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ELECTRONIC SUPPORTING INFORMATION

pH-Triggered Changes in the Supramolecular Self-assembly of Cu(II) Malonate Complexes

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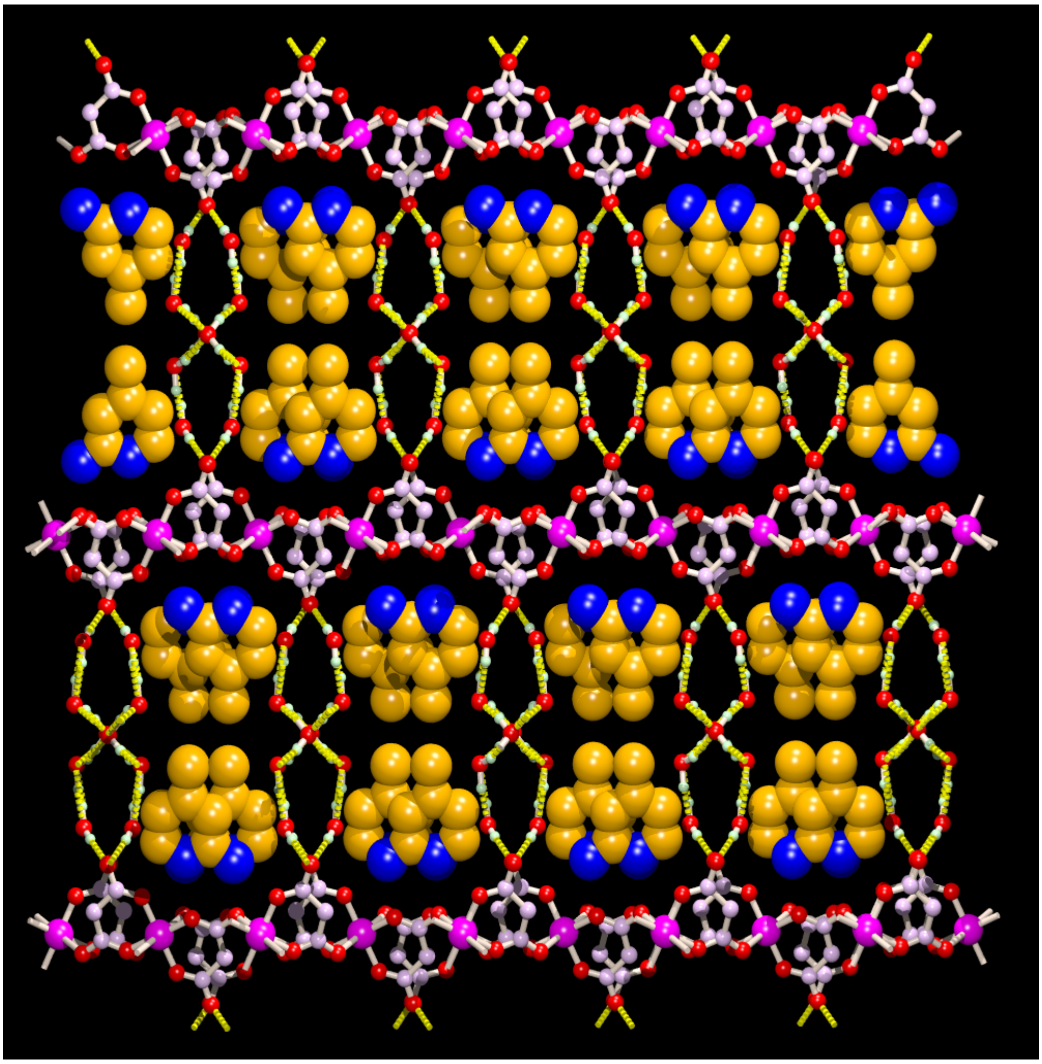

Figure S1. The Cu(II)-malonate planes in 2 are supported by water chains forming rectangular channels incorporating picoline molecules (shown in CPK). Protonation on picoline is not shown for clarity.

