

SUPPORTING INFORMATION

Crowned Tetrameric Spirocyclic Water Chain – An Unusual Building Block of a Supramolecular Metal Organic Host

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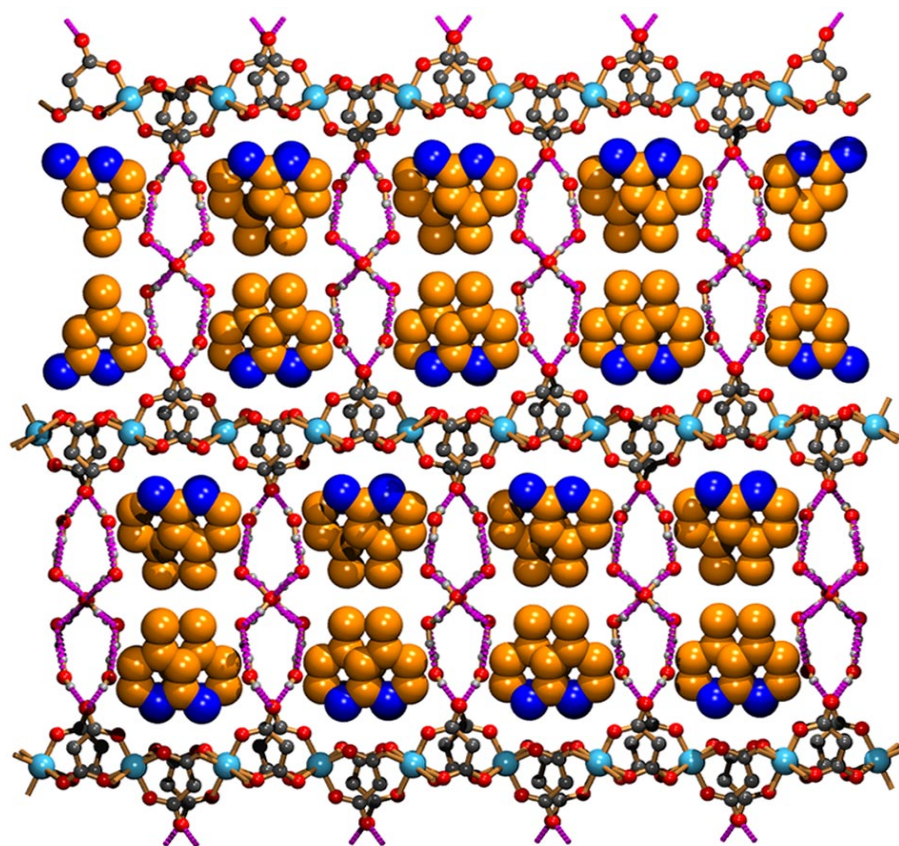


Figure S1. Guest 2-amino-4-picoline molecules (protonation not shown) entrapped within the supramolecular channel

