Contents

Single Crystal X-ray diffraction

Crystallographic data were collected for **1** and **2** at 100 K using Mo-Kα radiation (λ = 0.71073 Å). For **1** a Bruker APEXII CCD diffractometer with an Oxford Cryosystems n-Helix low-temperature device mounted on a sealed tube generator was used; for **2** a Rigaku AFC12 goniometer equipped with an (HG) Saturn724+ detector mounted on an FR-E+ SuperBright rotating anode generator with HF Varimax optics (100µm focus).[1] All the structures were solved using SHELXT[2] and refined using full-matrix least squares refinement on F^2 using SHELX2014[3] within OLEX2.[4] Unless otherwise stated below positional and anisotropic adps were refined for all non-H atoms and hydrogen atoms were placed in geometrically calculated positions and included as part of a riding model, except those from the NH_2 groups in complex **1** (*vide infra*). Rigid-bond restraints (RIGU)[5] have been applied to both **1** and **2**.

For **1** there was some disorder present in the structure with one CH_3CN molecule modelled over 2 partially occupied sites with occupancies refined competitively for the two parts. Distance restraints were applied and isotropic adps retained for the nitrogen atoms and carbon atoms of the minor component. Similarly for O4s and O5s, lattice water molecules, which were refined to sum to an occupancy of 1 and are approx 0.75 and 0.25 occupied respectively. The NH_2 hydrogen atoms were located from difference Fourier maps and refined with distance restraints and Uiso=1.2U(eq) for N.

For **2** disorder is also present in the HEt_3N^+, with one ethyl group modelled over two partially occupied sites with 0.8:0.2 occupancies. Distance restraints were applied and all partially occupied sites were refined with isotropic adps. The minor disorder component overlaps with a partially occupied CH_3OH molecule modelled as 0.7 occupied, also with isotropic adps. A second partially occupied CH_3OH (0.3) is present in the lattice. Hydrogen atoms were not included explicitly in the model for the partially occupied CH_3OH molecules but are included in the unit cell contents and all values derived from them. SQUEEZE was used to account for a region of disordered solvent which calculated 4 symmetry equivalent voids of 190 Å^3 containing 42 electrons, approximately corresponding to 4 molecules of H_2O per complex.

Table S1 Crystal data and structure refinement parameters for complexes **1** and **2**.

Complex	**1**	**2**
T/K	100(2)	100(2)
Crystal system	monoclinic	monoclinic
Space group	$P2_1/n$	$P2_1/n$
a/Å, b/Å, c/Å	12.1753(12), 23.756(3), 26.951(3)	12.0222(3) 12.0473(4) 49.8716(12)
β/°	95.658(3)	90.877(2)
V/Å^3	7757.0(14)	7222.3(3)
Z	4	4
ρ_{calc}/mg/m^3	1.547	1.430
μ/mm^{-1}	0.880	0.918
F(000)	3728.0	3192.0
2θ range for data collection	3.038 to 50.122°	4.702 to 50.054°
Index ranges	$-14 \leq h \leq 14$, $-28 \leq k \leq 28$, $-32 \leq l \leq 32$	$-12 \leq h \leq 14$, $-14 \leq k \leq 14$, $-59 \leq l \leq 54$
Reflections collected	117295	54397
Data/restraints/parameters	13738/1097/1071	12756/988/855
GOF on F^2	1.046	1.228
Final R indexes [$I \geq 2\sigma(I)$]	$R_1 = 0.0381$, $wR_2 = 0.0939$	$R_1 = 0.0896$, $wR_2 = 0.2087$
Final R indexes [all data]	$R_1 = 0.0496$, $wR_2 = 0.1018$	$R_1 = 0.1027$, $wR_2 = 0.2144$
Largest diff. peak/hole/e Å^{-3}	0.81/-0.59	0.93/-0.72

Figure S1 Structure of the anionic complex in **2**. C, grey; Mn, lavender; N, blue; O, red; Hydrogen atoms and crystallisation molecules are omitted for clarity. Only crystallographically unique Mn, N and O atoms are labelled.