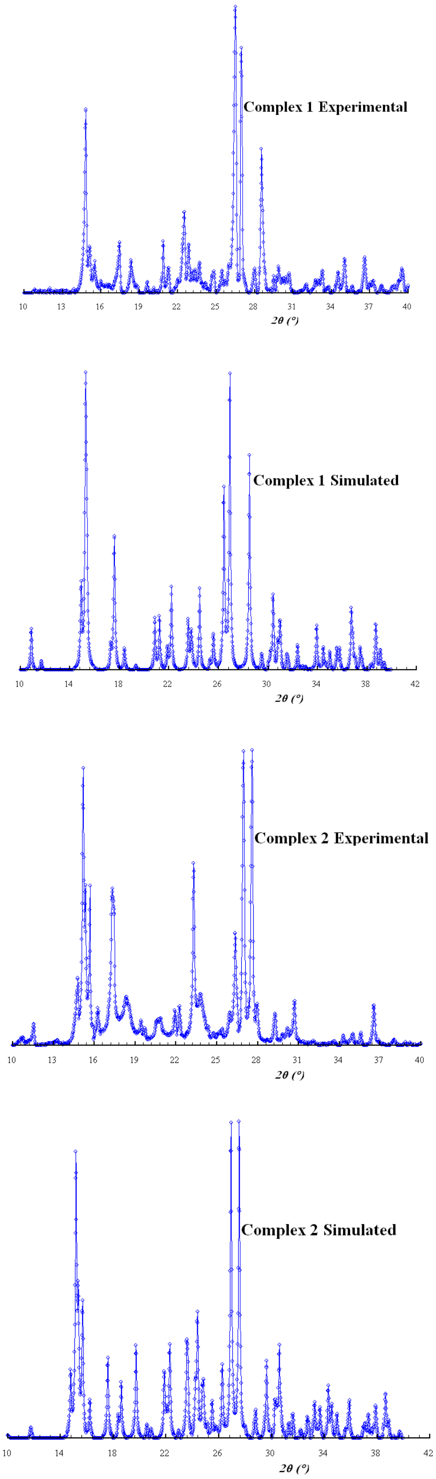

Figure S2. **XRPD patterns of 1 and 2. All intensity data were scaled such that the maximum peak is 100.**

Table S1. Comparison of crystal and structure refinement data of 1 and 2

Complex	**1**	**2**
Formula	$CuC_6H_4O_8$, $2(C_6H_9N_2)$, $2(H_2O)$	$CuC_6H_4O_8$, $2(C_6H_9N_2)$, $5(H_2O)$
M	521.97	576.02
Crystal system	Monoclinic	Monoclinic
Space group	$P2_1/c$ (No. 14)	$C2/c$ (No. 15)
a (Å)	15.4913(8)	36.290(15)
b (Å)	9.6377(4)	9.659(4)
c (Å)	7.4509(3)	7.363(3)
α (°)	90	90
β (°)	102.594(2)	97.289(12)
γ (°)	90	90
V (Å^3)	1085.66(8)	2560.1(18)
Z	2	4
T (K)	273	150
ρ_{calc}/ Mg m^{-3}	1.597	1.495
λ (Mo Kα)/ Å	0.71073	0.71073
μ (Mo Kα)/ mm^{-1}	1.070	0.923
F(000)	542	1204
S (Goodness of fit)	1.06	1.06
R1, $I > 2\sigma(I)$ (all)	0.0228	0.0619
wR2, $I > 2\sigma(I)$ (all)	0.0674	0.1591
Measured reflections	9672	12572
Observed data [$I > 2\sigma(I)$]	2316	2561

Electronic spectra

Both the complexes exhibit exactly identical optical spectra in aqueous solution indicating the presence of same species in aqueous solutions of either **1** or **2**. A broad band has been observed at 736 nm ($\varepsilon = 33.9\ M^{-1}\ cm^{-1}$) and this may be assigned to a to a d-d transition of Cu(II) ions in a distorted octahedral environment. Two other bands were observed at 231 nm ($\varepsilon = 2.03 \times 10^4\ M^{-1}\ cm^{-1}$) and at 294 nm ($\varepsilon = 1.48 \times 10^4\ M^{-1}\ cm^{-1}$). These may be assigned to an intra-ligand and/or CT transition in the Cu(II) chromophore.

