Supporting Information

A Truncated [Mn^{III}_{12}] Tetrahedron from Oxime-based [Mn_3O] Building Blocks.

Jamie M. Frost, Sergio Sanz, Thayalan Rajeshkumar, Mateusz B. Pitak, Simon J. Coles, Gopalan Rajaraman, Wolfgang Wernsdorfer, Jürgen Schnack, Paul. J. Lusby and Euan K. Brechin

Experimental Procedures

^{1}H and ^{13}C NMR spectra were recorded on an ava 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 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 is 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: $MnBr_2{\cdot}4H_2O$ (143 mg, 0.5 mmol), 1-(3-((bis(2-hydroxyethyl)amino)methyl)-2-hydroxy-5-methyl)phenyl)ethanone oxime (140 mg, 0.5 mmol) and trimesic acid (105 mg, 0.5 mmol) were dissolved in MeOH (25 ml). After 15 minutes of stirring, NEt_3 (0.3 mL, 2 mmol) was added, and the solution stirred for a further 3 h, before being filtered and allowed to stand. Dark-black rod-like X-ray quality crystals were obtained after room temperature evaporation of the mother liquor during 5 days. Elemental analysis (%) calculated (found) for $C_{204}H_{328}Mn_{12}N_{24}O_{96}$ (5311.94): C 46.12 (45.53), H 6.22 (5.97), N 6.33 (6.42).

Crystallographic details

Crystal data for 1:

Formula: $C_{204}H_{252}Mn_{12}N_{24}O_{77;}$ M_r = 4931.58; crystal dimensions: 0.15 × 0.03 × 0.03 mm; crystal system: Tetragonal; space group : $I4_1/a$; a = 39.8049(17) Å, b = 39.8049(17) Å, c = 37.7169(16) Å, α = β = γ = 90°; V = 59760(6) Å^3, Z = 8; ρ_{calc} = 1.096 Mg/m^3; μ = 0.558 mm^{-1}; *T* = 100 K; 128515 measured reflections; 26144 unique reflections [R_{int} = 0.0912] , 11542 with $F^2 > 2\sigma$, R(F, F2>2σ) = 0.0850; R_w(F^2, all data) 0.2596; $\Delta\rho_{min/max}$ =1.139/ -0.637 e Å^{-3}; θ_{max} = 25.027°. The X-ray data were collected at 100K 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]. X-ray data were recorded and integrated using Rigaku

CrystalClear[3] software. Crystal Structure was solved by charge-flipping methods using SUPERFLIP [4] and refined on F_o^2 by full-matrix least squares refinement using SHELX-2013[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. Black column crystals of **1** were highly sensitive to solvent loss. Spot intensities decay rapidly with $\sin\theta/\lambda$ with no significant data observed beyond 0.84 Å resolution. Crystal structure contains large accessible voids (~33% of the unit cell) occupied by highly disordered solvent (MeOH/H_2O). SQUEEZE[6] routine of PLATON[7] was used to remove highly diffused electron density from the crystal lattice. This results in better model and led structure refinement to satisfactory convergence. Furthermore, to maintain sensible geometries and model better atomic displacement parameters of librating diethanolamine groups, vibrational restraints (SIMU/DELU) and distance/angle restraints DFIX/DANG were used in SHELXL refinement. Some atoms have been restraint to have approximate isotropic behaviour with ISOR. In the crystal structure centre of the molecular cage is occupied by highly diffused partially occupied H_2O/MeOH molecules disordered over symmetry element (2-fold axis), however only one water molecule (O100) located at special has been refined. CCDC 949848.