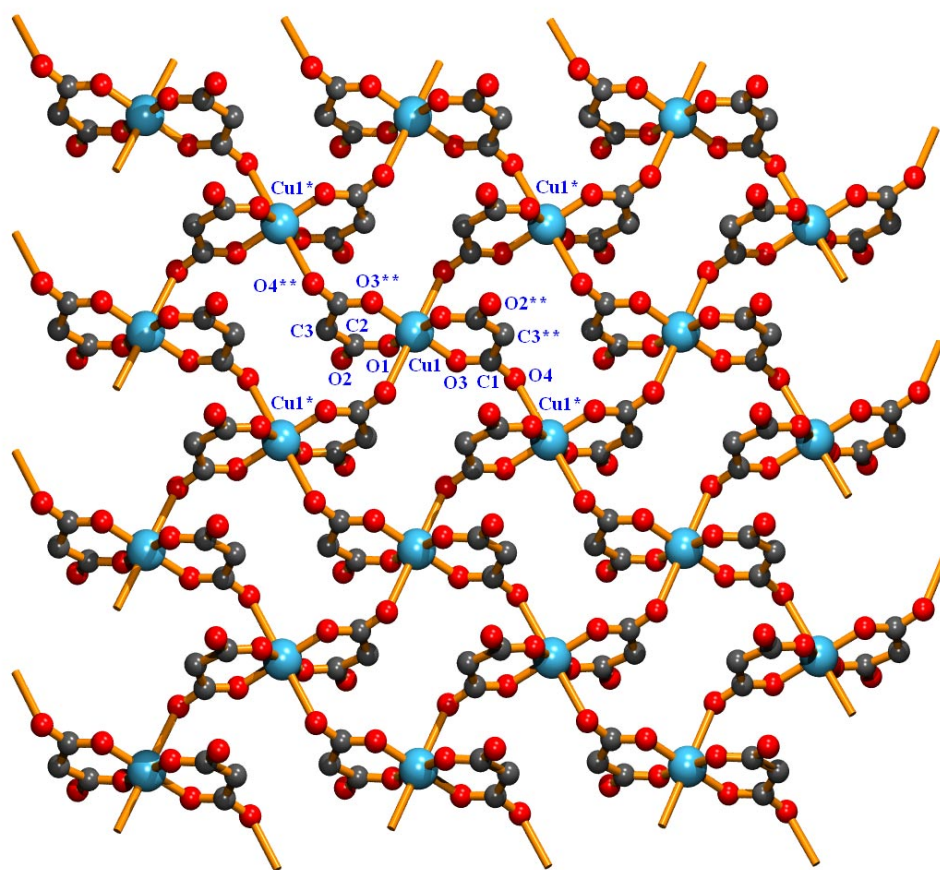


Figure S2. The Cu(II)-malonate sheets with atoms labeled

***Ab-initio* calculations and results**

For a quantitative understanding about the stability of the water chain obtained in our crystal, at first we have retrieved the tetrameric unit, $(\text{H}_2\text{O})_4$ from the crystal structure and performed *ab-initio* geometry optimization of the H-atom positions with 6-31G basis set by freezing the positions of the heavy oxygen atoms. In the next set of calculations we have considered two adjacent corner-shared tetrameric units, $(\text{H}_2\text{O})_7$, which is the basic repeating unit of the whole chain and performed the *ab-initio* geometry optimization of the H-atom positions keeping oxygen atoms fixed. We consider the stabilization energy of cluster association having n number of water molecules ($\Delta E_{n\text{-mer}}$) to be equal to $E_{n\text{-mer}} - (n \times E_{\text{monomer}})$. Monomer energy was calculated by optimizing a single H_2O molecule at the same level of theory. The stabilization energy of the tetramer and two adjacent corner shared tetramer have been given in the table below. In the calculation of stabilization energy the basis set superposition error (BSSE) was taken into account following Morokuma decomposition scheme. Zero point vibrational energy (ZPVE) was taken into account for the optimized geometry. All calculations have been performed using the PC GAMESS package.¹

Reference

- (1) Schmidt, M. W.; Baldridge, K. K.; Boatz, J. A.; Elbert, S. T.; Gordon, M. S.; Jensen, J. H.; Koseki, S.; Matsunaga, N.; Nguyen, K. A.; Su, S. J.; Windus, T. L.; Dupuis, M.; Montgomery Jr., J. A. *PC GAMESS version 6.4. J. Comput. Chem.* **1993**, *14*, 1347–1363.

***Ab-initio* computational results**

Units	<i>ab-initio</i> uncorrected stabilization Energy (kcal mol ⁻¹)	BSSE Correction (kcal mol ⁻¹)	ZPVE Correction (kcal mol ⁻¹)	Corrected Stabilization Energy (kcal mol ⁻¹)
Tetramer (H ₂ O) ₄	-39.88	5.02	7.90	-27.77
Adjacent tetramers (H ₂ O) ₇	-77.83	11.25	15.46	-51.12