Infrared spectroscopy

Both the complexes exhibit very similar IR spectra. The band at 3437 cm^{-1} can be assigned to the stretching vibration, υ (O-H), of the hydroxyl groups in the water molecules and the 3307 cm^{-1} band to the stretching vibration, υ (N-H), of the primary aromatic amine. The next band at 2909 cm^{-1} corresponds to the stretching vibration, υ (C-H), of the malonate ligands. υ_{as} (OCO) and υ_s (OCO) absorptions appeared, respectively, at 1589 cm^{-1} and 1434 cm^{-1}. δ (OCO) absorptions were located at 786 and 742 cm^{-1}. All the stated frequencies are both for **1** and **2**.

Thermal Study

Thermogravimetric analysis (Figure S3) of **1** shows that dehydration starts at 50 °C with an endothermic process centered at 99 °C and all water molecules are lost at 120 °C (calculated for two water molecules 6.89%, found 6.62%). The range of temperature for dehydration might be indicative of sufficiently strong hydrogen bonding interactions of the water molecules. Complete decomposition of the dehydrated complex was achieved at 480 °C with a strong exothermic process centered at 430 °C.

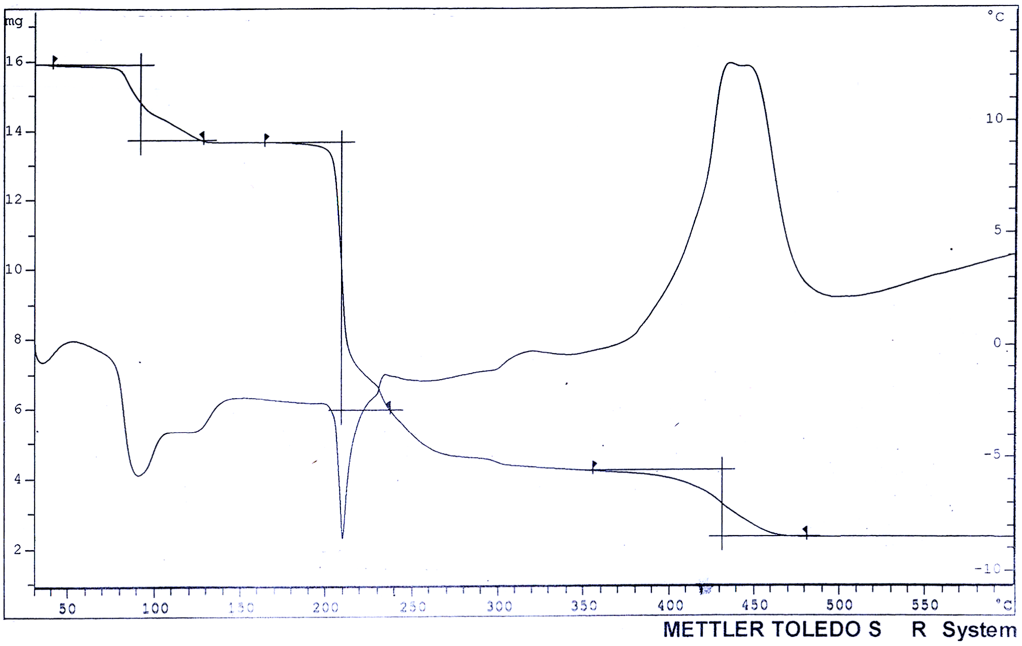

Figure S3. TG and SDTA curves of pure 1 at normal condition.

Comments: Dehydration starts at 50 °C with an endothermic process centered at 99 °C and all water molecules are lost at 120 °C (calculated for two water molecules 6.89%, found 6.62%). The range of temperature for dehydration might be indicative of sufficiently strong hydrogen bonding interactions of the water molecules. Complete decomposition of the dehydrated complex was achieved at 480 °C with a strong exothermic process centered at 430 °C.

