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Electronic Supplementary Information

A Heterobimetallic [$\mathrm{Mn^{II}}_5\mathrm{Cu^{II}}_5$] Nanowheel Modulated by a Flexible Bis-Oxamate Type Ligand

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Synthesis and Materials

$MnCl_2 \cdot 4H_2O$ and dimethylsulfoxide were purchased from Sigma-Aldrich and used as received. The precursor $(Bu_4N)_4[Cu_2(edpba)_2] \cdot 4H_2O$ was prepared according to a previously reported procedure.[1]

$[Mn^{II}_5Cu^{II}_5(edpba)_5(dmso)_7(H_2O)_5] \cdot 2dmso \cdot 4H_2O$ was obtained as follows: $(Bu_4N)_4[Cu_2(edpba)_2] \cdot 4H_2O$ (0.050 g, 0.03 mmol) dissolved in 1.0 mL of dimethylsulfoxide was introduced in a test tube; then, 7.0 mL of a 1:1 dmso:water (v/v) mixture was slowly poured into the tube; finally, 2.0 mL of an aqueous solution of $MnCl_2 \cdot 4H_2O$ (0.030 g, 0.15 mmol) was added dropwise. The resulting solution was allowed to diffuse at room temperature in a test tube and X-ray quality dark green prismatic crystals were grown after four weeks. Yield: 45%. Anal. Calcd for $C_{108}H_{132}Cu_5Mn_5N_{10}O_{48}S_9$ (**1**): C, 40.29; H, 4.13; N, 4.35; Cu, 9.87; Mn, 8.53%. Found: C, 40.61; H, 3.88; N, 4.58; Cu, 10.22; Mn, 8.91%. IR/cm^{-1}: 3427 (νO-H), 1618, 1603 and 1583 (νC=O), 1568 (νC=C), 1485, 1450 and 1342 (δ-CH_2-) and 1015 (νS=O).

This formula was determined by elemental analysis and TG curves in both atmospheres (please, see below).

Physical Measurements

Elemental analysis (for C, H, N) was performed with a Perkin-Elmer 2400 analyzer**.** The manganese and copper contents were determined by atomic absorption spectrometry with a Hitachi Z-8200 Polarized Atomic Absorption Spectrophotometer. The thermal studies (TG/DTA) of polycrystalline sample were conducted on a Shimadzu TG-60 thermal analyzer by using *ca.* 3.0–5.0 mg of the product packed in an alumina crucible. The samples were heated at 10 °C min^{-1} from room temperature to 900 °C in a dynamic air and nitrogen atmospheres (flow rate = 50 cm^3 min^{-1}). The infrared spectrum was recorded on a Perkin-Elmer FTIR spectrophotometer using KBr pellets in the range 4000–400 cm^{-1} with an average of 128 scans and 4 cm^{-1} of spectral resolution. The magnetic susceptibility measurements were carried out on crushed single crystals in the temperature range 1.9–295 K with a Quantum Design SQUID magnetometer and using applied magnetic fields of 0.1 T ($T \geq 100$ K) and 100 G ($T < 100$ K).

Diamagnetic corrections of the constituent atoms were estimated from Pascal's constants[2] as -151×10^{-6} cm^3 mol^{-1} K per one mole of copper(II) ions. Experimental susceptibilities were also corrected for the temperature-independent paramagnetism [60 x 10^{-6} cm^3 mol^{-1} per copper(II)] and the magnetization of the sample holder for **1**. X-ray diffraction data were collected in the Bragg/Brentano mode (deg s^{-1}) using monochromatic Cu-Kα radiation.

Crystal Data Collection and Refining

X-ray diffraction data collections were performed on an Oxford-Diffraction GEMINI diffractometer by using Graphite-Enhance Source Cu-K_{α} radiation (λ = 1.5418 Å). The measurement was performed at 150 K as shown in Table S1. Data integration and scaling of the reflections for compound **1** was carried out with the *Crysalis* suite of programs.[3] Final unit cell parameters were based on the fitting of all reflections positions. Analytical[3] absorption corrections were performed using the *Crysalis* suite of programs and the space group identification was done with *XPREP*[4]. The structure of compound **1** was solved *via* direct methods using the *SUPERFLIP*[5] program. The positions of all atoms could be unambiguously assigned on consecutive difference Fourier maps. 5 DMSO non-coordinated solvent molecules were included in the structure and refined with occupation lower than 1 Refinements were performed by using *SHELXL*[4] based on F^2 through a full-matrix least squares routine. All atoms except hydrogen atoms and non-coordinated water molecules were refined with anisotropic atomic displacement parameters. All hydrogen atoms were located in difference maps and included as fixed contributions according to the riding model.[6] For organic moieties C–H = 0.97 Å and $U_{iso}(H) = 1.2\ U_{eq}(C)$ for methylene groups and aromatic carbon atoms. Methyl groups C–H = 0.97 Å and $U_{iso}(H) = 1.5\ U_{eq}(C)$. During the refinement it was noticed some remarkable disordered solvent molecules in the structure. The occupancy of all disordered atoms were fitted to better U_{iso} between them and the remaining structure. After all molecules could be assigned, a high residual difference Fourier map was observed. Having in mind the distance between the $[Mn^{II}_5Cu^{II}_5]$ moieties and being supported by other characterization techniques, we conclude these voids are occupied by disordered solvent molecules. Squeeze techniques were applied using *PLATON*[7] suite in **1** to remove the spread and unsigned density maxima in Fourier map. The voids left after the procedure are compatible to molecular structure proposed for this compound and are supported by other chemical characterizations. Mercury program[8] was used to perform the graphical manipulations and to simulate the X-ray powder diffraction pattern from the atomic positions obtained from the single crystal structure analysis. The crystal data and structure refinement of **1** are listed in Table S1.