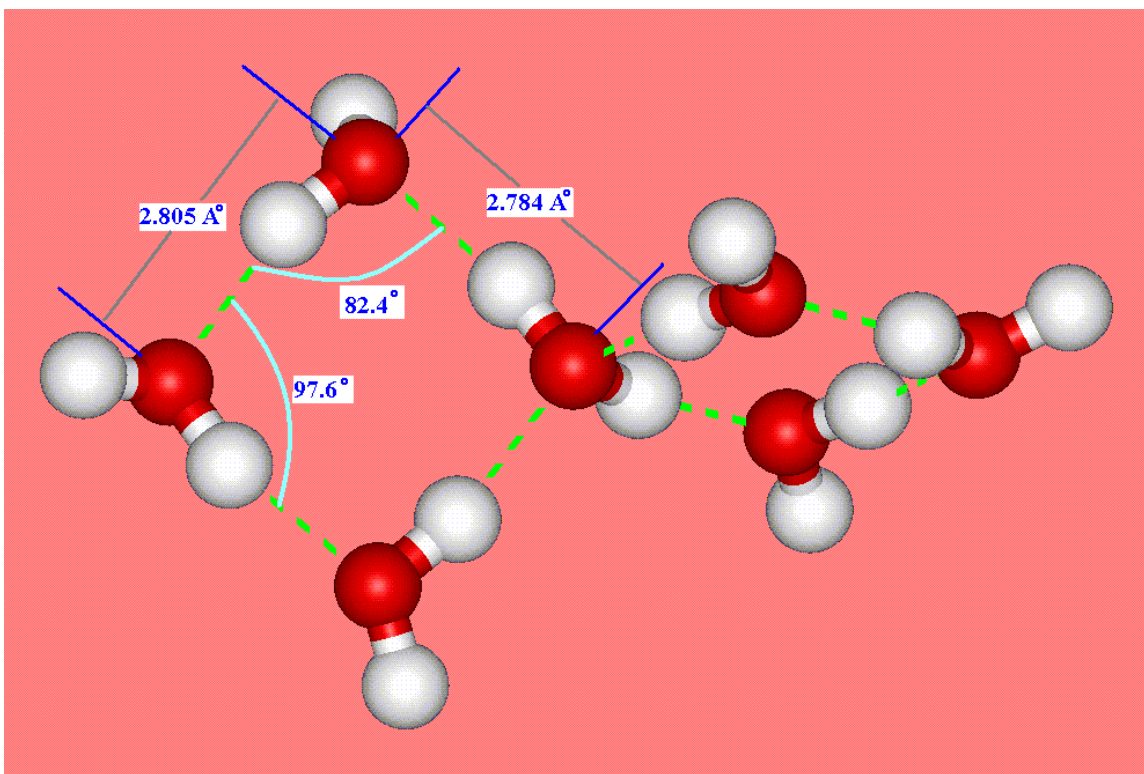


Figure S3. Building block of the spirocyclic chain as obtained from *ab-initio* calculations

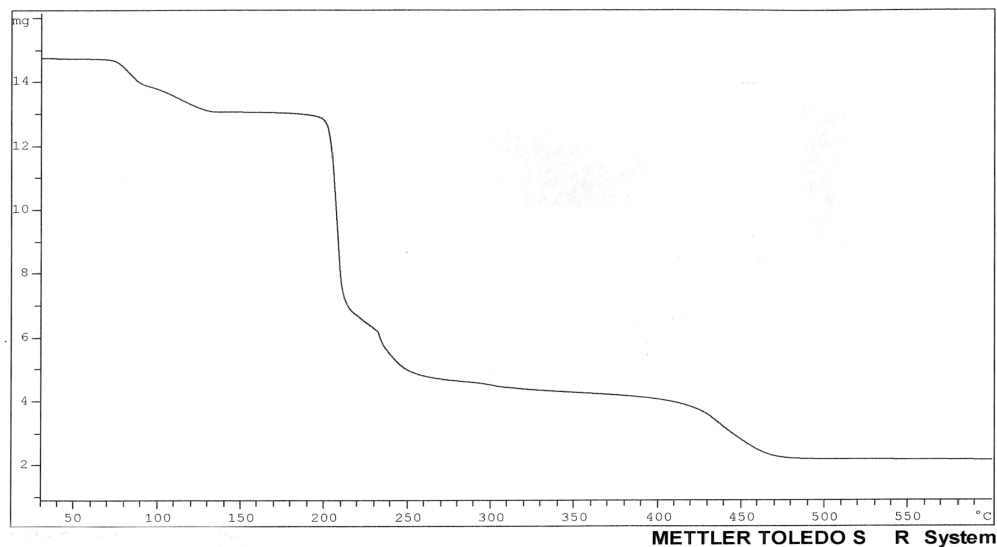


Figure S4. TG curve of 1. Heating rate 10° C per minute

Comment: Dehydration starts at 60° C and all lattice water are lost at 130° C. Calculated loss for five water molecules 15.15%, found 14.85%. The complete removal of water at such elevated temperature might suggest a strong hydrogen-bonding interaction of the water molecules.