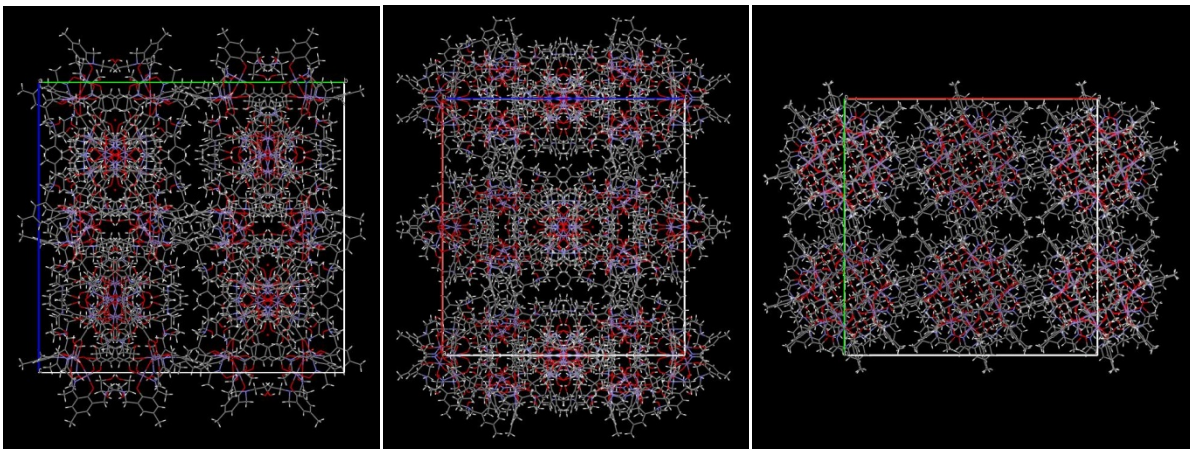

Figure S1. The packing of the molecules in the crystal, viewed down the *a*- (left), *b*- (middle), and *c*- (right) axes.

Computational Details:

The exchange parameter values (*J*) between Mn^{III} ions were calculated using Noodleman's broken symmetry method.[8,9] The B3LYP[10] functional along with TZV[11] basis sets for the Mn^{III} ions and SVP[12] basis sets for remaining atoms were employed in our calculations as implemented in the G09[13] suite of programs. For extracting the *J* values, the following spin Hamiltonian was used:

$$\hat{H} = -2J_1(S_{Mn1}S_{Mn2} + S_{Mn1'}S_{Mn2'} + S_{Mn4}S_{Cu6} + S_{Mn4'}S_{Mn6'}) - 2J_2(S_{Mn2}S_{Mn3} + S_{Mn2'}S_{Mn3'} + S_{Mn4}S_{Mn5} +$$

The *J* values were evaluated by solving the linear equations from different BS solutions. See Table S1. The exchange between different [Mn_3] triangles was evaluated using the HS and BS4 solutions.

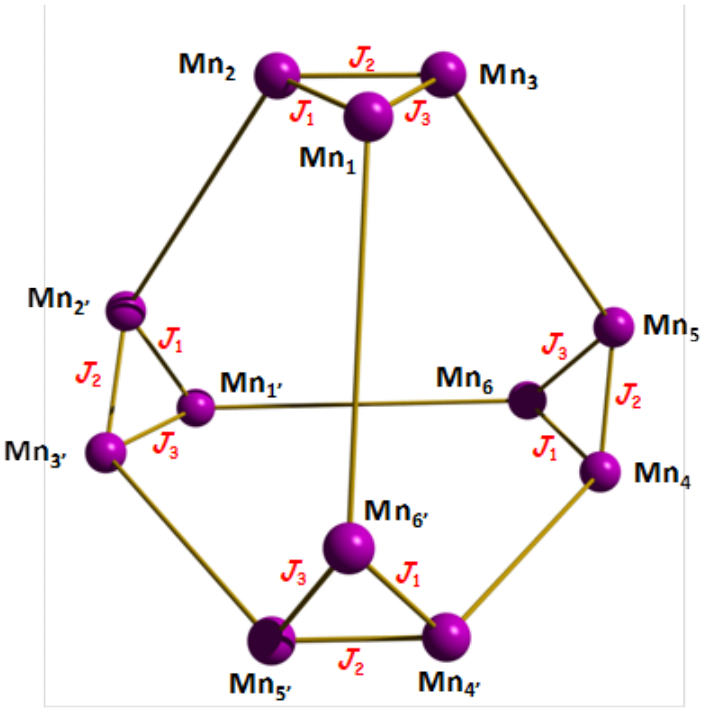

Figure S2. The intra-triangle exchange pathways (J_1-J_3) in **1**.

