

Electronic Supporting Information (ESI) for the manuscript:

**Self-Assembly of a Chiral Three-Dimensional Manganese(II)-
Copper(II) Coordination Polymer with a Double Helical
Architecture**

Thais Grancha, Clarisse Tourbillon, Jesús Ferrando,* Miguel Julve, Francesc Lloret,
Jorge Pasán, Catalina Ruiz-Pérez, Oscar Fabelo, and Emilio Pardo*

Experimental Section

Physical techniques. Elemental analyses (C, H, N) were performed at the Servicio Central de Soporte a la Investigación (SCSIE) from the Universitat de València (Spain). FT-IR spectra were recorded on a Perkin-Elmer 882 spectrophotometer as KBr pellets.

Materials. All chemicals were of reagent grade quality. They were purchased from commercial sources and used as received. (*S*)-trimethyl(1-phenylethyl)ammonium iodide {[(*S*)-(1-PhEt)Me₃N]I} and (Na)₄[Cu₂(mpba)₂] · 10H₂O were prepared according to literature methods.¹ [(*S*)-(1-PhEt)Me₃N]₄[Cu₂(mpba)₂] · 8H₂O/[(*S*)-(1-PhEt)Me₃N]₂(ox) were obtained by metathesis through the reaction of (Na)₄[Cu₂(mpba)₂] · 10H₂O or (NH₄)₂ox with AgNO₃ and [(*S*)-(1-PhEt)Me₃N]Cl in methanol.

[(*S*)-(1-PhEt)Me₃N]₄[Mn₂(ox)Cu₂(mpba)₂(H₂O)₂] · 3H₂O (1). Well-formed green rectangular prisms of **1**, suitable for single-crystal X-ray diffraction with synchrotron radiation, were obtained, after three weeks, by slow diffusion, in an H-shaped tube at 16 °C, of aqueous solutions containing stoichiometric amounts of [(*S*)-(1-PhEt)Me₃N]₄[Cu₂(mpba)₂] · 8H₂O/[(*S*)-(1-PhEt)Me₃N]₂(ox) (0.057 g, 0.04 mmol/0.0164 g, 0.04 mmol) on one side of the tube and Mn(NO₃)₂ · 4H₂O (0.020 g, 0.08 mmol) on the other side. The crystals were filtered on paper and air-dried. Yield: 0.031 g, 48%; Anal. calcd (%) for C₄₄H₅₄Cu₂Mn₂N₆O₂₁ (1239.9): C 42.62, H 4.39, N 6.78; found: C 42.79, H 4.59, N 6.66; IR (KBr): $\nu = 1619$ and 1593 cm^{-1} (C=O).

The synthesis of compound **1** was repeated up to five times to ensure the reproducibility of the method.

¹ (a) M. Clemente-León, E. Coronado, J. C. Díaz, A. Soriano-Portillo, R. D. Willett, *Inorg. Chem.*, 2008, **47**, 6458. (b) I. Fernández, R. Ruiz, J. Faus, M. Julve, F. Lloret, J. Cano, X. Ottenwaelde, Y. Journaux, M. C. Muñoz, *Angew. Chem. Int. Ed.* 2001, **40**, 3039.