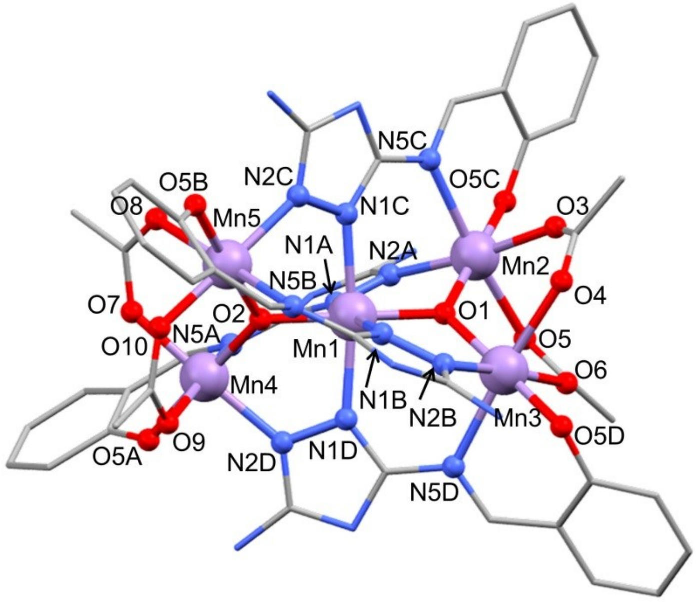

Figure S2 Detail of the core in **1**. The planes formed by the different {Mn_3O} units are shown in blue (Mn1, Mn2, Mn3) and green (Mn1, Mn4, Mn5).

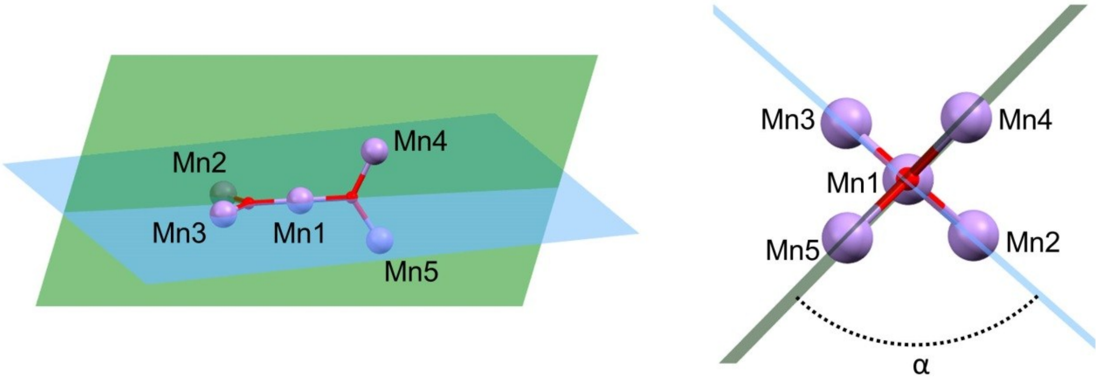

Figure S3 Crystal packing diagram of **1** highlighting the N-H···N interaction (orange) between two adjacent molecules as viewed along the a-axis

