Supplementary Information

All-Round Robustness of the Mn_{19} Coordination Cluster System: Experimental Validation of a Theoretical Prediction

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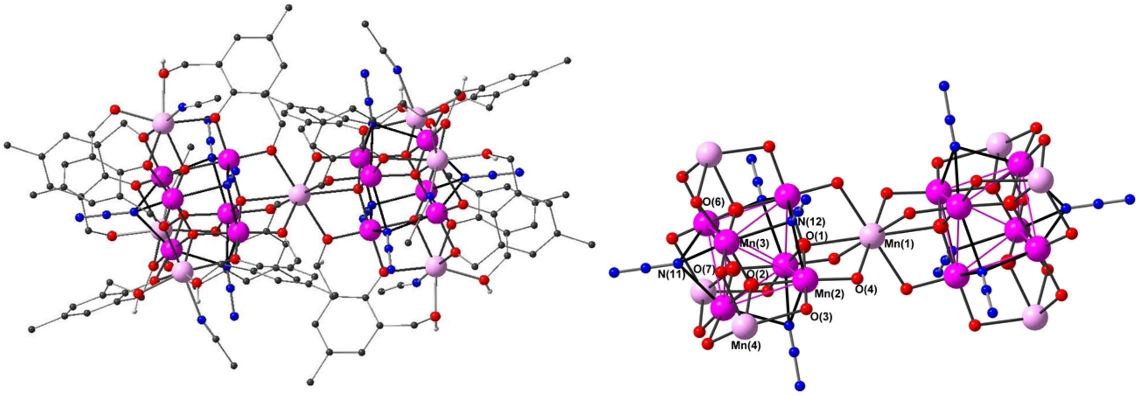

Fig. S1. Molecular structure of **1** (left) in the crystal and metallic core with partial atom numbering scheme (right). Carbon-bound hydrogen atoms, counter ions, and noncoordinated solvent molecules have been omitted for clarity. Colour code: Mn^{III}, dark pink; Mn^{II}, pale pink; O, red; N, blue.

Experimental Section

General details: Unless otherwise stated all reactions were carried out under aerobic conditions. Reagents were obtained from commercial sources, and were used as received, without further purification. Elemental analyses (CHN) were performed using an Elementar Vario EL analyzer.

FTIR spectra were measured on a Perkin Elmer Spectrum One spectrometer with samples prepared as KBr pellets.

$[Mn^{III}_{12}Mn^{II}_{7}(\mu_4\text{-}O)_8(\mu_3\text{-}Cl)_6(\mu_3\text{-}OMe)_2(HL^{Me})_{12}(MeOH)_5(MeCN)]Cl_2\cdot 5MeOH\cdot 5MeCN\cdot 2H_2O$ (2)

A slurry of $MnCl_2\cdot 4H_2O$ (0.1 g, 0.5 mmol), Et_3N (0.081 g, 0.8 mmol) and H_3L^{Me} (0.084 g, 0.5 mmol) in 15 mL MeCN and 3 mL MeOH was stirred for 2 h at ambient conditions to afford a dark brown solution, which was then filtered. Dark brown blocks **2** were obtained overnight and dried *in vacuo*. Yield: 34 % (based on Mn). Elemental analysis (%) calcd for **2**$\cdot 4MeOH\cdot 2H_2O$ (3913.08): C 37.14; H 4.46; N 0.37 %; found: C 37.18; H 4.46; N 0.15. Selected IR data (KBr pellet, cm^{-1}): 476 (w), 556 (s), 634 (s), 814 (m), 862 (w), 995 (m), 1030 (m), 1160 (m), 1222 (s), 1256 (s), 1384 (w), 1470 (s), 1653 (w), 2922 (m), 3401 (b,s). The same complex is obtained if the reaction mixture that produced **6** is additionally refluxed refluxed for 2 h.

$[Mn^{III}_{12}Mn^{II}_{7}(\mu_4\text{-}O)_8(\mu_3\text{-}\eta^1Br)_7(\mu_3\text{-}\eta^1OH)(HL^{Me})_{12}(MeCN)_6]Br_2\cdot 16H_2O\cdot 11MeOH$ (3)

A slurry of $MnBr_2\cdot 4H_2O$ (0.15 g, 0.5 mmol), Et_3N (0.081 g, 0.8 mmol) and H_3L^{Me} (0.084 g, 0.5 mmol) in 15 mL MeCN and 3 mL MeOH was stirred for 1 h at ambient conditions then refluxed for 2 h to afford a dark brown solution, which was then filtered. Dark brown blocks of **3** were obtained overnight and dried *in vacuo*. Yield: 38 % (based on Mn). Elemental analysis (%)calcd for **3**$\cdot 11MeOH$ (4500.83): C 34.96; H 4.09; N 1.86%; found: C 35.69; H 4.96, N1.27. Selected IR data (KBr pellet, cm^{-1}): 555 (m), 618 (s), 811 (m), 864 (w), 985 (m), 1026 (m), 1160 (m), 1225 (m), 1254 (s), 1470 (s), 1564 (w), 2938 (m), 3210 (b,s).

