Experimental Procedures

^{1}H and ^{13}CNMR spectra were recorded on an av 500 MHz spectrometer. 1-(3-((Bis(2-hydroxyethyl)amino)methyl)-2-hydroxy-5-methyl)phenyl)ethanone was prepared by published procedures.[1] Solvents and reagents were used as received from commercial suppliers.

Synthesis of (H_4L) 1-(3-((Bis(2-hydroxyethyl)amino)methyl)-2-hydroxy-5-methyl)phenyl)ethanone oxime

1-(3-((Bis(2-hydroxyethyl)amino)methyl)-2-hydroxy-5-methyl)phenyl)ethanone (10.8 g, 40 mmol), hydroxylamine hydrochloride (3.5 g, 50 mmol) and sodium acetate (4.14 g, 50 mmol) were dissolved in 500 mL of ethanol. The mixture was refluxed under N_2 for 4 h. A white precipitate was filtered off from the warm ethanol solution. The solvent evaporated to dryness, CH_2Cl_2 added and a white product collected after filtration (10.16 g, 90%). ^{1}H NMR (500 MHz, DMSO): δ 7.12 (bs, 1H), 7.05 (bs, 1H), 3.60 (s, 2H), 3.54 (t, *J*=6.2 Hz, 4H), 2.53 (t, *J*= 6.2 Hz, 4H), 2.23 (s, 3H), 2.22 (s, 3H).^{13}C NMR (500 MHz, DMSO): δ 157.28 (1C, C_{ar}OH), 153.86 (1C, *C*NOH), 131.34 (1C, *C*H), 127.61 (1C, *C*H), 126.99 (1C, *C*), 124.34 (1C, *C*), 121.01 (1C, *C*), 59.14 (2C, CH_2), 56.51 (2C, CH_2), 54.78 (1C, CH_2), 21.69 (1C, CH_3), 12.73 (1C, CH_3).

Synthesis of compound 1: $MnCl_2 \cdot 4H_2O$ (125 mg, 0.5 mmol), (126 mg, 0.5 mmol) 1-(3-((Bis(2-hydroxyethyl)amino)methyl)-2-hydroxy-5-methyl)phenyl)ethanone (133 mg, 0.5 mmol), and NaOMe (81 mg, 1.5 mmol) were dissolved in MeOH (30 mL). The solution stirred for 3 h, before being filtered and allowed to stand. Dark-brown hexagonal prism-like X-ray quality crystals were obtained after room temperature evaporation of the mother liquor during 3 days. Elemental analysis (%) calculated (found) for $C_{84}H_{108}ClMn_6N_6NaO_{24}$ (1973.84): C 51.11 (51.22), H 5.52 (5.27), N 4.26 (4.04).

Synthesis of compound 2: $MnCl_2 \cdot 4H_2O$ (300 mg, 1.5 mmol), 1-(3-((Bis(2-hydroxyethyl)amino)methyl)-2-hydroxy-5-methyl)phenyl)ethanone oxime (140 mg, 0.5 mmol), and ^{t}BuONa (240 mg, 2.5 mmol) were dissolved in MeOH (30 mL). After 5 minutes of stirring, NEt_3 (0.28 mL, 2 mmol) was added, and the solution stirred for a further 3 h, before being filtered and allowed to stand. Dark-brown plate-like X-ray quality crystals were obtained after room temperature evaporation of the mother liquor during 5 days. Elemental analysis (%) calculated (found) for $C_{80}H_{148}Mn_{12}N_8O_{40}$ (2521.34): C 38.11 (38.37), H 5.92 (6.11), N 4.44 (4.25).

Crystallographic details

For weakly diffracting crystals of complex **1,** X-ray data were collected using synchrotron radiation at the Diamond Light Source UK, beamline I19 (λ=0.6889Å) situated on an undulator insertion device with a combination of double crystal monochromator, vertical and horizontal focussing mirrors and a series of beam slits (primary white beam and either side of the focussing mirrors). X-ray data were collected on a Crystal Logic diffractometer and Rigaku Saturn 724+ detector. The X-ray data for complex **2** were collected at 100 K on Rigaku AFC12 goniometer equipped with an enhanced sensitivity (HG) Saturn 724+ detector mounted at the window of an FR-E+ Superbright MoKα (λ=0.71075 Å) rotating anode generator with HF Varimax optics.[2] Unit cell parameters were refined against all data. An empirical absorption correction was carried out using CrystalClear software.[3] The crystal structure of complex **1** was solved by the charge-flipping method implemented in SUPERFLIP,[4] whereas for complex **2** direct methods were used as implemented in SHELXS-

97.[5] Both crystal structures were refined on Fo^2 by full-matrix least-squares refinements using SHELX-2013 software.[5] All non-hydrogen atoms were refined with anisotropic displacement parameters. All hydrogen atoms were added at calculated positions and refined using a riding model with isotropic displacement parameters based on the equivalent isotropic displacement parameter (U_{eq}) of the parent atom. Both crystal structures contain large accessible voids occupied by heavily disordered solvent molecules of MeOH/H_2O which have been removed with the PLATON/SQUEEZE routine.[6,7] This improves models and led structure refinement to satisfactory convergence. Even with the use of synchrotron radiation on crystals of complex **1,** the diffraction pattern was weak and intensity spots decayed quickly for higher resolution shells. Additionally, the crystal was sensitive to radiation damage.