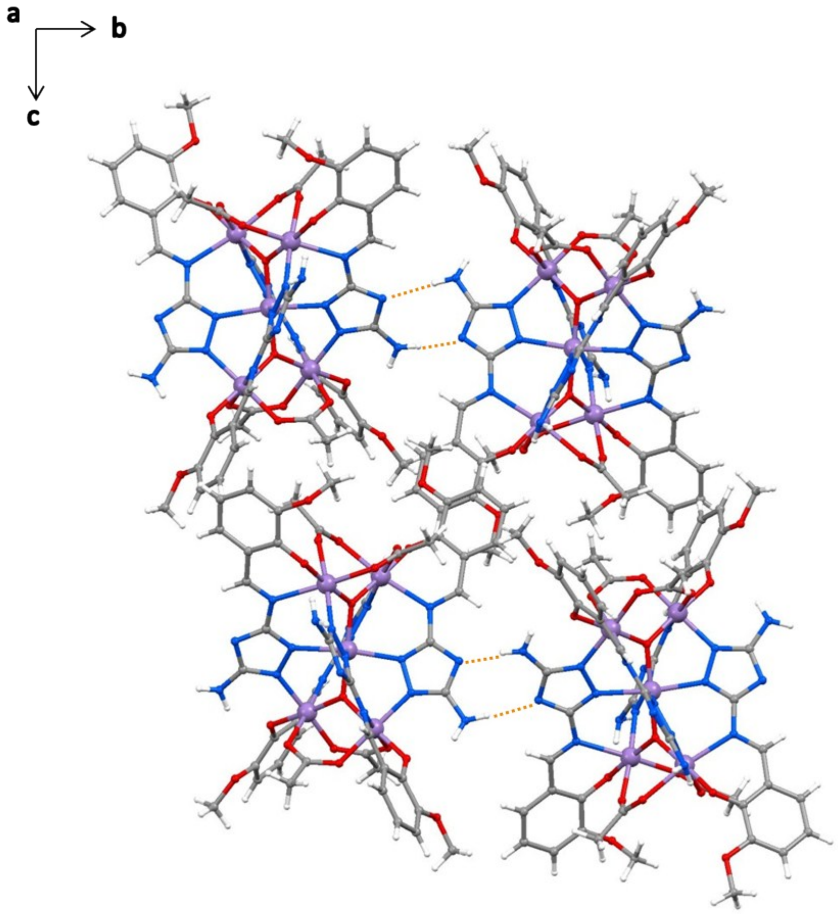

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Table S2 Bond valence sum values for complexes **1** and **2** calculated using the equation $s = e^{[(r_0 - r)/B]}$ with the appropriate values taken from the literature.[6–8]

		Bond Distance (Å)		Mn (II) BVS Value		Mn (III) BVS Value	
		1	2	1	2	1	2
Mn1	**N1A**	2.097	2.163	0.5115703	0.42799291	0.49524499	0.41433474
Mn1	**N1B**	2.094	2.153	0.51573503	0.43971802	0.49927682	0.42568568
Mn1	**N1C**	2.169	2.070	0.42110846	0.55029692	0.40766998	0.53273576
Mn1	**N1D**	2.154	2.078	0.4385312	0.53852631	0.42453673	0.52134079
Mn1	**O1**	1.875	1.885	0.74282314	0.72301571	0.67943991	0.6613226
Mn1	**O2**	1.870	1.877	0.75292942	0.73881871	0.68868385	0.67577717
Sum				3.38269754	3.41836859	**3.19485227**	**3.23119673**

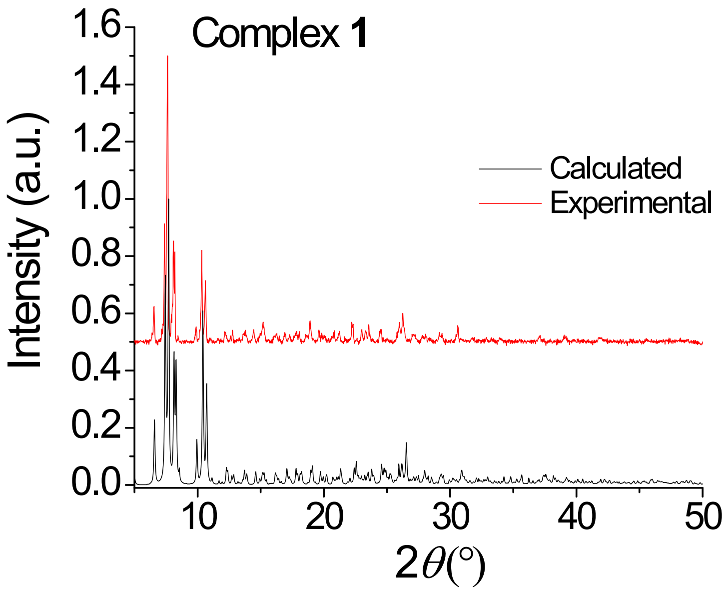
		Bond Distance (Å)		Mn (II) BVS Value		Mn (III) BVS Value	
		1	**2**	**1**	**2**	**1**	**2**
Mn2	**O1**	1.893	1.884	0.70755073	0.72497245	0.6471772	0.66311237
Mn2	**O3**	1.963	1.966	0.58559015	0.58086132	0.53562321	0.53129788
Mn2	**O5**	2.196	2.192	0.31196482	0.31535571	0.28534564	0.28844719
Mn2	**O5C**	1.878	1.88	0.7368246	0.73285251	0.67395321	0.67032005
Mn2	**N5C**	2.293	2.29	0.30119421	0.30364625	0.29158246	0.29395625
Mn2	**N2A**	2.044	2.025	0.59035748	0.62146501	0.57151791	0.60163273
Sum				3.23348199	3.27915325	**3.00519964**	**3.04876648**