X-ray crystallographic data collection and structure refinement. Single-crystal X-ray diffraction data of **1** were collected on at 100 K at the ESRF synchrotron at BM16 beamline (Grenoble, France) using $\lambda = 0.7379 \text{ \AA}$. Data were indexed, integrated and scaled using the HKL2000 program.² All hydrogen atoms of the ligands were set in calculated positions and refined as riding atoms except those of the water molecules which were neither found nor set. The structures were solved by direct methods and refined by a full matrix least-squares technique based on F^2 using SHELXL 97 program.³ The final geometrical calculations and the graphical manipulations were carried out with WinGX, PLATON and CRYSTAL MAKER programs, respectively.^{4,5,6} A good model for the solvent molecules cannot be achieved because of the severe disorder. Thus, to obtain a good refinement of the structures, the SQUEEZE subroutine in the PLATON software package⁵ was applied to mask the electron density allocated in the cavities with the exception of those related with the counter cations and the O(3w) and O(4w) crystallization water molecules, which were kept in the final model. A total of 248.2 electrons per unit cell, corresponding roughly to 25 water molecules, were included in the SQUEEZE mask in a total void volume of $5049.3 \text{ \AA}^3/\text{cell}$. Some carbon atoms [C(52), C(58), C(59) and C(60)] of the (*S*)-trimethyl(1-phenylethyl)ammonium cation defined by the N(6) nitrogen atom, which occupy the pores in the crystal structure of **1**, exhibit larger anisotropic displacement parameters than usual. Crystallographic data (excluding structure factors) for the structure reported in this paper have been deposited with the Cambridge

2 *HKL2000* (Otwinowski & Minor, 1997)

3 *SHELXTL*, Bruker Analytical X-ray Instruments, Madison, WI, 1998.

4 L.J. Farrugia, *J. Appl. Cryst.*, 1999, **32**, 837.

5 A. L. Spek, *J. Appl. Cryst.*, **2003**, *36*, 7-13

6 D. Palmer, *CRYSTAL MAKER*, Cambridge University Technical Services, Cambridge, 1996.

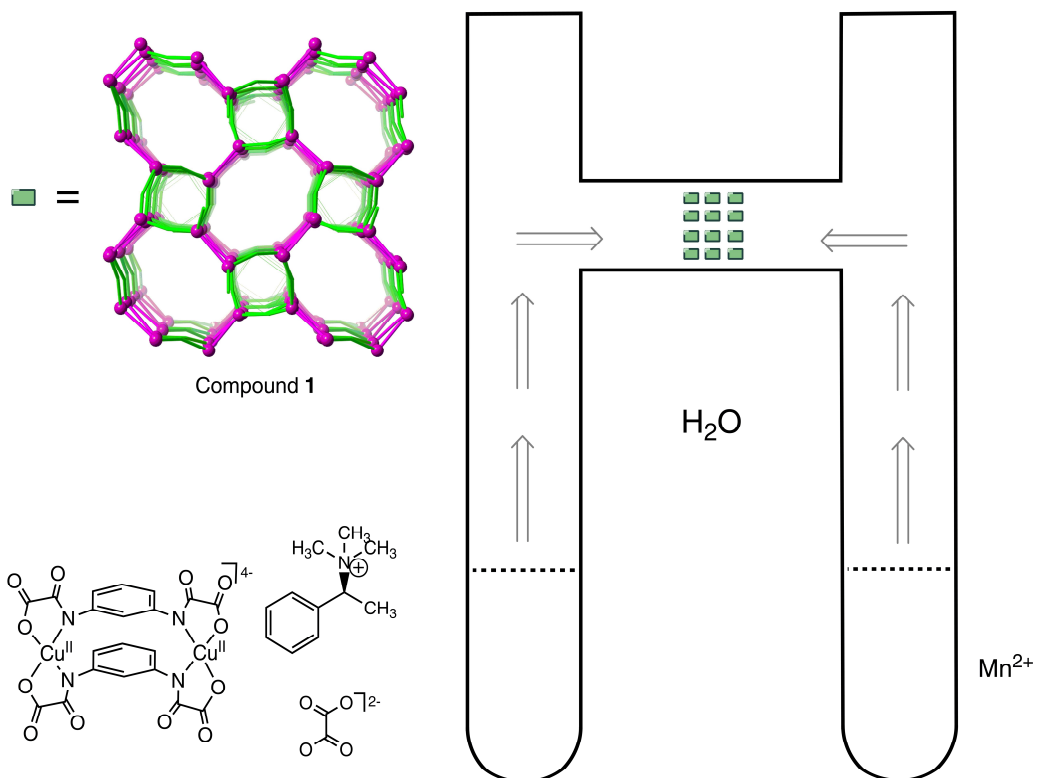
Crystallographic Data Centre as supplementary publication number CCDC-941373. Copies of the data can be obtained free of charge on application to CCDC, 12 Union Road, Cambridge CB21EZ, UK [fax: (+44) 1223-336-033; e-mail: deposit@ccdc.cam.ac.uk].