Table S2. Selected Bond Lengths (Å) and Angles (deg) for 1 and 2

	1		
Cu1-O1	1.9224(9)	C1-C2^{ii}	1.5188(18)
Cu1-O2	1.9458(9)	C2-C3	1.5150(18)
Cu1-O3^{i}	2.6143(10)	C1-O4	1.2502(16)
C1-O1	1.2712(16)	C3-O3	1.2493(16)
C3-O2	1.2757(15)		
O1-Cu1-O2	92.94(4)	C3-O2-Cu1	128.82(8)
O1-Cu1-O2^{ii}	87.06(4)	O4-C1-O1	122.24(12)
C1-C2-C3	121.57(11)	O3-C3-O2	121.93(11)
C1-O1-Cu1	129.08(9)		
	2		
Cu1-O1	1.918(3)	C2-C3	1.513(5)
Cu1-O3	1.948(3)	C1-C3^{iv}	1.510(5)
Cu1-O4^{iii}	2.601(3)	C1-O4	1.248(5)
C1-O3	1.280(5)	C2-O2	1.249(5)
C2-O1	1.272(5)		
O1-Cu1-O3	87.15(12)	Cu1-O3-C1	128.4(3)
O1-Cu1-O3^{iv}	92.85(12)	O1-C2-O2	121.9(3)
C1^{iv}-C3-C2	121.6(3)	O4-C1-O3	121.5(3)
Cu1-O1-C2	129.1(2)		

Symmetry codes: (i) = 1-x,1/2+y,1/2-z; (ii) = 1-x,1-y,-z; (iii) = x,2-y,-1/2+z; (iv)=1/2-x,3/2-y,-z.

Table S3. Hydrogen bonding interactions in 1 and 2

D-H···A	D-H (Å)	H···A (Å)	D···A (Å)	<D-H···A (°)
1				
N1-H1C···O2	0.81	2.11	2.9129(16)	173
N2-H2···O3	0.86	1.87	2.7232(15)	172
N1-H2C···O5	0.84	2.06	2.8995(17)	171
O5-H5A···O4^{i}	0.84	2.00	2.8092(15)	162
O5-H5B···O4^{ii}	0.80	1.98	2.7642(15)	171
C2-H3A···O3^{iii}	0.97	2.55	3.3438(16)	139
C8-H8···O4^{iii}	0.91	2.50	3.3068(18)	147
2				
N1-H1A···O3^{iv}	0.88	2.02	2.897(5)	171
N1-H1B···O5	0.88	2.04	2.905(5)	166
N2-H2···O4^{iv}	0.90	1.86	2.754(5)	174
O5-H5A···O2^{v}	0.86	1.88	2.742(4)	174
O6-H6A···O7^{vi}	1.03	1.79	2.784(6)	162
O7-H7A···O6^{vii}	0.94	1.91	2.805(6)	158
C5-H6···O2^{viii}	0.95	2.39	3.249(5)	150

Symmetry codes: (i) = 1-x, 1/2+y, 1/2-z (ii) = 1-x, -y, -z; (iii) = 1-x,-y,-z; (iv) = 1/2-x,-1/2+y,1/2-z; (v) = 1/2-x,1/2-y,-z; (vi) = x,y,-1+z; (vii) = x,y,-1+z; (viii) = 1/2-x,1/2+y,1/2-z.