		Bond Distance (Å)		Mn (II) BVS Value		Mn (III) Value	
		1	**2**	**1**	**2**	**1**	**2**
Mn3	O1	1.889	1.896	0.71524143	0.70183703	0.65421167	0.64195104
Mn3	O4	2.196	2.214	0.31196482	0.2971514	0.28534564	0.27179622
Mn3	O6	1.975	1.950	0.56690272	0.60653066	0.51853033	0.55477692
Mn3	O5D	1.888	1.884	0.71717713	0.72497245	0.6559822	0.66311237
Mn3	N2B	2.043	2.031	0.5919552	0.61146847	0.57306464	0.5919552
Mn3	N5D	2.295	2.263	0.29957053	0.32663272	0.29001059	0.31620917
Sum				3.20281181	3.26859273	**2.97714508**	**3.03980092**

		Bond Distance (Å)		Mn (II)		Mn (III)	
		1	**2**	**1**	**2**	**1**	**2**
Mn4	O2	1.894	1.889	0.70564101	0.71524143	0.64543044	0.65421167
Mn4	O7	1.975	1.958	0.56690272	0.59355724	0.51853033	0.54291049
Mn4	O9	2.167	2.180	0.33739987	0.32575112	0.30861039	0.2979556
Mn4	O5B/O5A	1.868	1.882	0.75701033	0.72890183	0.69241654	0.66670647
Mn4	N2C/N2D	2.027	2.035	0.6181148	0.6048936	0.59838943	0.58559015
Mn4	N5B/N5A	2.311	2.308	0.28689223	0.28922784	0.27773688	0.27999796
Sum				3.27196096	3.25757306	**3.04111401**	**3.02737234**

		Bond Distance (Å)		Mn (II)		Mn (III)	
		1	**2**	**1**	**2**	**1**	**2**
Mn5	O2	1.889	1.892	0.71524143	0.70946562	0.65421167	0.6489287
Mn5	O8	2.205	2.208	0.30446803	0.30200935	0.27848854	0.27623965
Mn5	O10	1.955	1.954	0.59838943	0.60000889	0.54733036	0.54881164
Mn5	O5A/O5B	1.879	1.889	0.73483587	0.71524143	0.67213417	0.65421167
Mn5	N2D/N2C	2.026	2.036	0.61978764	0.60326096	0.60000889	0.58400961
Mn5	N5A/N5B	2.291	2.268	0.3028267	0.32224845	0.29316285	0.31196482
Sum				3.27554909	3.2522347	**3.04533648**	**3.02416609**

Figure S4 A Powder X-ray diffraction (PXRD) pattern obtained from a powdered polycrystalline sample of **1** (red) compared to the pattern calculated using Mercury based on the .cif of the crystal structure (black).



Note that for **2**, it was not possible to compare the experimental and calculated PXRD patterns. This is likely due to structural differences caused by solvent exchange between the sample and the environment.

Figure S5 Energy of the spin states derived from the exchange-coupling model shown in Figure 4 for 1 (top) and 2 (bottom).

