 kOe (△) of **2**. (b) Magnetization versus H measured at 1.80 K (□) and 3.10 K (○) for **2**.

$T_c = 2.6$ K is determined by the peak of $d(\chi_M'T)/dT$ or the appearance of nonzero χ_M''. The weak frequency dependence of χ_M'' suggests a degree of glassy behavior. The magnetization at 1.83 K (Figure 2b) increases very rapidly in low field, as expected for a magnet, and reaches 1.0 Nβ/mol at 70 kOe, which corresponds to the theoretical saturation value for $S = {}^1/_2$, $g = 2.0$. Furthermore, a characteristic hysteresis loop is observed at 1.82 K with a remanent magnetization (M_r) of 0.18 Nβ/mol and a coercive field (H_c) around 28 Oe (inset of Figure 2b). These results are all indicative of an ordered ferromagnetic state.

The magnetic susceptibility of **2** in the range 70−200 K obeys the Curie−Weiss law with Curie constant $C = 0.372(1)$ cm^3 mol^{-1} K (Figure S3), the positive Weiss constant θ of 12 K suggests an overall ferromagnetic interaction between Cu ions, which is consistent with the reported data (5−300 K) in ref 14. However, the $\chi_M - T$ plot (Figure 3) shows a cusp around 3.3 K at a field lower than 30 kOe, which disappears at high field. This indicates an antiferromagnetic (AF) ground state, and a transition from AF to ferromagnetic state occurs when the applied field is large enough below 3.3 K. The temperature dependence of the ac magnetic susceptibility verifies the AF transition at ca. 3.2 K (T_N) and the absence of frequency dependence (Figure S4). The field dependence of magnetization at 1.80 K shown in Figure 3b shows a sigmoidal shape, characteristic of a metamagnetic behavior. The critical field for such a metamagnetic transition is approximately 30 kOe at 1.80 K (Figure S5).

In general, carboxylate bridges in *syn*−*anti* configuration promote ferromagnetic coupling, while those in *anti*−*anti* conformation favor antiferromagnetic coupling.[2−12] In the case of **1**, the Cu···Cu distance through *syn*−*anti* mal is shorter than that through *anti*−*anti* mal, suggesting that ferromagnetic interaction dominates over AF in **1**. When the malonate bridges extend to all three directions of space, long-range ferromagnetic ordering occurs. In the case of **2**, the overall magnetic behavior is ferromagnetic above 5 K as stated in ref 14 and is verified in this work. On the basis of the Cu···Cu distances and the dihedral angles between the basal planes of adjacent copper atoms through different bridges (*syn*−*anti*-a, *syn*−*anti*-b, pyz), the magnetic coupling through short *syn*−*anti*-a OCO should be ferromagnetic, and the strongest one, the coupling via long *syn*−*anti*-b OCO, might be weak ferro- or antiferromagnetic, while the magnetic interaction mediated by pyrazine bridges should be weak AF in character. At very low temperatures, the AF interactions must be considered. It is the weak AF coupling that yields a weak three-dimensional AF ordering state below 3.2 K. This weak AF interaction can be overcome by a large applied field to give a ferromagnetic state.

Acknowledgment. We acknowledge support from the National Science Fund for Distinguished Young Scholars (20125104, 20221101), National Key Project for Fundamental Research (G1998061305), and the Research Fund for the Doctoral Program of Higher Education (20010001020). This work is also supported by a CityU Strategic Research Grant (7001180).

Supporting Information Available: Synthesis of **1** and **2**, Figure S1 (OPTEP drawing and projection of **2**), Figure S2 (plot of $\chi_M T - T$ and $\chi_M^{-1} - T$ of **1**), Figure S3 (plot of $\chi_M T - T$ and $\chi_M^{-1} - T$ of **2**), Figure S4 (plot of χ_M', $\chi_M'' - T$ at different frequencies of **2**), Figure S5 (plot of χ_M', $\chi_M'' - H$ at 1.8 and 3 K of **2**), and X-ray crystallographic files for compounds **1** and **2** in CIF format. This material is available free of charge via the Internet at http://pubs.acs.org.

IC034346X