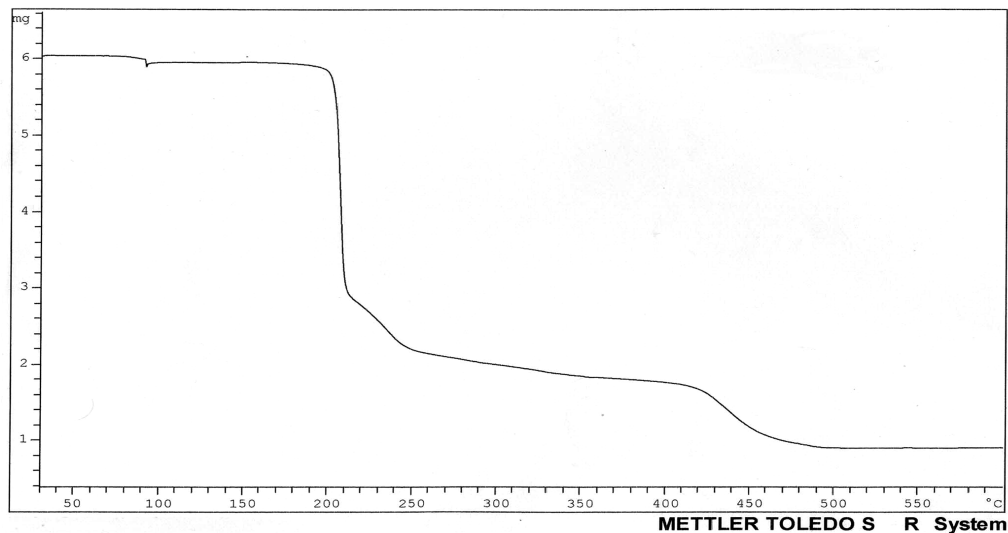


Figure S5. TG curve of heated (130 °C) sample. Heating rate 10° C per minute.

Comment: Water loss (irreversible) steps completely disappeared.

