

Supplementary Information

Accompanying

The self-assembly between C_2 -symmetric (methanol)₆ or S_6 -symmetric (ethanol)₆ cyclohexamers and paddle-wheel dinuclear copper units leads to unique 1D polymer chains

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1. Synthesis of $[\text{Cu}_2(\text{HL})_4(\text{CH}_3\text{OH})_2] \cdot 4\text{CH}_3\text{OH}$ (**1**)

To a solution of $\text{Cu}(\text{acetate})_2 \cdot \text{H}_2\text{O}$ (160 mg, 0.8 mmol) in MeOH (20 mL), a solution of 3,5-Di-*tert*-butylsalicylic acid hydrate ($\text{H}_2\text{L} \cdot \text{H}_2\text{O}$) (400 mg, 1.6 mmol) in MeOH (10 mL) was added at room temperature, causing an instantaneous colour change from blue to dark green. The reaction mixture was left standing in air for one week, during which time the solvent slowly evaporated to yield green rectangular crystals of $[\text{Cu}_2(\text{HL})_4(\text{CH}_3\text{OH})_2] \cdot 4\text{CH}_3\text{OH}$ (**1**), which were collected by filtration and dried under vacuum for one day to afford **1** in 85% yield. Elemental analysis: Calc. for: $\text{C}_{66}\text{H}_{108}\text{Cu}_2\text{O}_{18}$: C 60.21, H 8.27; Found: C 59.55, H 8.40.

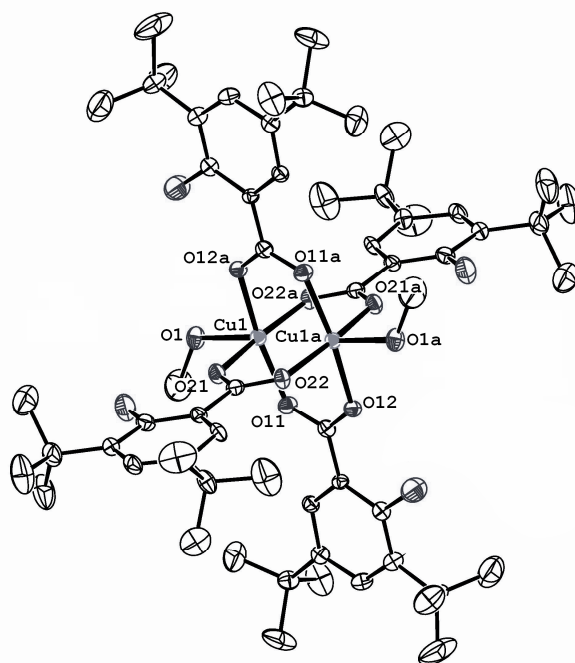


Fig. S1 ORTEP representation at the 50% level of $[\text{Cu}_2(\text{HL})_4(\text{CH}_3\text{OH})_2] \cdot 4\text{CH}_3\text{OH}$ (**1**). Hydrogen atoms and lattice methanol molecules are omitted for clarity. Selected bond distances (Å) and angles (deg): Cu1–O1 = 2.155(4), Cu1–O11 = 1.961(3), Cu1–O21 = 1.976(3), Cu1–O12a = 1.986(3), Cu1–O22a = 1.970(3), Cu1–Cu1a = 2.586(1); O12a–Cu1–O22a = 88.47(14), O22a–Cu1–O11 = 90.53(14), O11–Cu1–O21 = 89.93(14), O21–Cu1–O12a = 89.20(14).^{1–3}

2. Synthesis of $[\text{Cu}_2(\text{HL})_4(\text{CH}_3\text{CH}_2\text{OH})_2]\cdot 4\text{CH}_3\text{CH}_2\text{OH}$ (**2**)

To a solution of $\text{Cu}(\text{acetate})_2\cdot\text{H}_2\text{O}$ (160 mg, 0.8 mmol) in EtOH (20 mL), a solution of 3,5-Di-*tert*-butylsalicylic acid hydrate ($\text{H}_2\text{L}\cdot\text{H}_2\text{O}$) (400 mg, 1.6 mmol) in EtOH (10 mL) was added at room temperature, causing an instantaneous colour change from blue to dark green. The reaction mixture was left standing in air for three weeks, during which time the solvent slowly evaporated to yield green rectangular crystals of $[\text{Cu}_2(\text{HL})_4(\text{C}_2\text{H}_5\text{OH})_2]\cdot 4\text{C}_2\text{H}_5\text{OH}$ (**2**), which were collected by filtration and dried under vacuum for one day to afford **2** in 73% yield. Elemental analysis: Calc. for: $\text{C}_{72}\text{H}_{116}\text{Cu}_2\text{O}_{18}$: C 61.91, H 8.37; Found: C 60.85, H 8.33.