Magnetic measurements. Variable-temperature (2.0–300 K) direct current (dc) magnetic susceptibility measurements under an applied field of 100 ($T < 50$ K) and 10000 G ($T \geq 50$ K) were performed with a Quantum Design SQUID magnetometer for a polycrystalline sample of **1**. The magnetic susceptibility data were corrected for the diamagnetism of the constituent atoms, as well as for the temperature-independent paramagnetism and the sample holder.

Table S1. Crystal data and structure refinement for **1**.

Empirical formula	C ₄₄ H ₅₀ Cu ₂ Mn ₂ N ₆ O ₂₁	
Formula weight	1235.86	
Temperature	100(2) K	
Wavelength	0.73790 Å	
Crystal system	Tetragonal	
Space group	P 4 ₁ 2 ₁ 2	
Unit cell dimensions	<i>a</i> = 20.467(3) Å	α = 90°
	<i>b</i> = 20.467(3) Å	β = 90°
	<i>c</i> = 34.344(7) Å	γ = 90°
Volume	14387(4) Å ³	
Z	8	
Density (calculated)	1.141 Mg/m ³	
Absorption coefficient	1.089 mm ⁻¹	
<i>F</i> (000)	5056	
Crystal size	0.09 x 0.08 x 0.07 mm ³	
Theta range for data collection	1.59 to 28.25°	
Index ranges	-26 ≤ <i>h</i> ≤ 26, -26 ≤ <i>k</i> ≤ 26, -44 ≤ <i>l</i> ≤ 44	
Reflections collected	127126	
Independent reflections	15896 [<i>R</i> (int) = 0.1041]	
Completeness to theta = 28.25°	99.7 %	
Refinement method	Full-matrix least-squares on <i>F</i> ²	
Data / restraints / parameters	15896 / 0 / 677	
Goodness-of-fit on <i>F</i> ²	1.078	
Final <i>R</i> indices [<i>I</i> > 2σ(<i>I</i>)]	<i>R</i> 1 = 0.0788, <i>wR</i> 2 = 0.2218	
<i>R</i> indices (all data)	<i>R</i> 1 = 0.0842, <i>wR</i> 2 = 0.2274	
Absolute structure parameter	0.088(17)	
Largest diff. peak and hole	1.235 and -0.724 e Å ⁻³	

$$^a R_1 = \sum(|F_o| - |F_c|) / \sum|F_o|. \quad ^b wR_2 = [\sum w(F_o^2 - F_c^2)^2 / \sum w(F_o^2)^2]^{1/2}. \quad ^c S = [\sum w(|F_o| - |F_c|)^2 / (N_o - N_p)]^{1/2}.$$



Scheme. S1 Slow diffusion strategy for the synthesis of compound 1.