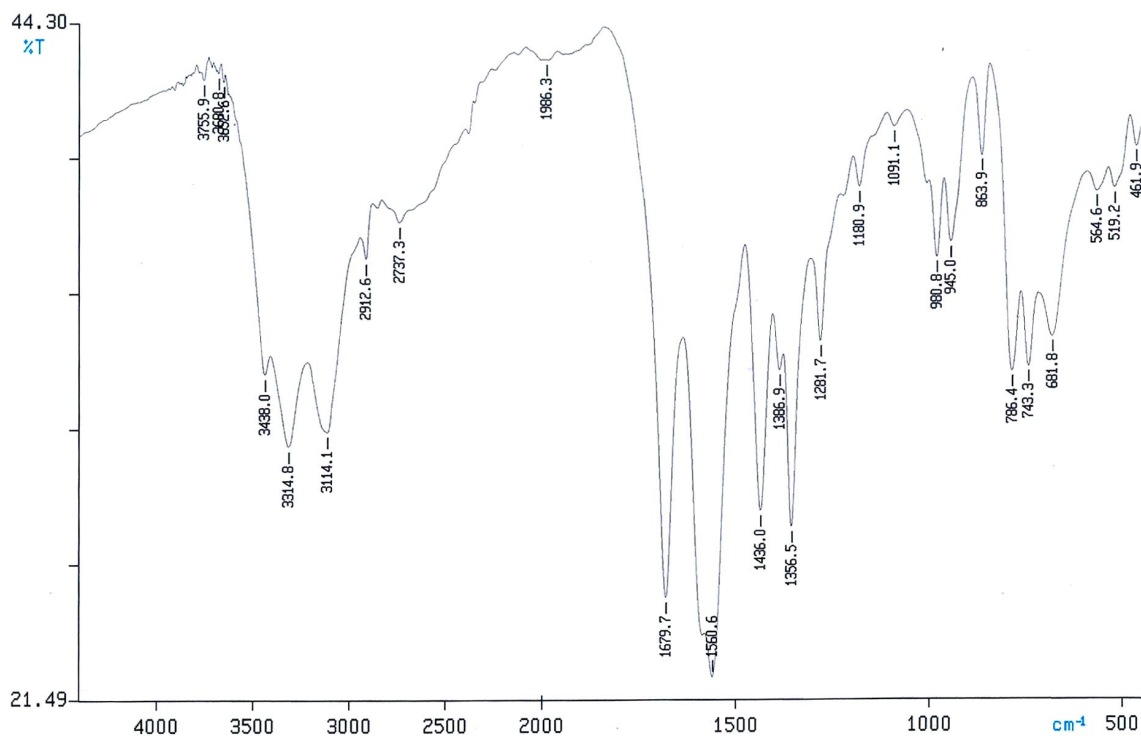


Figure S6. FTIR spectrum of **1** recorded on a Perkin Elmer RXI FT-IR spectrophotometer with the sample prepared as a KBr pellet.

Comment: The band at 3438 cm⁻¹ may be assigned to O–H stretching. On deliberate exposure to ambient atmosphere for a few days (34–36 °C, relative humidity 85–88%), the heated sample (two hours at 130 °C under 0.1 mm Hg) did not reabsorb water as evidenced from no characteristic O–H stretching. Water loss is thus found to be irreversible.

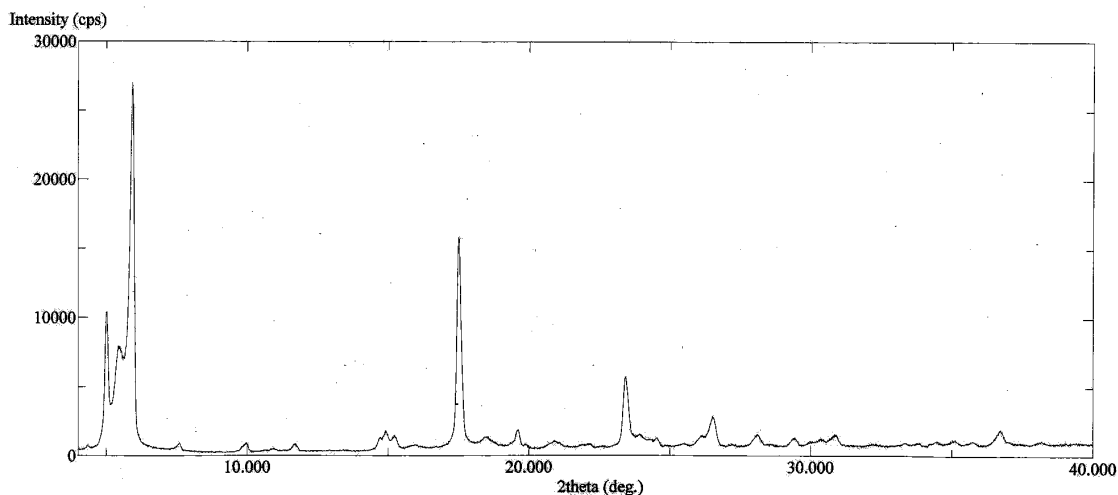


Figure S7. XRPD pattern of 1. Measured with Cu K α radiation using a Rigaku Miniflex X-ray diffractometer

