

Ferromagnetic ordering and metamagnetism in malonate bridged 3D diamond-like and honeycomb-like networks: $[\text{Cu}(\text{mal})(\text{DMF})]_n$ and $\{[\text{Cu}(\text{mal})(0.5\text{pyz})]\cdot\text{H}_2\text{O}\}_n$ (mal = malonate dianion, DMF = *N,N*-dimethylformamide, pyz = pyrazine)

Tian-Fu Liu,[†] Hao-Ling Sun,[†] Song Gao,^{*,†} Shi-Wei Zhang[†] and Tai-Chu Lau^{*,‡}

Supporting materials

Synthesis of 1 and 2:

Caution: Whilst no problems were encountered in the course of this work, perchlorate mixtures are potentially explosive and should therefore be handled with appropriate care.

Synthesis of the compound 1 $[\text{Cu}(\text{mal})(\text{DMF})]_n$. An aqueous solution of Malonic acid (0.104 g, 1 mmol, 10 ml) and sodium hydroxide (0.080 g, 2 mmol) was mixed with an aqueous solution of copper(II) perchlorate (0.372 g, 1 mmol, 10 ml). After 30 min stirred, 20 ml DMF (dimethyl formamide) was added to the mixture. Deep-blue prismatic single crystals were obtained after three days (Yield 53%). *Anal. Calc.* for $\text{C}_6\text{H}_9\text{NO}_5\text{Cu}$: C, 30.16; H, 3.77; N, 5.87. Found: C, 30.23; H, 3.68; N, 5.90%; IR (KBr cm^{-1}) 1657(m), 1618(m), 1588(m), 1566(s); 1442(m), 1368(m), 1356(m); 737(w), 701(w).

Compound 2 $[\text{Cu}(\text{mal})(0.5\text{pyz})]\cdot\text{H}_2\text{O}$: An aqueous solution of sodium malonate (1 mmol, 10 ml) was mixed with an aqueous solution of copper perchlorate (1 mmol, 10 ml). After 30 min stirred, a DMF solution of pyrazine (1 mmol, 5ml) was added to the mixture. Deep blue block single crystals were obtained after one months (Yield 43%). *Anal. Calc.* for $\text{C}_{10}\text{H}_{12}\text{N}_2\text{O}_{10}\text{Cu}_2$: C, 26.84; H, 2.68; N, 6.26%. Found: C, 26.74; H, 2.92; N, 6.08. IR (KBr cm^{-1}) 3599(w), 3444(w), 1582(vs), 1565(vs), 1457(w), 1428(w), 1376(m).

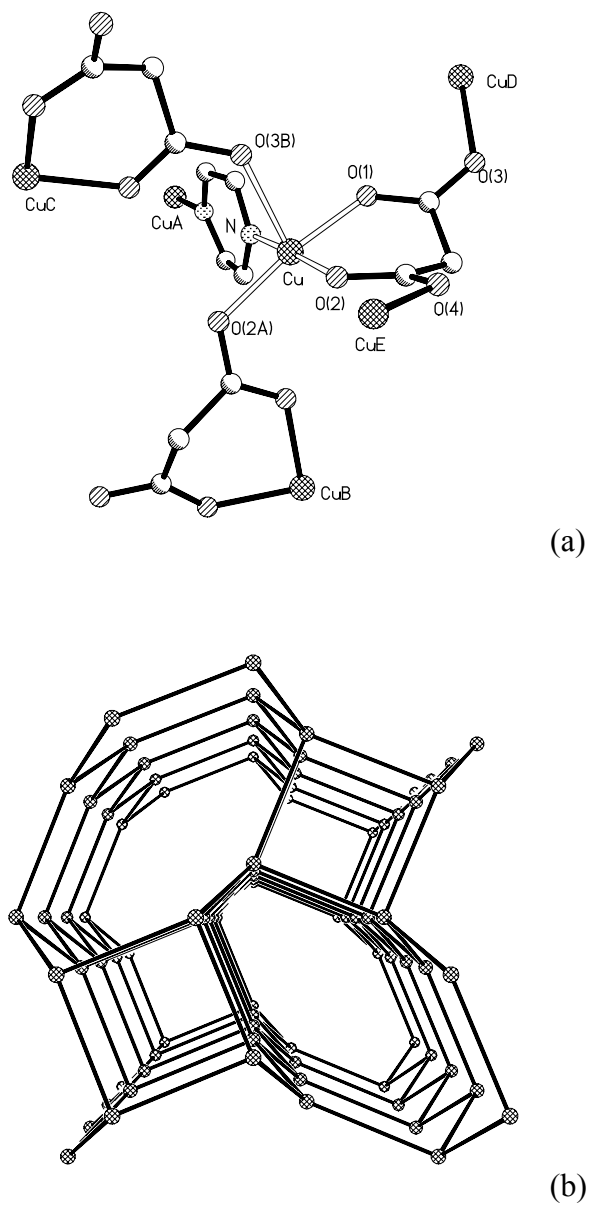


Figure S1. (a) An ORTEP drawing of **2** (Hydrogen atoms are omitted for clarity); (b) Projection of **2** from *c*-axis formed by copper ions.