Configurations	Mn1	Mn2	Mn3	Mn4	Mn5	Mn6	Mn7	Mn8	Mn9	Mn10	Mn11	Mn12
HS	↑	↑	↑	↑	↑	↑	↑	↑	↑	↑	↑	↑
BS1	↓	↑	↑	↑	↑	↑	↑	↑	↑	↑	↑	↑
BS2	↑	↑	↓	↑	↑	↑	↑	↑	↑	↑	↑	↑
BS3	↓	↑	↓	↑	↑	↑	↑	↑	↑	↑	↑	↑
BS4	↓	↓	↓	↑	↑	↑	↑	↑	↑	↑	↑	↑

Table S1. The different spin configurations employed in the calculations of the magnetic exchange.

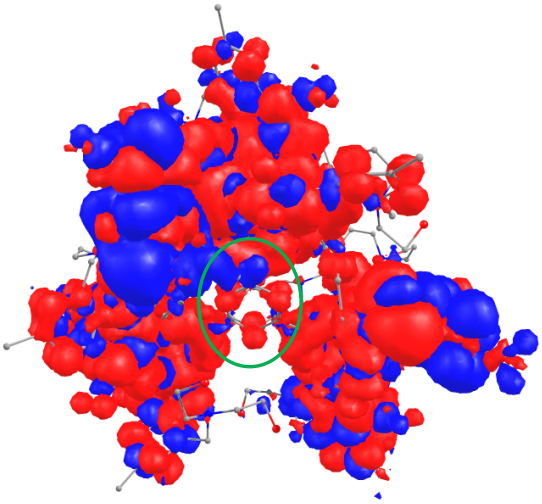

Figure S3. Computed spin density plot for the HS state of complex **1**. The spin densities on the benzene ring of the TMA ligands are highlighted to show spin polarisation.

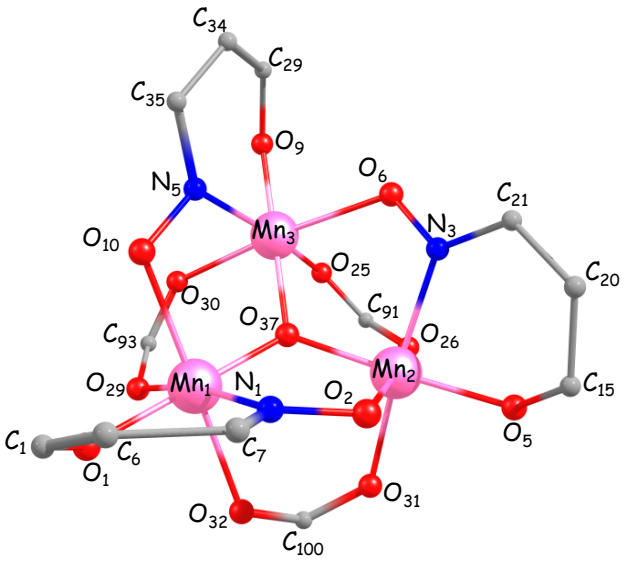

Figure S4. The [Mn_3] triangle of complex **1.** See Table S2 for structural parameters.

	Bond distance (Å)		Bond angle (˚)		Dihedral angle (˚)
Mn1-O37	1.871	Mn1-O37-Mn2	118.12	Mn1-O10-N5-Mn3	23.60
Mn1-O10	2.180	Mn1-O37-Mn3	119.16	Mn1-N1-O2	15.82

N5-O10	1.356	Mn1-N1-O2	115.10	Mn2-N3-O6-Mn3	10.18
Mn1-O29	1.953	Mn1-O10-N5	115.54		
Mn1-O1	1.853	Mn1-O29-C93	128.95		
Mn1-N1	1.984	Mn1-O32-C100	127.99		
N1-O1	1.368	Mn1-O1-C1	124.91		
Mn1-O32	2.220	Mn2-N3-O6	115.90		
Mn2-O37	1.889	Mn2-O2-N1	116.37		
Mn2-N3	2.017	Mn2-O31-C100	128.66		
N3-O6	1.333	Mn2-O5-C15	125.62		
Mn2-O5	1.896	Mn2-O26-C91	127.69		
Mn2-O31	1.981	Mn2-O37-Mn3	118.76		
Mn2-O2	2.181	Mn3-N5-O10	113.50		
O2-N1	1.368	Mn3-O6-N3	117.25		
Mn2-O26	2.206	Mn3-O9-C29	113.75		
Mn3-O6	2.132	Mn3-O25-C91	123.90		
Mn3-O9	1.903	Mn3-O30-C93	126.86		
Mn3-N5	2.018				
Mn3-O37	1.839				
Mn3-O25	2.001				
Mn3-O30	2.219				

Table S2. Selected structural parameters for the [Mn_3] triangle. See Figure S4 for atom labels.