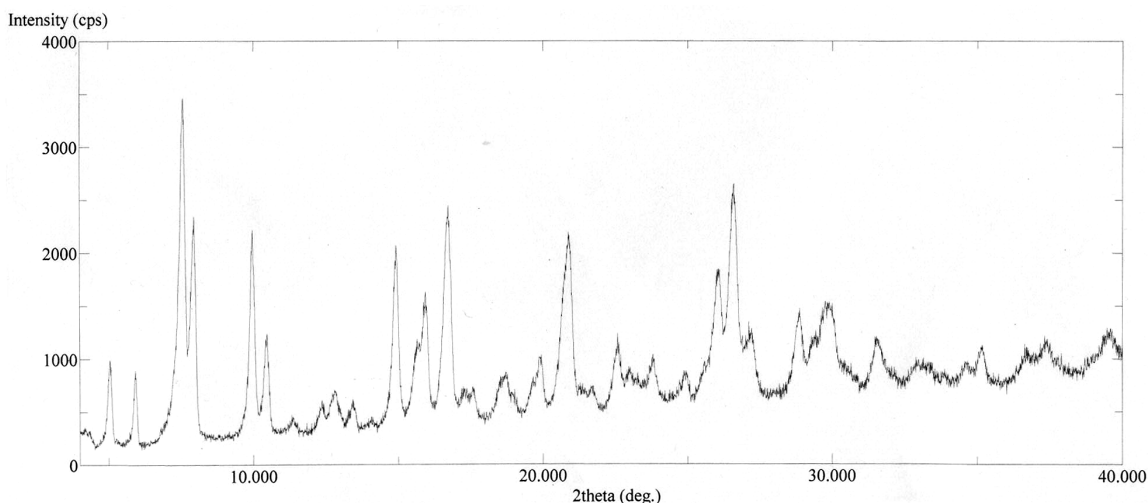


Figure S8. XRPD pattern of sample immediately after heating at 130 °C. This pattern remained unaltered when this heated sample was kept to ambient atmosphere for a few days (34–36 °C, relative humidity 85–88%)

Comment: Figures S7 and S8 show major changes both in the peak positions and their intensities before and after water expulsion, suggesting a complete breakdown of the 3D host lattice due to the removal of crystal water.

Magnetic studies of **1**

The magnetic properties of **1** in the form $\chi_M T$ vs T [χ_M being the molar susceptibility per copper(II) ion] are shown in Figure 1. $\chi_M T$ at room temperature is $0.406 \text{ cm}^3 \text{ mol}^{-1} \text{ K}$, a value which is as expected for a magnetically isolated spin doublet with $g = 2.08$. The $\chi_M T$ product increases slightly when cooling down and sharply below 15K, reaching a value of $0.64 \text{ cm}^3 \text{ mol}^{-1} \text{ K}$ at 2K. This behaviour is indicative of weak ferromagnetic coupling between the copper(II) ions. The M vs H plot (inset, Figure 1), clearly shows that the magnetization values are higher than the Brillouin law for $S = 1/2$ and $g = 2.078$, thus supporting the ferromagnetic interaction in this compound. When the field reaches 50 kG, the magnetization trends to the expected saturation value of $1 N\beta$. In keeping with the structure of **1**, in which each Cu(II) ion is linked to four different Cu(II) ions through carboxylate bridges in *syn-anti* fashion (figure S1), the magnetic data were fitted to the expression of the susceptibility derived by Baker et al.¹ from high-temperature series expansion for an isotropic ferromagnetic quadratic lattice with $S = 1/2$. The series takes the following form:

$$\chi_M = \frac{Ng^2\beta^2}{k_B T} \left[1 + \sum_{n \geq 1} \frac{\alpha_n}{2^n n!} x^n \right]$$

with n = integer values ranging from 1 to 10, $x = J/k_B T$ and α_n the coefficients for the square lattice. The best fit parameters are $J = 0.312(2) \text{ cm}^{-1}$ and $g = 2.072(1)$. The value of the exchange parameter is comparable with magnetic data found in the literature for other *syn-anti* carboxylate-bridged Cu(II) complexes with $d_{x^2-y^2}$ magnetic orbitals and carboxylate bridges linking a basal position (short Cu-O distance) and a axial position (long Cu-O distance).²⁻⁴ This exchange pathway produces a very poor overlap between

magnetic orbitals due to the low spin density of the unpaired electron at the axial position (the $d_{x^2-y^2}$ magnetic orbital is mainly located in the equatorial bismalonate copper(II) plane) and therefore the coupling through the bridging ligand is always very small (ferro- or antiferromagnetic) regardless of the structural parameters of the bridge. Moreover, because of the relatively long Cu-O axial distance of 2.600 (9) Å, the J coupling is lower than those observed for other malonate *syn-anti* carboxylate-bridged Cu(II) complexes with equatorial (short) - axial (long) coordination mode (J values in the range 1.2-1.9 cm^{-1}).²