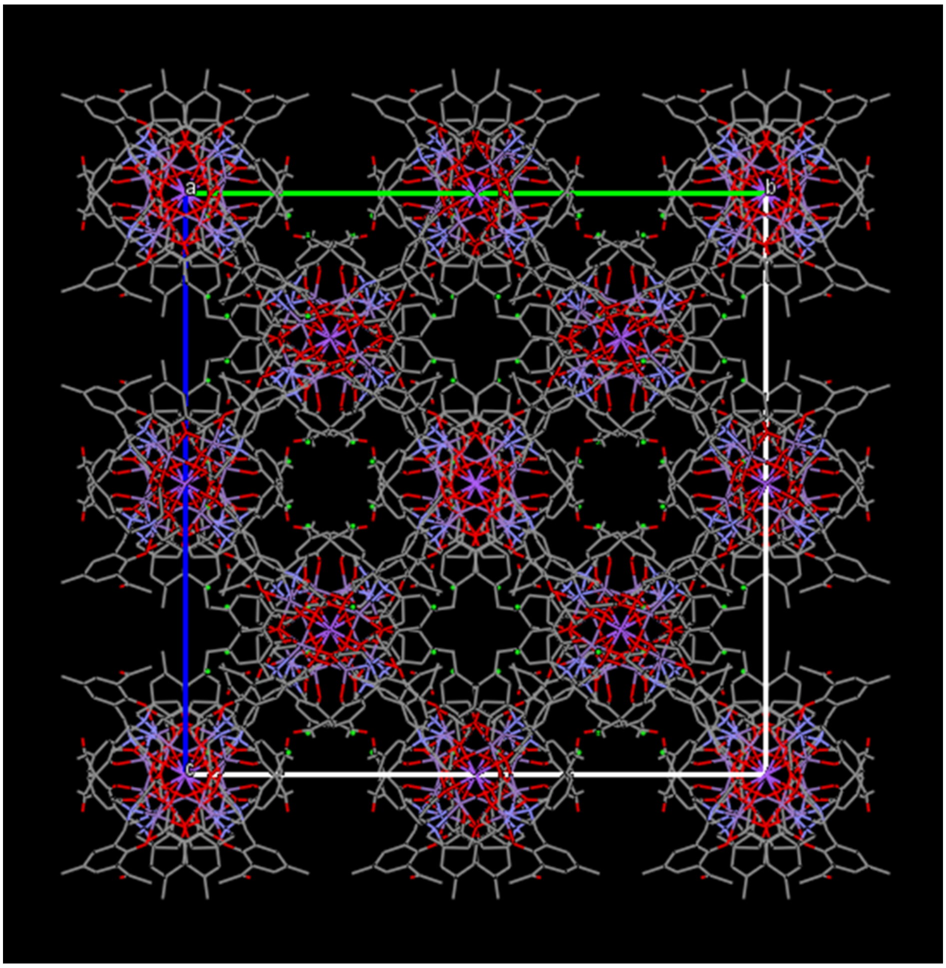

Figure S1. Packing of the molecules of **1** in the crystal. H-atoms removed.