Beta/Alpha	xz	xy	z^2	yz	x^2-y^2
xy	0.10	0.01	-0.01	0.02	-0.09
yz	0.10	0.00	-0.05	0.03	-0.01
z^2	-0.04	0.01	**0.02**	-0.03	-0.05
xz	-0.13	0.03	0.00	-0.31	-0.01
x^2-y^2	-0.07	0.13	-0.02	0.02	0.15

Table S3. Calculated overlap integral values corresponding to J_2 in complex **1**.

Beta/Alpha	z^2	xz	yz	xy	x^2-y^2

xy	0.03	-0.03	0.12	0.02	-0.19
yz	0.07	-0.07	0.10	-0.01	0.07
z^2	**0.26**	0.01	0.03	-0.01	0.02
xz	0.03	-0.07	0.14	0.11	0.05
x^2-y^2	-0.11	0.01	0.03	0.02	-0.15

Table S4. Calculated overlap integral values corresponding to J_3 in complex **1**.

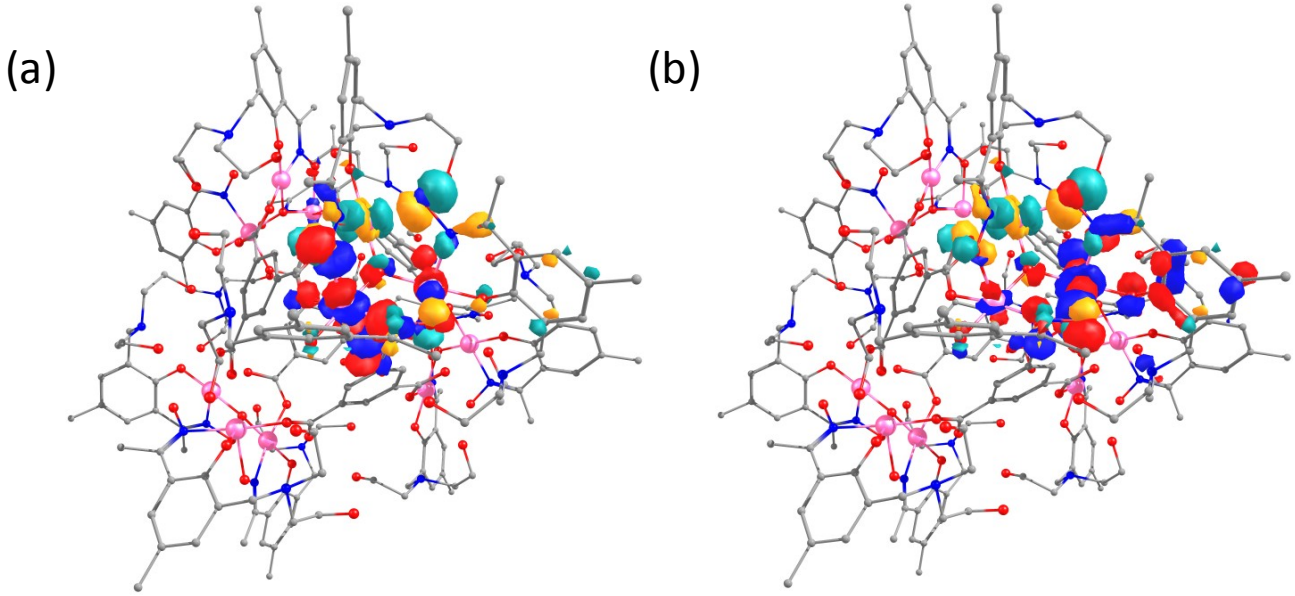

Figure S5. The superimposed d_z^2 orbitals of the Mn^{III} ion corresponding to: (a) the J_2 interaction; (b) the J_3 interaction. See Table S3 and S4 for the computed overlap integral values.