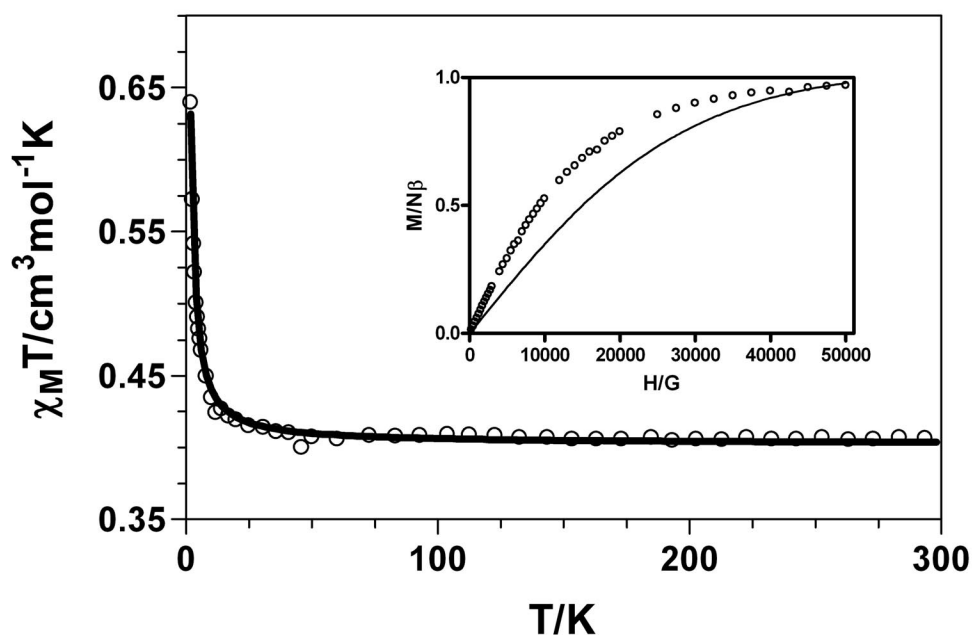


Figure S9. Plot of $\chi_M T$ versus T for 1.

References

- (1) Baker Jr., G. A.; Gilbert, H. E.; Eve, J.; Rushbrooke, G. S. *Phys. Lett.* **1967**, 25A, 207–209.

- (2) Ruiz-Pérez, C.; Sanchiz, J.; Molina, M. H.; Lloret, F.; Julve, M. *Inorg. Chem.* **2000**, *39*, 1363–1370.
- (3) Dey, S. K.; Bag, B.; Abdul Malik, K. M.; El Fallah, M. S.; Ribas, J.; Mitra, S. *Inorg. Chem.* **2003**, *42*, 4029–4035.
- (4) Colacio, E.; Ghazi, M.; Kivekäs, R.; Moreno, J. M. *Inorg. Chem.* **2000**, *39*, 2882–2890.

Experimental details for the preparation of 1

Synthesis of $\{[\text{Cu}(\text{mal})_2](\text{picH})_2 \cdot 5\text{H}_2\text{O}\}_n$, 1

Copper(II) acetate monohydrate (0.199 gm, 1 mM) was allowed to react with malonic acid (0.208 gm, 2 mM) in water (25 mL) resulting a clear blue solution. A hot (60 °C) aqueous solution (20 mL) of 2-amino-4-picoline (0.216 gm, 2 mM) was added drop wise to the above blue solution with continuous stirring. The pH of this solution was raised to 4.8 by adding dilute NaOH solution and kept for crystallization. Flat, pale blue, single crystals suitable for X-ray analysis were separated after several days from the mother liquor by slow evaporation at room temperature. The crystals were separated by filtration, washed with cold water, and air dried (yield 32%). Anal. Calcd for $\text{C}_{18}\text{H}_{32}\text{N}_4\text{O}_{13}\text{Cu}$: C, 37.53; H, 5.58; N, 9.73%. Found: C, 37.32; H, 5.42; N 9.67%.