Table S1. Crystal Data Details of the Structure Determination for **1**.

	1
Formula	$C_{111.50} H_{140.50} Cu_5 Mn_5 N_{10} O_{48.75} S_{10.75}$
Formula weight	3337.88
Crystal size (mm)	0.60 × 0.21 × 0.13
Crystal System	Monoclinic
Space group	$P2_1/c$
T (K)	150 (2)
a (Å)	23.2646 (19)
b (Å)	31.545 (2)
c (Å)	23.7317 (7)
α (Å)	90
β (Å)	102.528 (5)
γ (Å)	90
V (Å^3)	17001.8 (18)
Z	4
D_{calcd} (g cm^{-3})	1.304
μ (mm^{-1})	5.422
F(000)	6846
R (F_o^2) [$I > 2\sigma(I)$]	0.1107
R_w (F_o^2) [$I > 2\sigma(I)$]	0.2962

Crystallographic data for the structure **1** was deposited with the Cambridge Crystallographic Data Centre with reference number CCDC 1031230.

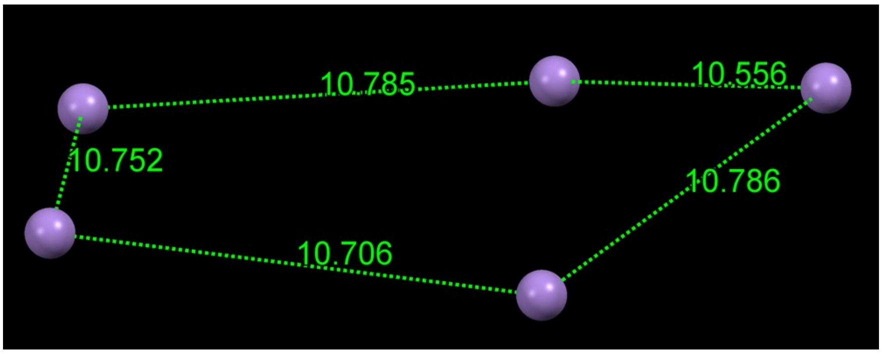

Fig. S1 Schematic representation of the wheel conformation of **1** involving the manganese(II) ions (here represented as purple balls). The green dashed lines show the distances between the manganese(II) ions.

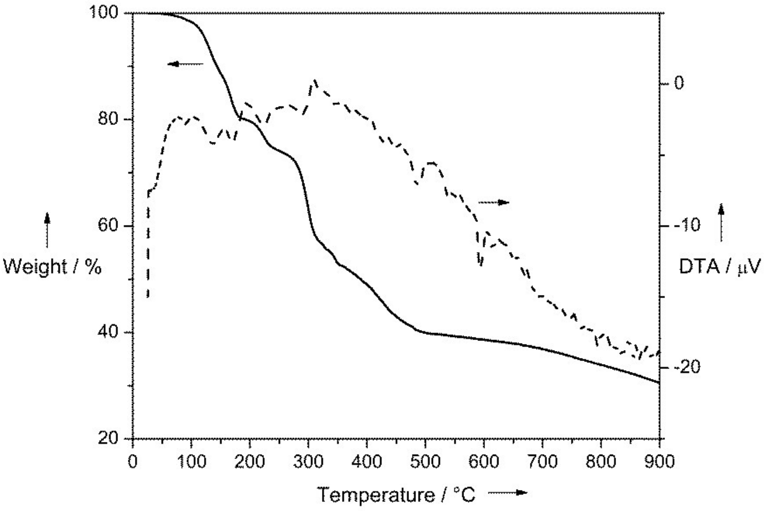

Fig. S2 TG and DTA curves of **1** collected in nitrogen atmosphere. The solid line represent TG curve whereas broken line is DTA curve.