X-ray Data Collection and Structure Refinement.

Data were collected at 100 K on a Bruker SMART Apex diffractometer (**2**) using a Mo-$K\alpha$ rotating-anode source. Data for **3** were measured at 150 K on the SCD beamline at the ANKA synchrotron, Karlsruhe, using a Bruker SMART Apex diffractometer and silicon-monochromated radiation with $\lambda = 0.8000$ Å (15.510 keV); f' and f'' for this wavelength were obtained by the method of Brennan and Cowan[S1] as implemented on http://skuld.bmsc.washington.edu/scatter/AS_periodic.html. Data were corrected for absorption.[S2] Structure solution by direct methods and full-matrix least-squares refinement against F^2 (all data) were carried out using the SHELXTL package.[S2] All ordered non-H atoms were refined anisotropically. Lattice solvent molecules and counterions were disordered, and those that could not be refined satisfactorily using partial occupancies were handled using the

SQUEEZE option in PLATON.[S3] Crystallographic data and structure refinement details for compounds **2** and **3** are listed in Table S1.

Table S1. Crystallographic Data

	(2)	**(3)**
formula	$C_{132}H_{188}Cl_8Mn_{19}N_6O_{58}$	$C_{131}H_{215}Br_9Mn_{19}N_6O_{72}$
Mr	4114.34	4789.22
crystal system	triclinic	trigonal
space group	*P*-1	*R*-3
T [K]	180(2)	150(2)
a [Å]	14.1015(10)	21.217(3)
b [Å]	16.5323(12)	
c [Å]	18.1689(15)	35.704(5)
V [Å^3]	4144.6(5)	13919(4)
Z	1	3
ρ_{calcd} [g/cm^{-3}]	1.648	1.714
λ [Å]	0.71073	0.8000
μ [mm^{-1}]	1.603	4.368
F(000)	2097	7257
reflections collected	45111	27023
unique data	16961	6425
R_{int}	0.0722	0.0508
data with [I>2σ(I)]	10434	4639
parameters/restraints	1030/53	331/3
S on F^2 (all data)	0.989	1.099
wR_2 (all data)	0.1467	0.2040
R_1 (I>2σ(I))	0.0583	0.0644
largest residuals [e Å^{-3}]	+0.60/-0.82	+1.95/-0.60
CCDC number	954052	954053

Magnetic Measurements

Magnetic susceptibility measurements were obtained using a Quantum Design SQUID magnetometer MPMS-XL over the temperature range 1.8-300 K, first using a dc field of 1000 Oe, and then in zero dc field with an oscillating ac field of 3 Oe and ac frequencies of 100 or 200 Hz. Magnetisation measurements were made over a range of temperatures 1.8-300 K with dc applied fields from 0 to 7 T. The measurements of *M* versus *H* at 100 K were additionally used to check for the presence of ferromagnetic impurities, which were found to be absent. All measurements were performed on freshly filtered crystalline samples (to minimise lattice solvent loss) which were finely ground and restrained in grease, and magnetic data were corrected for the sample holder and the diamagnetic contribution which was calculated from Pascal's constants.[S4]

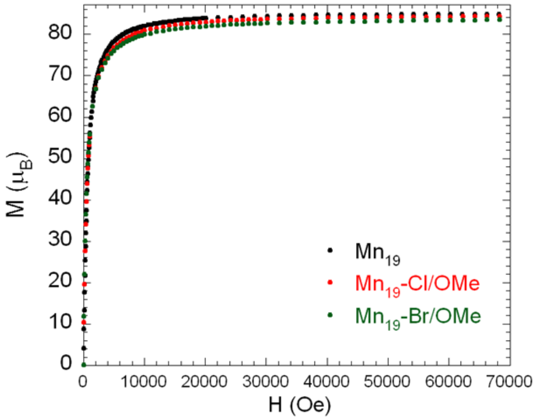

Fig.S2 Field dependence of the magnetization at 1.8 K for compounds **1-3**.