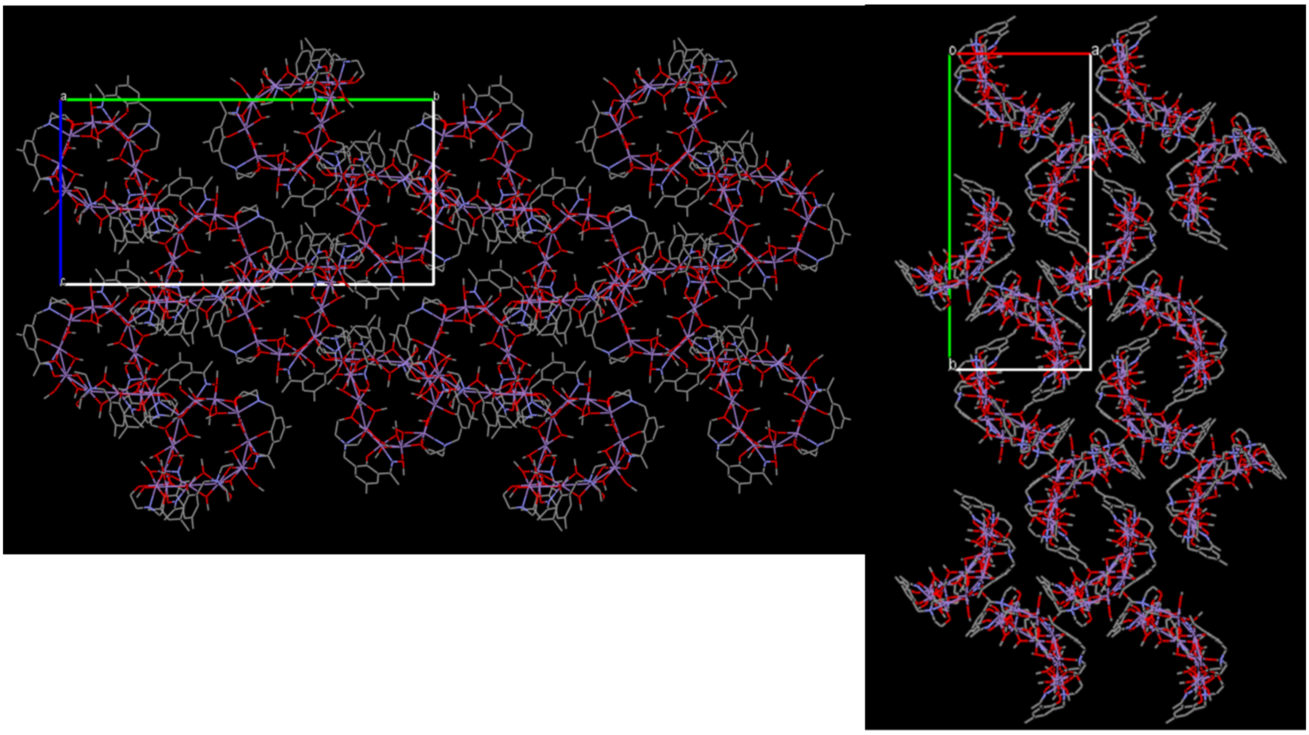

Figure S2. Packing of the molecules of **2** in the crystal, as viewed down the *a*-(left) and *c*-axes (right). H-atoms removed.

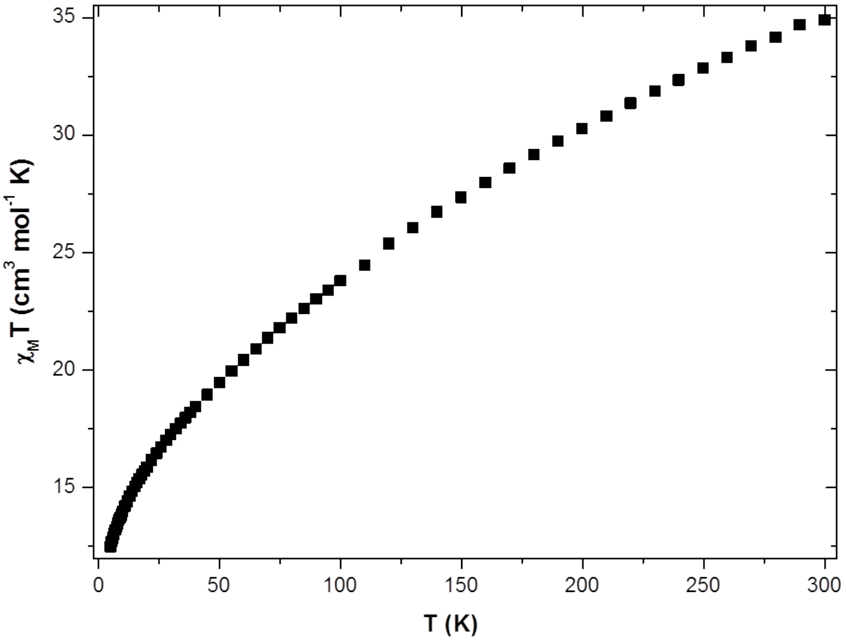

Figure S3. Plot of the $\chi_M T$ product versus T for **2**.

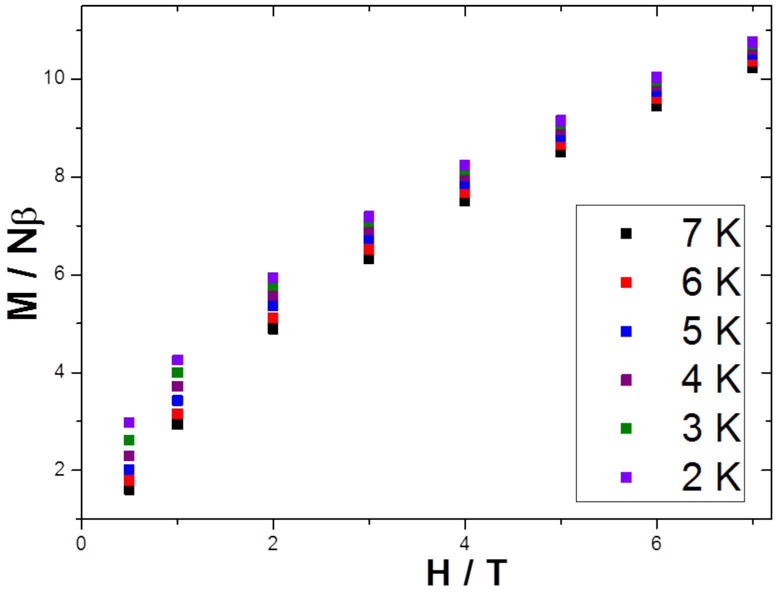

Figure S4. Plot of *M / Nβ vs H* for **2** in the indicated field and temperature ranges.

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