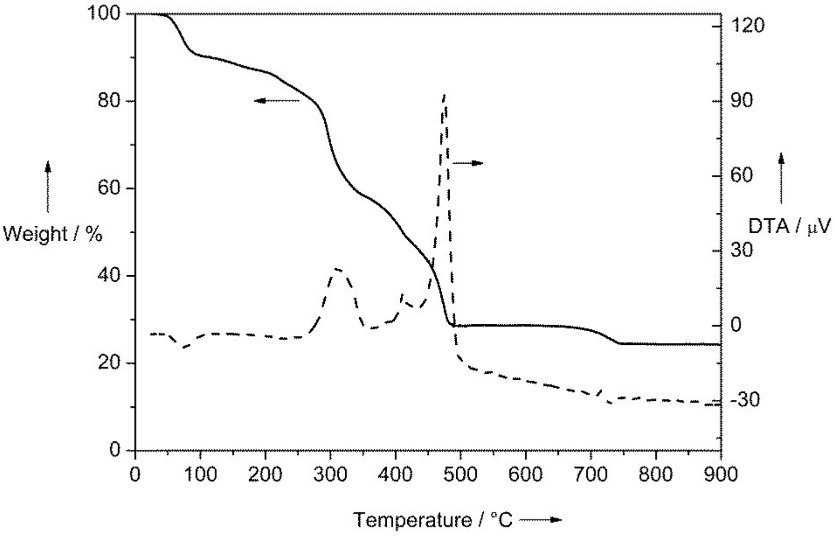

Fig. S3 TG and DTA curves of **1** collected in air atmosphere. The solid line represent TG curve whereas broken line is DTA curve.

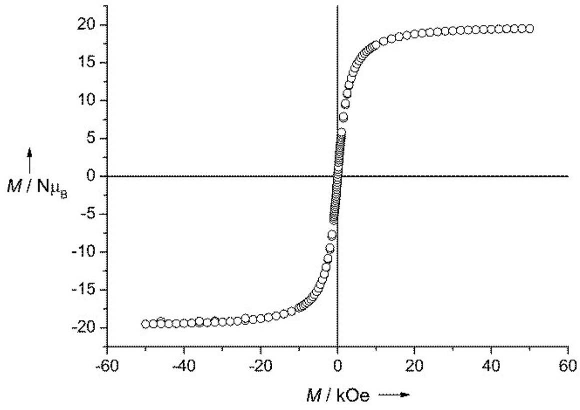

Fig. S4 Hysteresis loop of **1** at 2 K.

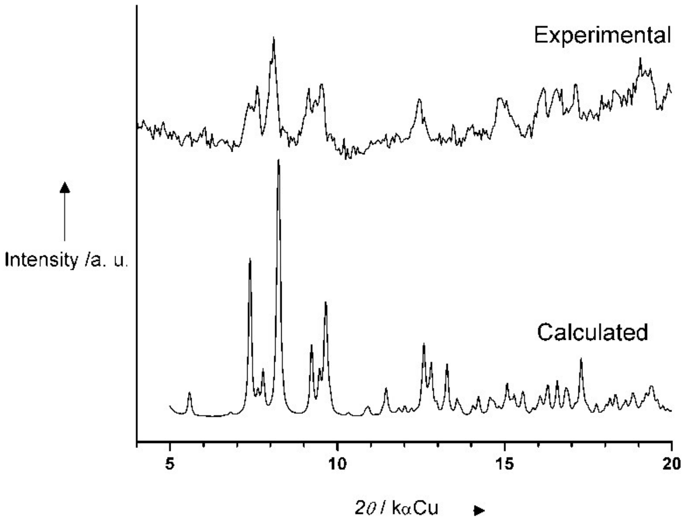

Fig. S5 X-ray diffraction pattern obtained by a collection of crushed single crystals of **1**.

References

1 W. D. do Pim, W. X. C. Oliveira, M. A. Ribeiro, E. N. de Faria, I. F. Teixeira, H. O. Stumpf, R. M. Lago, C. L. M. Pereira, C. B. Pinheiro, J. C. D. Figueiredo-Júnior, W. C. Nunes, P. P. de Souza, E. F. Pedroso, M. Castellano, J. Cano, M. Julve, *Chem. Commun.,* 2013, **49**, 10778.

2 O. Kahn, Molecular Magnetism, VCH, New York, 1993.

3 Xcalibur CCD system, CrysAlisPro Software system, version 1.171.35.15 (Agilent Technologies UK Ltd, Oxford 2011).

4 G. M. Sheldrick, *Acta Crystallogr.*, 2008, **A64**, 112.

5 L. Palatinusz, G. Chapuis, SUPERFLIP - a computer program for the solution of crystal structures by charge flipping in arbitrary dimensions. *J. Appl. Cryst.*, 2007, **40**, 786.

6 C. K. Johnson, ORTEP, Crystallographic Computing, edited by F. R. Ahmed, pp 217-219, Copenhagen, Denmark.

7 A.L. Spek, *Acta Cryst.,* 2009, **D65**, 148.

8 C. F. Macrae, I. J. Bruno, J. A. Chisholm, P. R. Edgington, P. McCabe, E. Pidcock, L. Rodriguez-Monge, R. Taylor, J. van de Streek, P. A. Wood, Mercury CSD 2.0 - New Features for the Visualization and Investigation of Crystal Structures. *J. Appl. Cryst.*, 2008, **41**, 466.