Electronic supplementary information

Three different types of bridging ligands in a 3d-3d'-3d'' heterotrimetallic chain

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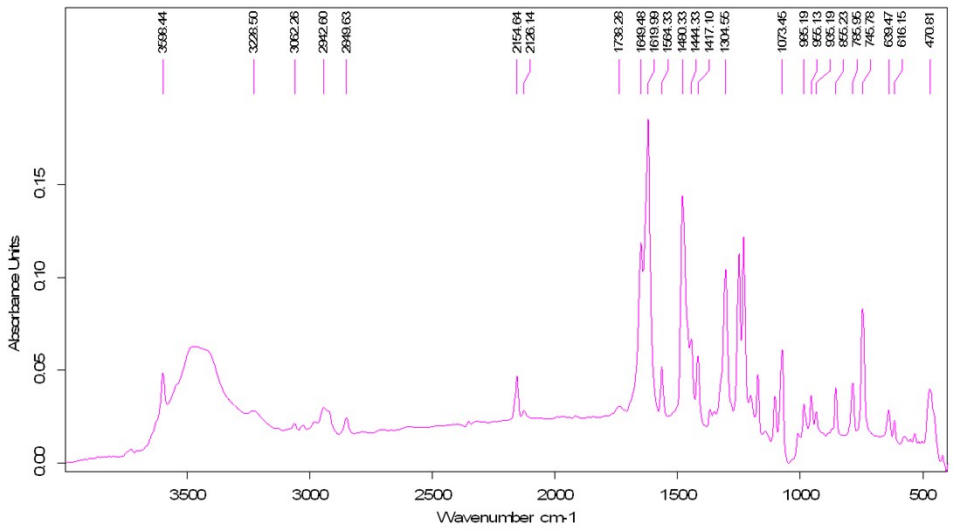

Figure S1. FTIR spectrum of **1**.

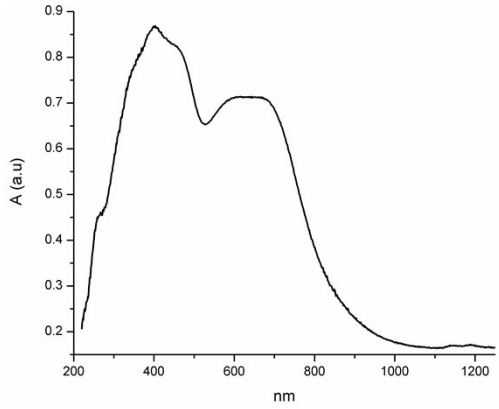

Figure S2. Solid-state UV-Vis spectrum of **1**.

The UV-Vis spectra of **1** exhibits three bands in the visible region: (i) the first peak at ca. 400 nm with a shoulder at 450 nm, which correspond most likely to the electronic transitions of the chromium(III) ion and (ii) two other absorptions at 610 and 705 nm that could be assigned to the d-d transitions of the square pyramidal copper(II) ions.

Lever, A.B.P. *Crystal Field Spectra Inorganic Electronic Spectroscopy*, 1st ed., Elsevier, Amsterdam, p. 249, (1968).

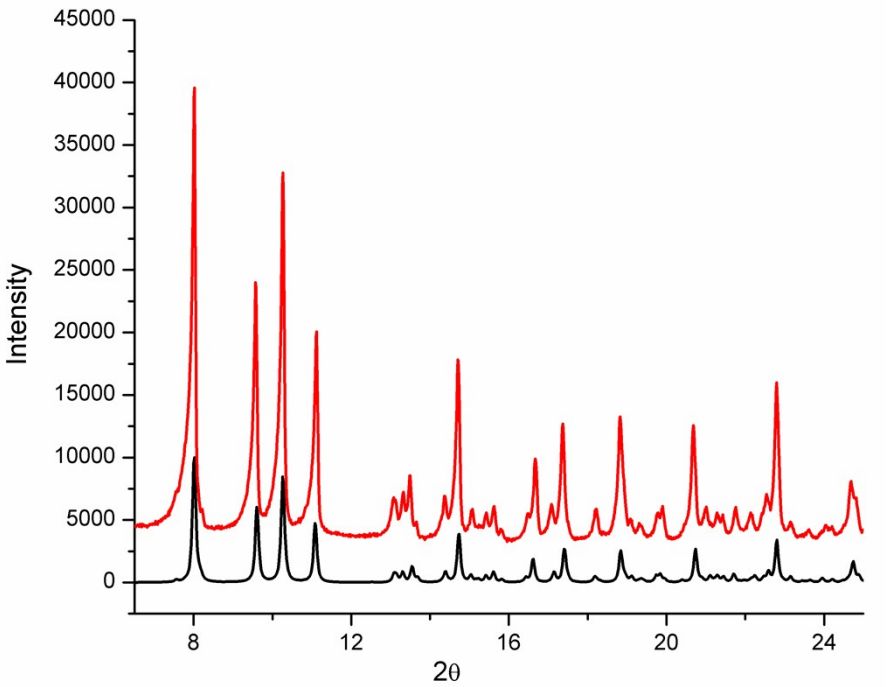

Figure S3. Experimental (red) and simulated (black) PXRD pattern for **1**.