Ab-initio computational studies: optimized geometry of the $–CH_3\cdots O_w$ interaction

In the crystal, the distance between methyl carbon atom (C9) and the water oxygen atom (O5) is 3.289(2) Å and the water molecules are positioned nearly vertically over the methyl groups (Figure S4). This is revealed by the near linear arrangement of C6, C9 and O5 atoms (<C6-C9···O5 = 169.12°) and nearly identical distances of O5 atom from the three methyl hydrogen atoms ($H9A\cdots O5^j$ = 3.21 Å; $H9B\cdots O5^j$ = 3.19 Å; $H9A\cdots O5^j$ = 2.92 Å; j = 1-x,-y,-z). This $–CH_3\cdots O$ interaction has been studied by *ab-initio* quantum chemical calculations to find out the optimized geometry and the energy of the $–CH_3\cdots O_w$ interaction. The calculations have been performed at the restricted Hartree-Fock (RHF) level. To perform these calculations, we have taken the initial geometry of the protonated picoline and water system as it was in the crystal structure of complex **1** and the dimeric system was optimized with no restrictions on the atomic coordinates. For all calculations 6-311++G** basis set was used. The basis set superposition error (BSSE) corrected energy of the interaction has been defined as $E_{int} = \{(E_{picoline-water-dimer} + BSSE_{picoline-water-dimer}) - (E_{picoline} + E_{water})\}$. All calculations have been performed using the PCGAMESS package.[1]

The optimized dimer geometry was found to be almost identical to the one that existed in the crystal, the distance between the picoline methyl carbon (C9) and water oxygen atom that was 3.29 Å in the crystal structure reduced to 3.21 Å in the theoretically obtained optimized configuration of the dimer indicating a slight enhancement of the interaction (Figure S5). The basis set superposition error (BSSE) corrected energy of the interaction which has been defined as $E_{int} = \{(E_{picoline-water-dimer} + BSSE_{picoline-water-dimer}) - (E_{picoline} + E_{water})\}$ was found to be –4.31 kcal mol^{-1} which places this interaction at the energy level of weak hydrogen bonds.

Results:

$E_{picoline\text{-}water\text{-}dimer} = –417.3115833921$ Hartree

$BSSE_{picoline\text{-}water\text{-}dimer} = 0.000339$ Hartree

$E_{picoline} = –341.2509310434$ Hartree

$E_{water} = –76.0534461651$ Hartree

$E_{int} = \{(E_{picoline\text{-}water\text{-}dimer} + BSSE_{picoline\text{-}water\text{-}dimer}) - (E_{picoline} + E_{water})\} = –0.0068671836$ Hartree $= –4.31$ kcal mol^{-1}.