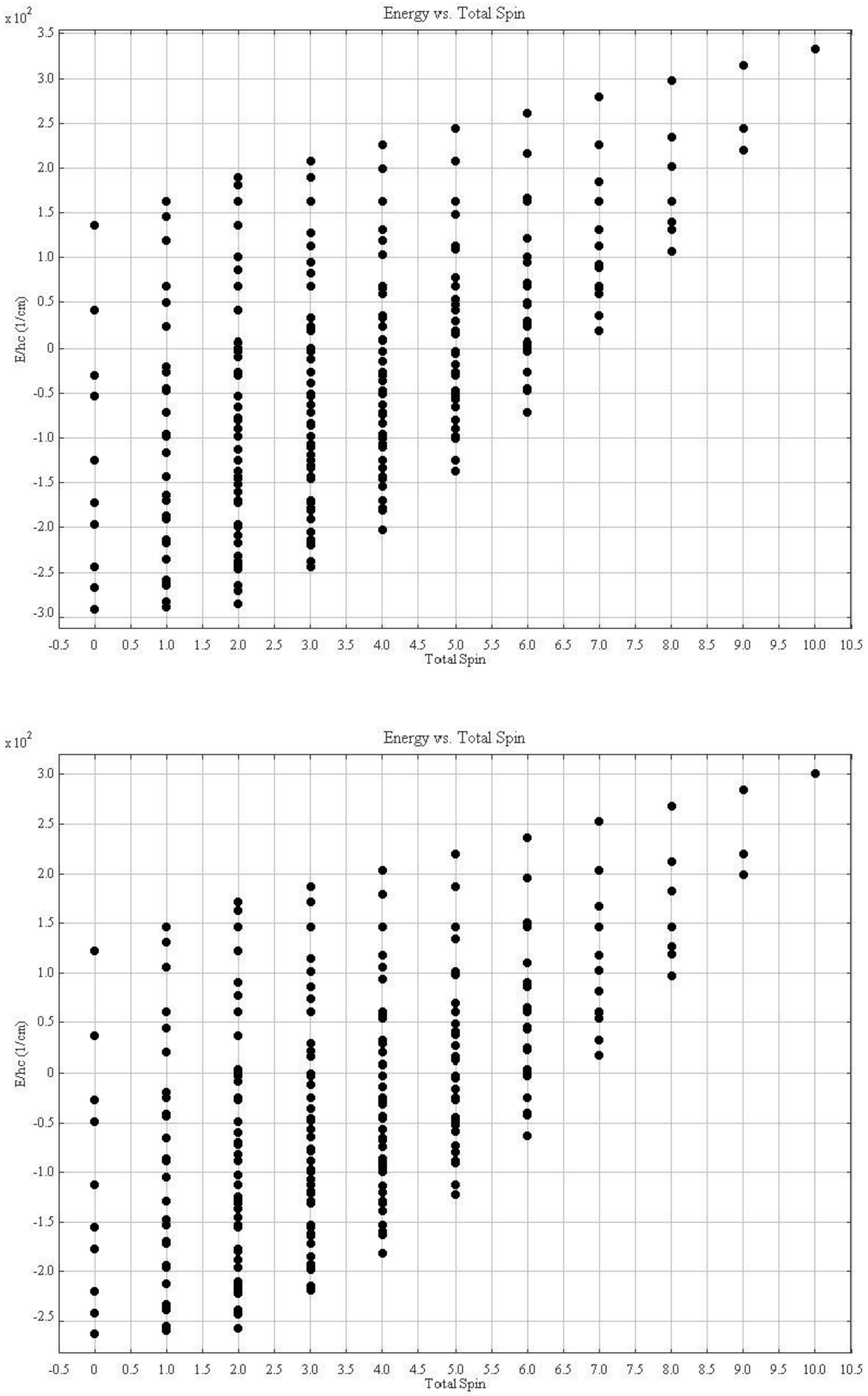


Figure S6 Magnetisation versus field at 2, 4 and 6 K for **1** (left) and **2** (right).