Table S1. Crystallographic data, details of data collection and structure refinement parameters

Empirical formula	$C_{45}H_{50}CrCu_2Mn_2N_{10}O_{15}$
Formula weight	1231.54
Temperature/K	293(2)
Crystal system	Triclinic
Space group	*P*-1
a/Å	12.6009(6)
b/Å	13.4206(10)
c/Å	18.2930(10)
α/°	101.278(5)
β/°	99.831(5)
γ/°	114.139(6)
V/Å^3	2657.7(3)
Z	2
D_{calc}/g cm^{-3}	1.574
μ/mm^{-1}	1.521
Crystal size/mm^3	0.2 × 0.05 × 0.02
θ_{min}, θ_{max} (deg)	3.06 to 25.03
Reflections collected	23304
Independent reflections	9327 [R_{int} = 0.0596]
Data/restraints/parameters	9429/0/681
GOF[c]	1.023
R_1[a] [$I > 2\sigma(I)$]	0.0565
wR_2[b] (all data)	0.0927

[a]$R_1 = \Sigma||F_o| - |F_c||/\Sigma|F_o|$. [b]$wR_2 = \{\Sigma[w(F_o^2-F_c^2)^2]/\Sigma[w(F_o^2)^2]\}^{1/2}$. [c] GOF = $\{\Sigma[w(F_o^2-F_c^2)^2]/(n-p)\}^{1/2}$, where *n* is the number of reflections and *p* is the total number of refined parameters.

Figure S4. Coordination geometry for Mn1 (distorted pentagonal pyramidal) and Mn2 (distorted monocapped trigonal prism).

Table S2. Results of the SHAPE1 analysis for $\{MnNO_6\}$, $\{MnN_2O_4\}$, $\{CuN_2O_2\}$ and $\{CuN_2O_3\}$ fragments in **1**.[a]

Structure [$MnNO_6$]	PBPY-7[a]	COC-7[a]	**CTPR-7[a]**	JPBPY-7[a]
	20.293	19.143	**17.682**	27.377
Structure [MnN_2O_4]	**PPY-6[b]**	OC-6[b]	TPR-6[b]	JPPY-5[b]
	33.054	39.270	34.418	36.861

[a]PBPY-7, D_{5h} Pentagonal bipyramid; COC-7, C_{3v} Capped octahedron; CTPR-7, C_{2v} Capped trigonal prism; JPBPY-7, D_{5h} Johnson pentagonal bipyramid (J13)
[b]PPY-6, C_{5v} Pentagonal pyramid; OC-6, O_h Octahedron; TPR-6, D_{3h} Trigonal prism; JPPY-5, C_{5v} Johnson pentagonal pyramid (J2).

[a] (1) M. Llunell, D. Casanova, J. Cirera, J. M. Bofill, P. Alemany, S. Alvarez, M. Pinsky and D. Avnir, SHAPE: Continuous shape measures of polygonal and polyhedral molecular fragments, 1.1b, University of Barcelona: Barcelona, 2005; (2) D. Casanova, M. Llunell, P. Alemany, S. Alvarez, *Chem. Eur. J.*, 2005, **11**, 1479.