References

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

The final coordinates are given below:

```
COORDINATES OF ALL ATOMS ARE (ANGS)

ATOM   CHARGE      X                  Y                  Z
 ----------------------------------------------------------------------
 O1W       8.0   5.0467103407  -0.5178193920   0.0559103884
 H1W       1.0   5.6222055953  -0.5810079630   0.7994423305
 H2W       1.0   5.5999077985  -0.6028422328  -0.7022616142
 N1        7.0  -2.2884280927   0.6378956159  -0.0674290179
 H2        1.0  -3.2640303321   0.8372366686  -0.1268687114
 C3        6.0  -1.8821681733  -0.6352349701  -0.0011828168
 C4        6.0  -0.5030303769  -0.8913975865   0.0800201480
 H5        1.0  -0.1752350396  -1.9116865736   0.1328029004
 C6        6.0   0.3931398756   0.1413803242   0.0897072615
 C7        6.0  -0.0958170380   1.4818470924   0.0174800084
 H8        1.0   0.5816290945   2.3131039350   0.0228835731
 C9        6.0  -1.4169982808   1.6908044101  -0.0587017700
 H10       1.0  -1.8670794552   2.6623939146  -0.1163473467
 C11       6.0   1.8707410831  -0.0960156268   0.1712951765
 H12       1.0   2.2755334321   0.3944164056   1.0498495022
 H13       1.0   2.1151738159  -1.1469051867   0.2169057629
 H14       1.0   2.3649734345   0.3366740403  -0.6908870462
 N15       7.0  -2.7950241174  -1.6052354421  -0.0152957955
 H16       1.0  -3.7704577742  -1.4236131155  -0.0726690834
 H17       1.0  -2.5111709829  -2.5561127098   0.0343663629
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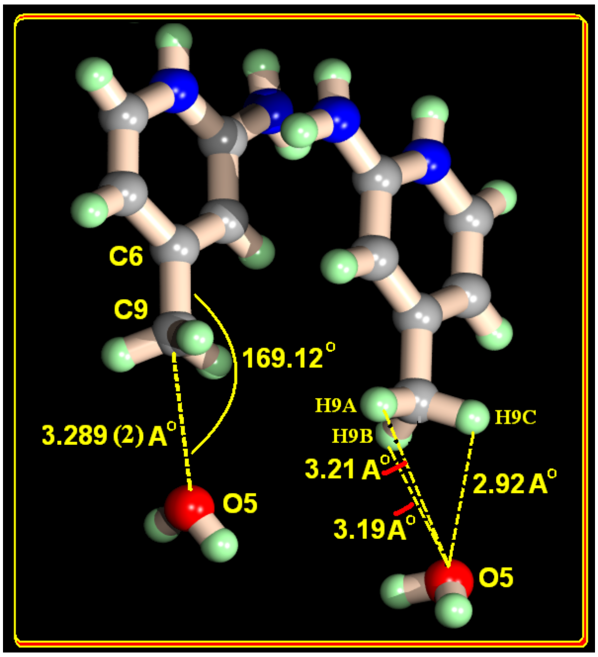

Figure S4. Interaction of water molecules with the methyl terminal of picoline: the $CH_3 \cdots O$ interaction as observed in the crystal structure of 1.

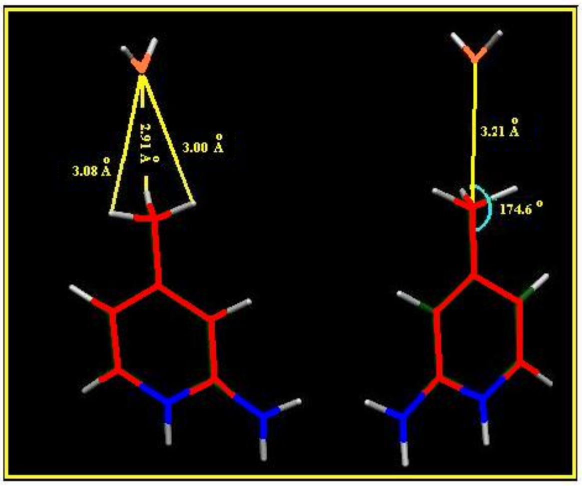

Figure S5. Interaction of water molecules with the methyl terminal of picoline: the $CH_3 \cdots O$ interaction as resulted from *ab-initio* calculations.

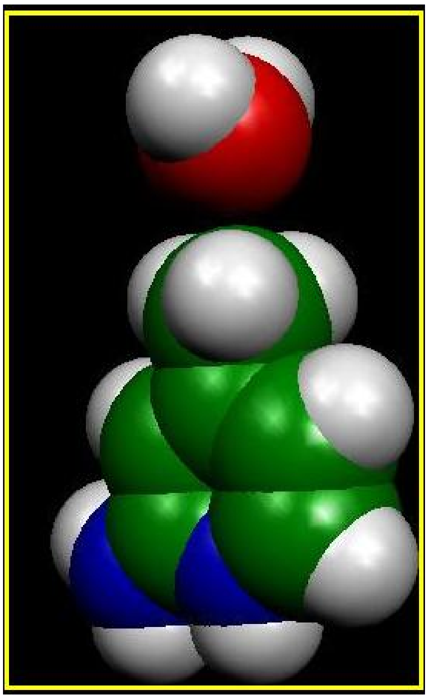

Figure S6. **The CPK view of the –$CH_3\cdots$Ow interaction.**

Magnetic studies of 1