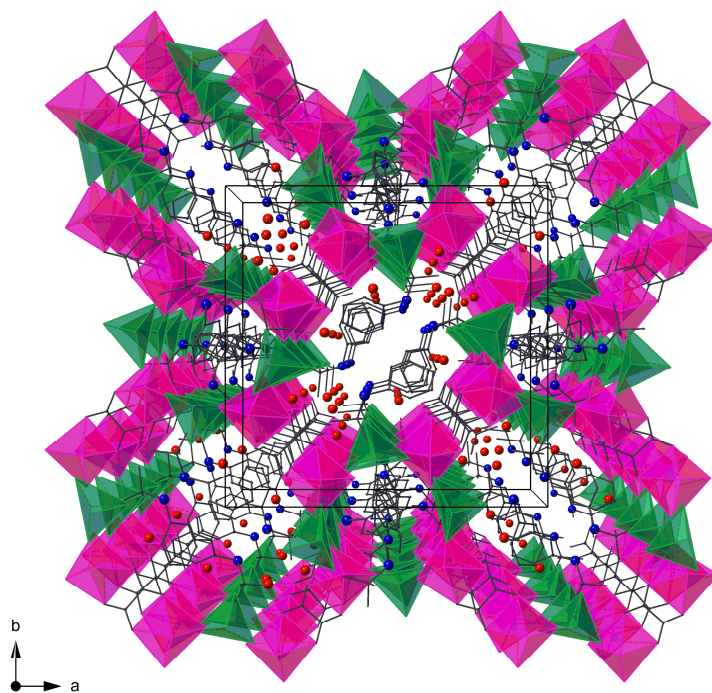


Fig. S1 Perspective view of the anionic 3D network of **1** showing the filling of the pores along the crystallographic *c* axis. Metal and ligand atoms of the anionic network are represented by polyhedra and sticks, respectively (Cu, green; Mn, purple). Hydrogen atoms are omitted for clarity.

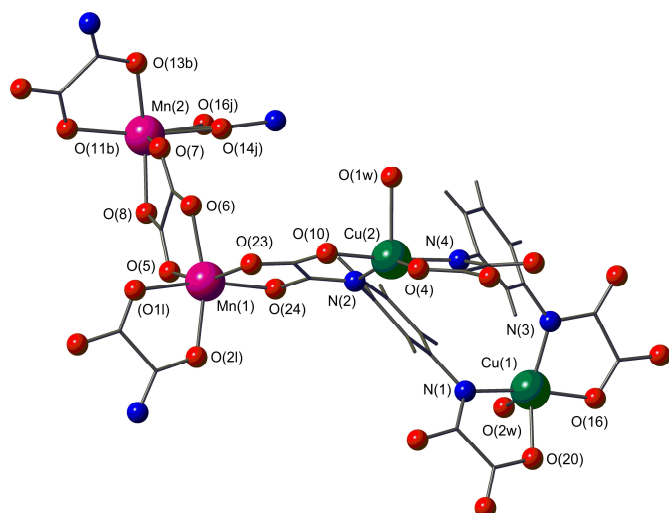


Fig. S2 Perspective view of a fragment of **1** with the labelling of the coordination metal environment [symmetry code: $b = -x+1/2, y+1/2, -z+1/4$; $j = x, y, -z$; $l = x-1/2, -y+1/2, z+1/4$].

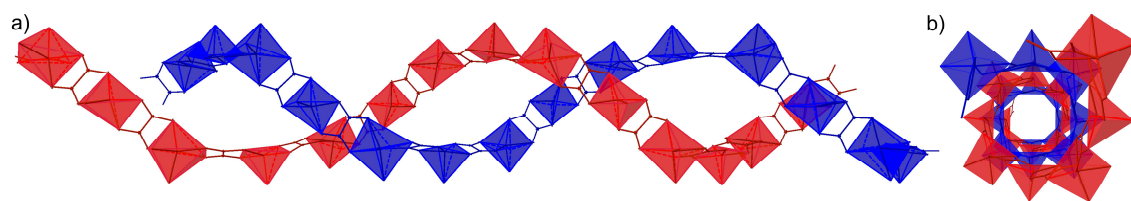


Fig. S3 Perspective (a) and lateral (b) views of a fragment of the double helical chain motif of **1**. Metal and ligand atoms are represented by polyhedra and sticks, respectively. Each Mn^{II}Cu^{II} chain of the double-stranded helix is depicted in red and blue colours. Hydrogen atoms, *m*-phenylene spacers, counteranions and crystallization water molecules are omitted for clarity.