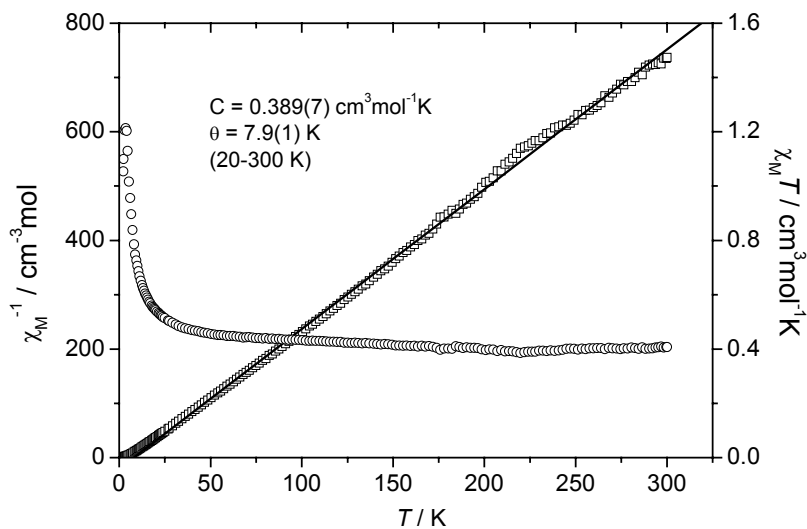


Figure S2. Temperature dependence of $\chi_M T$ and χ_M^{-1} of **1** at 10 kOe field. The solid line represents the best fit to the Curie-Weiss expression.

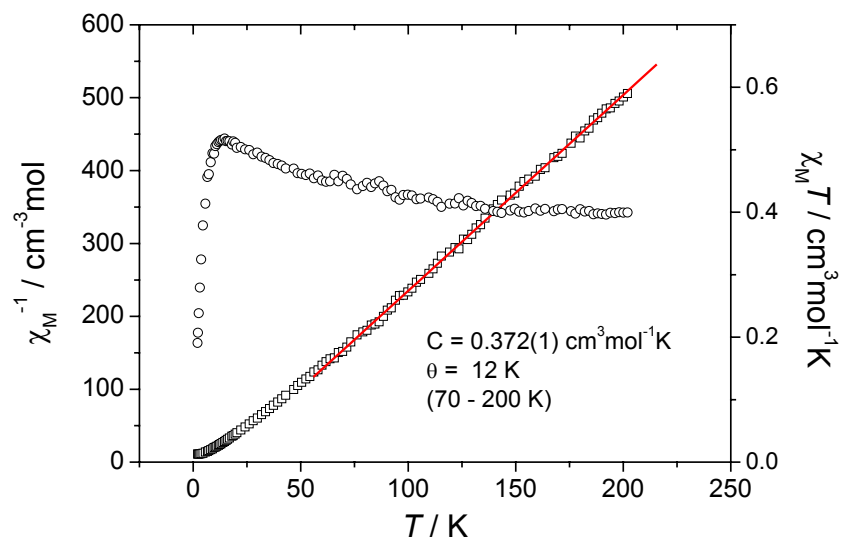


Figure S3. Temperature dependence of $\chi_M T$ and χ_M^{-1} of **2** at 20 kOe field. The solid line represents the best fit to the Curie-Weiss expression.

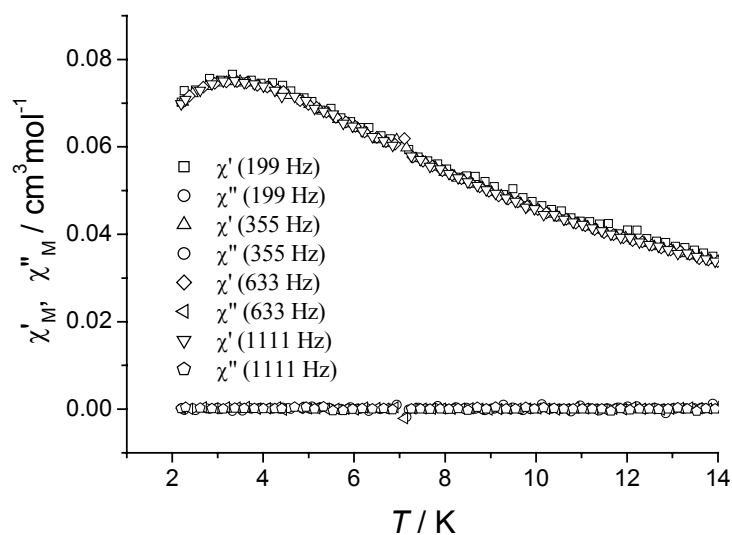


Figure S4. Real (χ_M') and imaginary (χ_M'') *ac* magnetic susceptibilities as a function of temperature in zero applied *dc* field and an *ac* field of 2 Oe at different frequencies (199, 355, 633, 1111 Hz) for **2**.

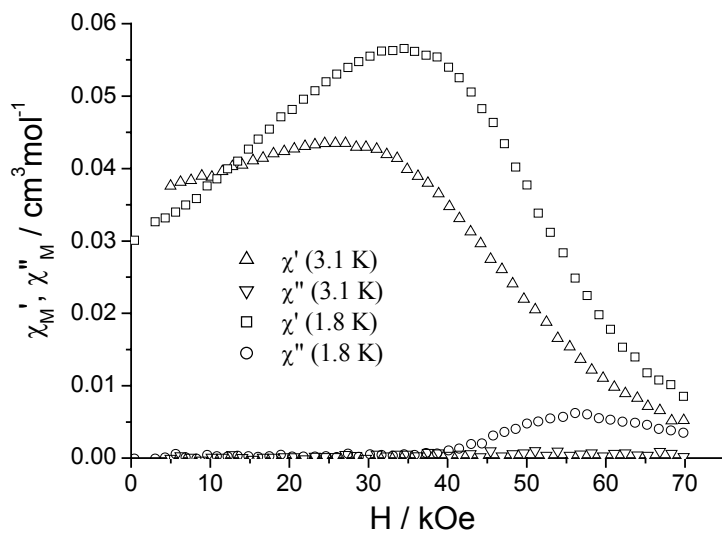


Figure S5. Real (χ_M') and imaginary (χ_M'') *ac* magnetic susceptibilities as a function of field are taken at 1.8 K and 3.1 K for **2**.