The magnetic properties of **1** in the form χ_MT *versus* T [χ_M being the molar susceptibility per copper (II) ion] are shown in Figure S7. χ_MT at room temperature is 0.44 cm^{3}mol^{-1}K, a value which is as expected for a magnetically isolated spin doublet with g = 2.16 whereas for complex **2**, χ_MT at room temperature was 0.406 cm^3 mol^{-1} K, and g = 2.08.[1] The χ_MT product increases slightly when cooling down and sharply below 15K, reaching a value of 0.64 cm^{3}mol^{-1}K at 2K (exactly the same value was obtained for complex **2**[1]). This behaviour is indicative of weak ferromagnetic coupling between the copper(II) ions. The M *versus* H plot (Figure S7, inset) clearly shows that the magnetization values are higher than the Brillouin law for S = 1/2 and g = 2.16, thus supporting the ferromagnetic interaction in this compound. When the field reaches 50 kG, the magnetization trends to the expected saturation value of 1 Nβ. 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 2 of the main manuscript), the magnetic data were fitted to the expression of the susceptibility derived by Baker *et al.*[2] 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 from 1 to 10, $x = J/k_B T$ and α_n the coefficients for the square lattice. The best fit parameters are J = 0.3(2) cm^{-1} and g = 2.157(2). The value of the exchange parameter is comparable with the magnetic data found in the literature for other *syn-anti* carboxylate-bridged copper(II) complexes with d_{x2-y2} magnetic orbitals and carboxylate bridges linking a basal position (short Cu-O distance) and a axial position (long Cu-O distance).[3-5] 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_{x2-y2} 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 2.614 (9) Å, the J coupling is lower than those observed for other malonate *syn-anti* carboxylate-bridged copper(II) complexes with equatorial (short) – axial (long) coordination mode (J values in the range 1.2-1.9 cm^{-1}).[3]

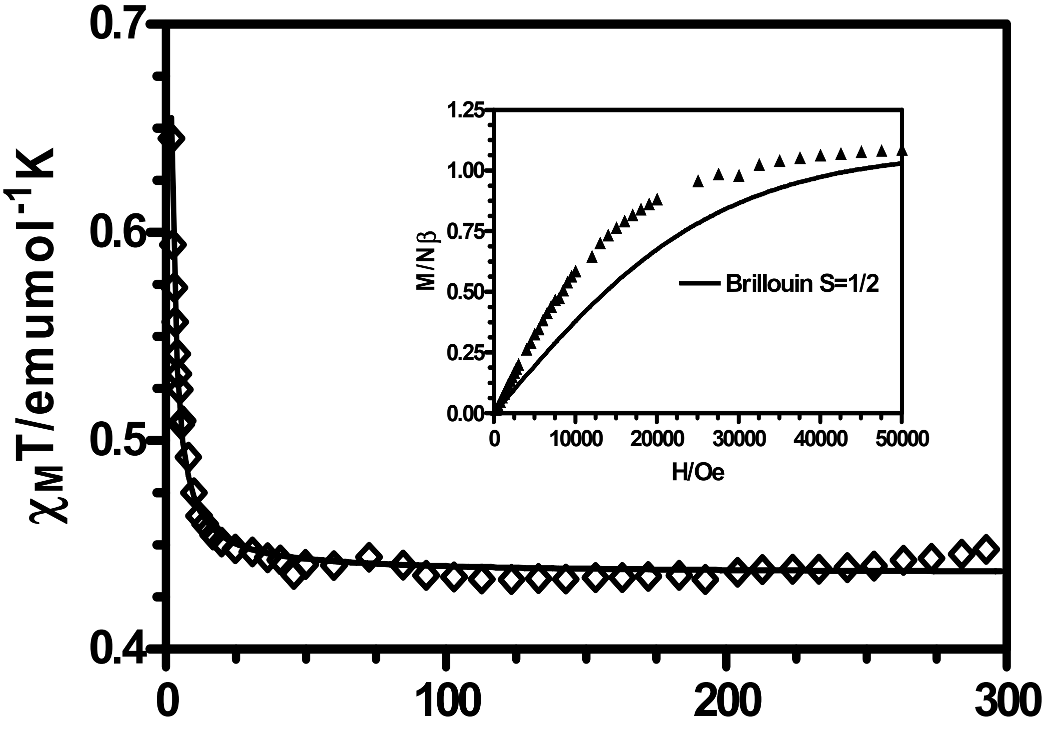

Figure S7. Plots of χ_MT versus T and M versus H for 1.

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