X-ray structure determination of $\{[\text{Cu}(\text{mal})_2](\text{C}_6\text{H}_8\text{N}_2\text{H})_2 \cdot 5\text{H}_2\text{O}\}_n$, 1

Crystal data were collected on a Bruker SMART APEX II diffractometer equipped with graphite monochromated $\text{MoK}\alpha$ radiation. Crystal Dimensions, $0.56 \times 0.49 \times 0.23$ mm; crystal system, monoclinic; space group, $C 2/c$ (No.15); $a = 36.290(15)$ Å; $b = 9.659(4)$ Å; $c = 7.363(3)$ Å; $\beta = 97.289(12)^\circ$; $V = 2560.1(17)$ Å³; $Z = 4$; $D_{\text{cal}} = 1.495$ g cm⁻³; $M = 576.02$; $F(000) = 1204$; $T = 150$ K; $\mu(\text{MoK}\alpha) = 0.923$ mm⁻¹; radiation $[\text{MoK}\alpha] = 0.71073$ Å; $\theta(\text{min-max}) = 2.18\text{-}27.85^\circ$. Total reflections 12572, unique reflections 3033, $R_{\text{int}} = 0.050$. The 2561 data $[I > 2\sigma]$ used for solution and refinement by full-matrix least squares on F^2 using SHELX-97 (G. M. Sheldrick, Program for the solution and refinement of crystal structures, University of Gottingen, Germany, 1997) package. The non-hydrogen atoms were refined anisotropically. Final $R = 0.0619$, $R_w = 0.1591$; H atoms of water molecules were located by difference Fourier and were kept fixed. Other

H atoms were treated by a riding model; maximum and minimum residual electron densities were 2.06 (near heavy atom) and $-0.82 \text{ e } \text{\AA}^{-3}$, respectively. CCDC-295384 contains the supplementary crystallographic data for this paper, that can be obtained free of charge from the CCDC via www.ccdc.cam.ac.uk/data_request/cif.

Table S1. Hydrogen-bonding parameters in complex 1

D–H...A	D–H (Å)	H...A (Å)	D...A (Å)	<D–H...A (°)
O5–H5A...O2 ^[a]	0.860	1.880	2.742 (4)	174.0
O5–H5B...O7 ^[b]	0.990	1.900	2.801 (5)	151.0
O6–H6A...O7 ^[c]	1.030	1.790	2.784 (6)	162.0
N1–H1B...O5	0.880	2.040	2.905 (5)	166.0
N1–H1A...O3 ^[d]	0.880	2.020	2.897 (5)	171.0
N2–H2...O4 ^[e]	0.900	1.860	2.754 (5)	174.0

Symmetry codes: [a], 1/2-x, 1/2-y, -z; [b], x, y, -1+z; [c], x, y, -1+z; [d] 1/2-x, -1/2+y, 1/2-z;

[e], 1/2-x, -1/2+y, 1/2-z

Table S2. Selected Bond Lengths (Å) and Angles (deg) for 1

C(1)–O(3)	1.279(5)	C(2)–O(2)	1.252 (5)
C(1)–O(4)	1.246(5)	Cu(1)–O(1)	1.918(3)
C(2)–C(3)	1.515(5)	Cu(1)–O(3)	1.949(3)
C(1)–C(3)	1.509(5)	Cu(1)–O(4)	2.610(9)
C(2)–O(1)	1.268(5)		
O(1)–Cu(1)–O(3)	87.16(12)	O(2)–C(2)–C(3)	115.9(3)
O(3)–Cu(1)–O(1)	92.84(12)	O(1)–C(2)–C(3)	122.0(3)
Cu(1)–O(1)–C(2)	129.0(3)	O(1)–C(2)–O(2)	122.0(4)
Cu(1)–O(3)–C(1)	128.4(3)	C(1)–C(3)–C(2)	121.6(3)
O(3)–C(1)–C(3)	121.5(3)		