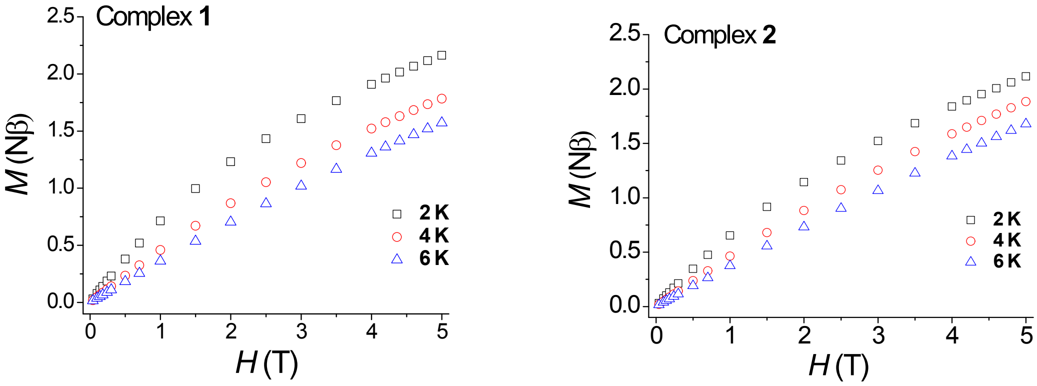


Figure S7 Variable frequency ac susceptibility with in-phase (χ') and out-of-phase (χ'') responses indicated for **1** (left) and **2** (right).

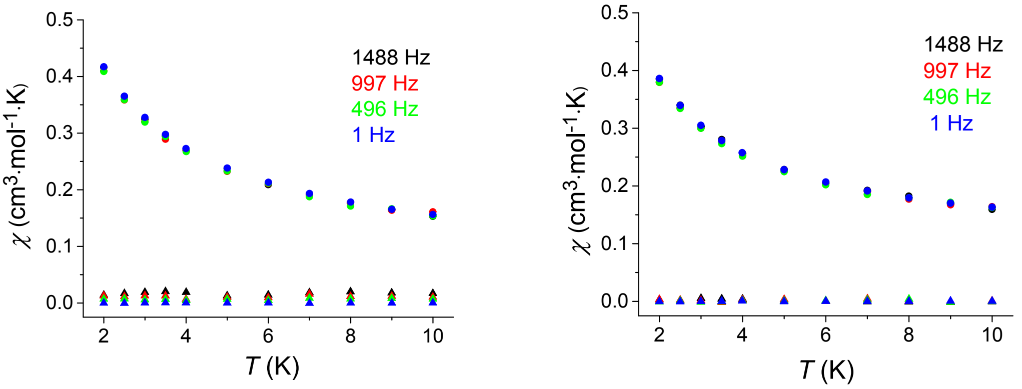
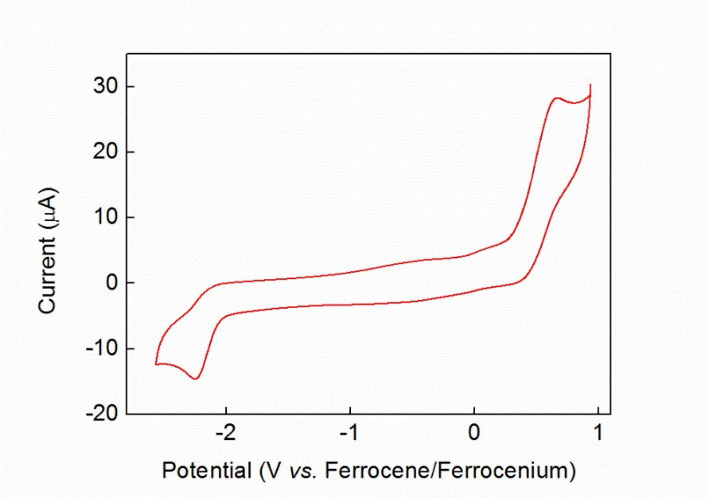


Figure S8 CV of a 2 mM solution of ligand H_2L1 at a scan rate of 100 mV/sec over the range +1 to −2.5 V *vs.* ferrocene/ferrocenium.



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