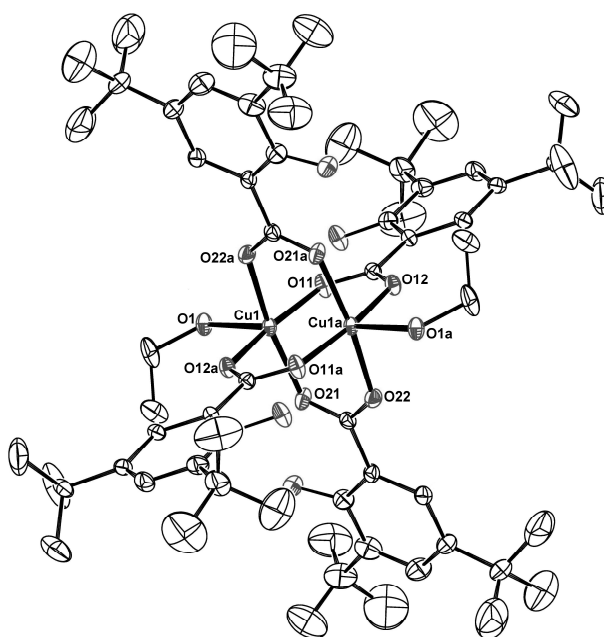


Fig. S2 ORTEP representation at the 50% level of $[\text{Cu}_2(\text{HL})_4(\text{CH}_3\text{CH}_2\text{OH})_2]\cdot 4\text{CH}_3\text{CH}_2\text{OH}$ (**2**). Hydrogen atoms and lattice ethanol molecules are omitted for clarity. Selected bond distances (Å) and angles (deg): Cu1–O1 = 2.154(4), Cu1–O21 = 1.962(3), Cu1–O12a = 1.968(4), Cu1–O22a = 1.976(3), Cu1–O11 = 1.961(4), Cu1–Cu1a = 2.599(1); O22a–Cu1–O11 = 89.64(17), O11–Cu1–O21 = 89.68(16), O21–Cu1–O12a = 89.57(16), O12a–Cu1–O22a = 89.20(17).¹⁻³

3. Magnetic susceptibility measurements for compound 1

The magnetic behaviour of a powdered sample of compound **1** was measured in the range of temperature 6 to 300 K (Figure S1). The χT vs. T curve shows a decrease of χT , from 0.42 cm³mol⁻¹K at 300K, (already much lower than that expected for a dinuclear copper(II) compound with two uncorrelated S = 1/2 spins expected at χT 0.750 cm³mol⁻¹K), to ca. 0 cm³mol⁻¹K at ca. 100K. This indicates an S = 0 ground state as a result of a strong antiferromagnetic interaction between the copper ions (d⁹, S = 1/2). The χT vs. T has been successfully modelled using the Hamiltonian H = -2J $S_a S_b$ (S_a = S_b = S_{Cu} = 1/2) and the derived Bleaney-Bowers equation (1).

$$\chi T = 2N_A g^2 \beta^2 / 3k_B [1/(3 + \exp(-2J/K_B T))] + \text{TIP} \quad (1)$$

The best fit was obtained with: TIP = 60·10⁻⁴ per copper atom, g = 2.18 and 2J = -355 cm⁻¹. The value of the strong exchange interaction, J, is in the range of those generally found for carboxylate bridged-dinuclear copper complexes; it is well known, for these type of compounds, that the carboxylates that bridge the two Cu(II) ions in the equatorial plane provide paths for the interaction to occur through the so-called super-exchange mechanism.⁴ This interaction parameter is also influenced by the donating ability of the apical ligand.⁴ In this case the presence of an oxygen donor with a Janteller elongated Cu-O bond (2.153 Å), makes the value of J obtained reasonable.^{4,5}

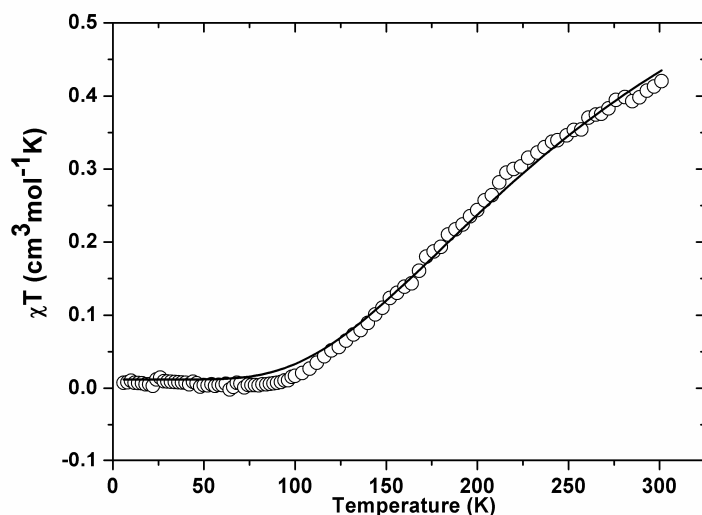


Figure S3. χT vs. T plot for **1**. The solid line represents the best fit by use of parameters: g = 2.18, 2J = -355 cm⁻¹ and TIP = 60·10⁻⁴ per copper atom.

References

1. G. M. Sheldrick, *Program for Crystal Structure refinement*, (1986) University of Göttingen, Göttingen, Germany.
2. G. M. Sheldrick, *Program for Crystal Structure refinement*, (1997) University of Göttingen, Göttingen, Germany.
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4. M. Melnik, *Coord. Chem. Rev.*, 1982, **42**, 259-293.
5. F. P. W. Agterberg, H. Kluit, W. L. Driessen, H. Oevering, W. Buijs, M. T. Lakin, A. L. Spek and J. Reedijk, *Inorg. Chem.*, 1997, **36**, 4321-4328.