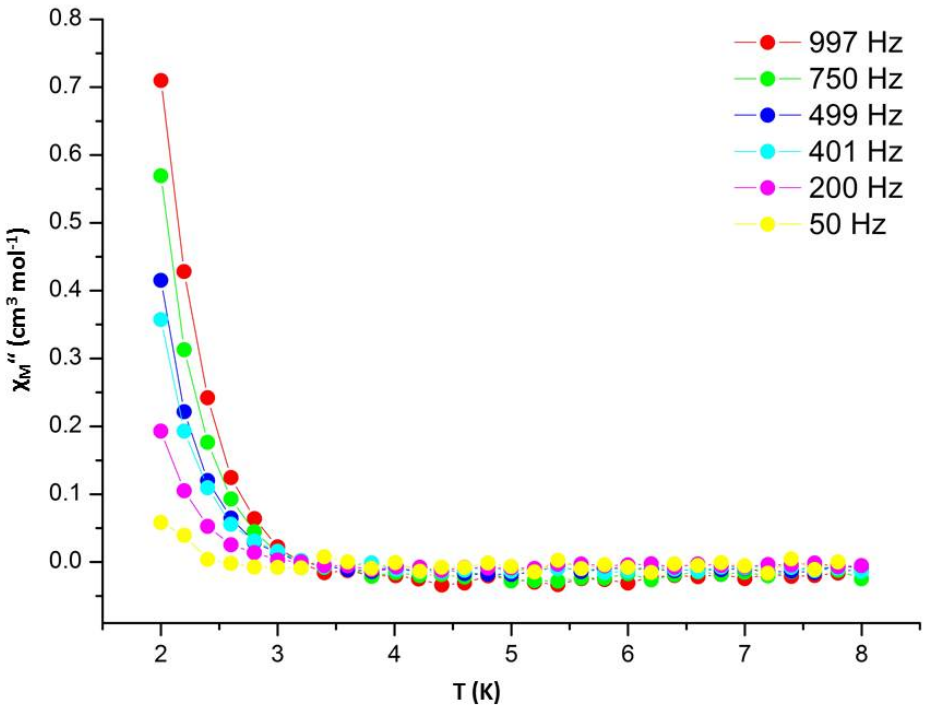

Figure S6. Out-of-phase (χ'') ac susceptibility data for complex **1** measured in the indicated field and temperature ranges.

FTLM calculations:

The curves in Fig. S7 depict various scenarios for J_1-J_3, and $\boldsymbol{d_i}$=$\boldsymbol{D}$. They do not represent fits, since this is impossible for such a huge quantum spin system, but are intended to qualitatively estimate the order of magnitude of exchange and anisotropy.

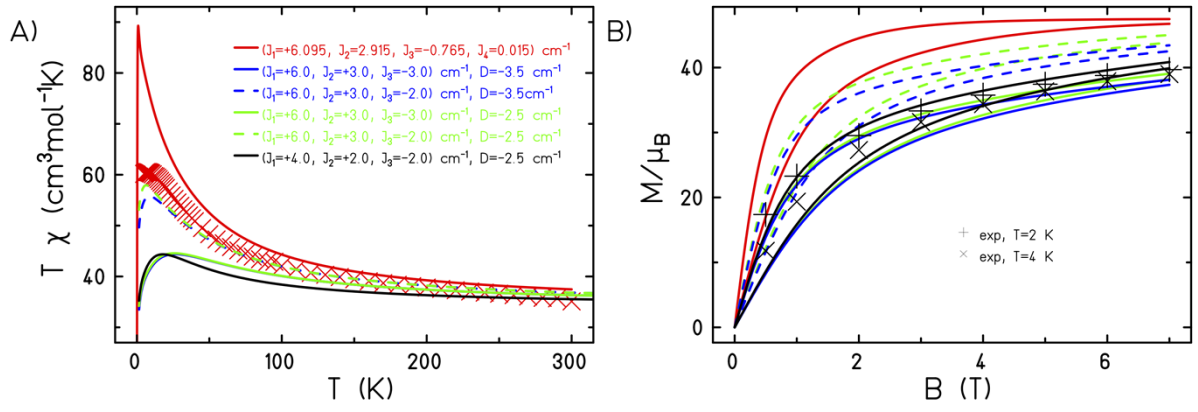

Figure S7. (A) The magnetic susceptibility of **1** at B=0.1 T (experimental data represented by crosses) and various simulations using g=1.98. (B) The magnetisation at T=2 K and T=4 K.

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