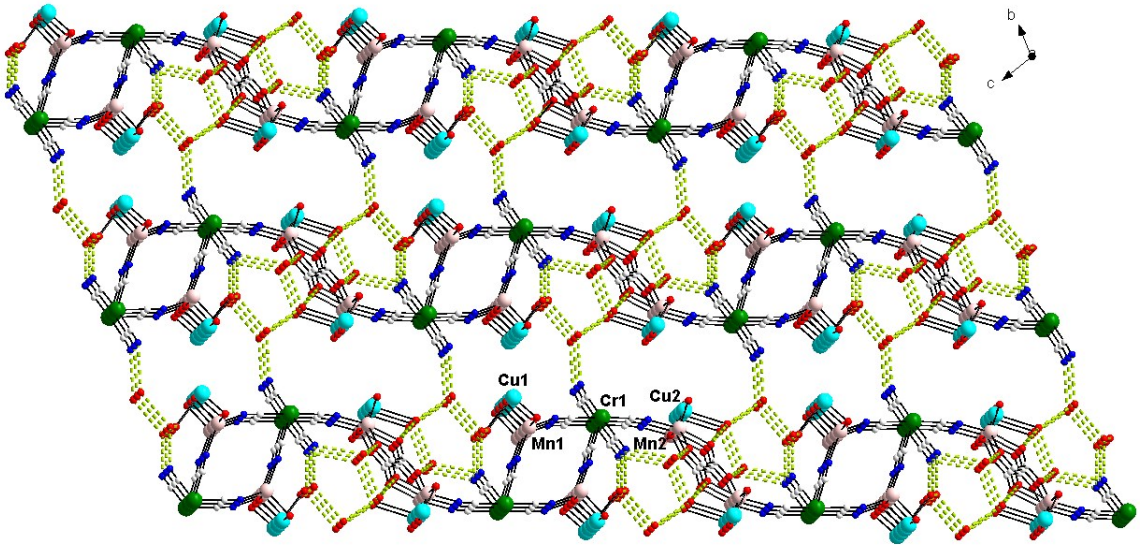

Figure S5. View of the fragment of the supramolecular 3 D supramolecular network of **1**. Hydrogen bonds are shown as dashed lines.

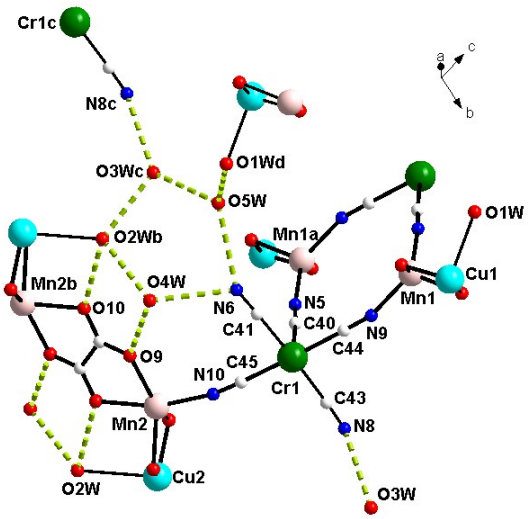

Figure S6. A detail of the hydrogen bonding in **1** illustrating the assembling role of the water molecules.

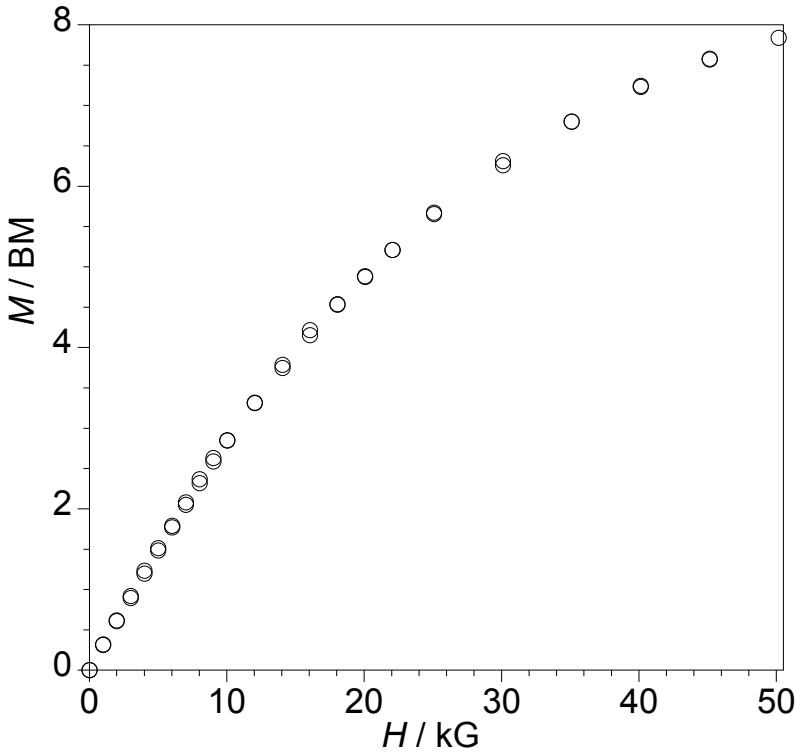

Figure S7. Filed dependence of the magnetization for **1** at 2 K

Table S3. Geometrical parameters associated to the hydrogen bonds in **1**[a,b]

D---H···A	D – H/ Å	H···A/ Å	D···A/ Å	D - H···A, deg
O3Wc ··· O2Wb	0.86	2.07	2.822(5)	145
O5W ··· N6	0.86	2.17	3.016(7)	168
O3Wc ··· N8c	0.86	2.14	2.971(6)	163
O1Wd ··· O5W	0.89	1.91	2.780(8)	168
O5W ··· O3Wc	0.85	1.99	2.823(6)	168
O2Wb ··· O4W	0.86	2.04	2.769(5)	142
O4W ··· N6	0.86	2.11	2.951(6)	167
O2Wb ··· O10	0.86	2.00	2.842(6)	164
O4W ··· O9	0.86	2.01	2.840(6)	161

[a] D = donor and A = acceptor; [b] Symmetry code: (b) = -*x*, -1-*y*, 1-*z*; (c) = *x*, -1+*y*, *z*; (d) = 2-*x*, -*y*, 2-*z*