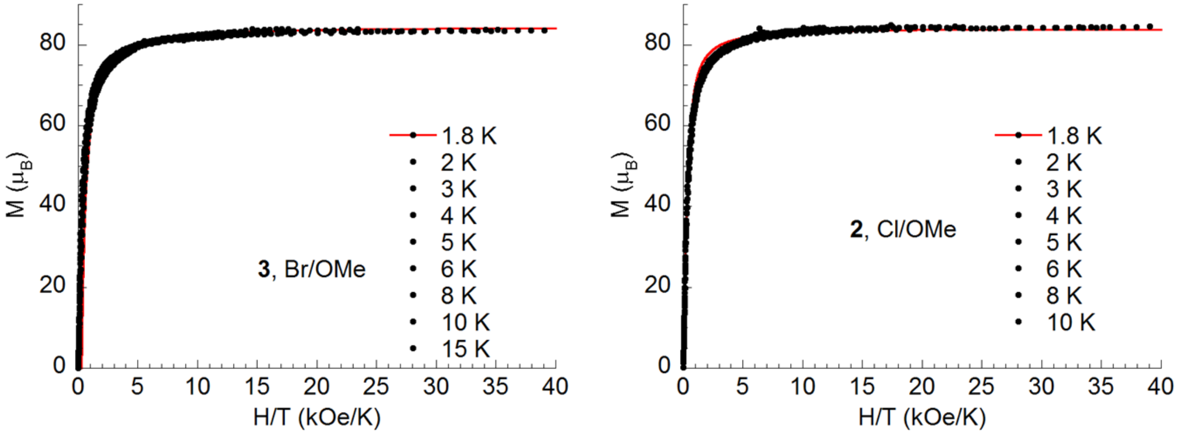

Fig. S3. M vs H/T plots. The red solid line at 1.8 K curve represents a Brillouin function of S = 83/2 with g = 2.03 for Br/OMe and g = 2.02 for Cl/OMe.

DFT Calculations

Table S2. Exchange Coupling Constants (J in cm^{-1}) together with metal-metal and metal-ligand distances (in Å) and metal-ligand-metal angle (in degrees).

	Bridging Ligands	Mn···Mn	Mn-X[a]	Mn-X-Mn	J
J_1	μ_4-O, μ_3-Cl	3.357	1.937, 1.924, 2.744, 2.744	120.8, 75.4	17.2
		3.346	1.932, 1.921, 2.683, 2.735	120.5, 76.3	
		3.337	1.931, 1.923, 2.734, 2.686	119.9, 76.0	
J_2	μ_4-O, μ_3-Cl	3.269	1.923, 1.910, 2.798, 2.735	117.0, 72.4	13.6
		3.263	1.921, 1.910, 2.885, 2.744	116.8, 70.8	
		3.257	1.924, 1.901, 2.724, 2.734	116.7, 73.3	
J_3	μ_4-O, μ_3-Cl	3.225	1.887, 1.869, 2.885, 2.744	118.3, 69.9	13.9
		3.224	1.887, 1.879, 2.798, 2.683	117.7, 72.0	
J_4	μ_4-O, μ_3-Cl	3.167	1.879, 1.869, 2.724, 2.686	115.3, 71.7	4.2
J_5	μ_4-O, μ_3-OMe	3.106	1.931, 1.910, 2.221, 2.211	108.8, 89.0	22.0
		3.101	1.937, 1.901, 2.221, 2.206	107.8, 88.9	
		3.098	1.932, 1.910, 2.211, 2.206	107.5, 89.0	
J_6	μ_4-O, μ_2-OR	3.448	1.887, 1.843, *2.579*, *2.314*	99.9, 111.6	2.1
J_7	μ_4-O, μ_2-OR	3.466	1.879, 1.847, *2.579*, *2.314*	100.9, 112.4	0.7
J_8	μ_4-O, μ_2-OR	3.408	1.869, 1.847, *2.579*, *2.253*	98.8, 112.1	-0.2
J_9	μ_4-O, μ_2-OR	3.338	1.937, 1.889, *2.253*, *2.402*	105.4, 101.5	5.5
J_{10}	μ_4-O, μ_2-OR	3.312	1.931, 1.893, *2.251*, *2.375*	104.5, 101.2	8.8
		3.292	1.932, 1.900, *2.239*, *2.352*	104.0, 100.9	
J_{11}	μ_4-O, μ_2-OR	3.285	1.923, 1.892, *2.251*, *2.324*	103.5, 101.9	6.2
		3.278	1.921, 1.898, *2.239*, *2.330*	103.7, 101.2	
J_{12}	μ_4-O, μ_2-OR	3.259	1.924, 1.883, *2.253*, *2.288*	102.3, 102.3	5.7
J_{13}	μ_4-O, μ_2-OR	3.220	1.910, 1.866, *2.251*, *2.197*	104.6, 101.1	1.5
J_{14}	μ_4-O, μ_2-OR	3.220	1.901, 1.885, *2.253*, *2.187*	104.0, 101.0	5.7
		3.214	1.910, 1.891, *2.239*, *2.202*	103.5, 101.5	

[a] Italic values are related to Mn^{II} cations.

$$
\begin{aligned}
\hat{H} = -J_1[&\hat{S}_3\hat{S}_7 + \hat{S}_{12}\hat{S}_{15} + \hat{S}_4\hat{S}_5 + \hat{S}_{11}\hat{S}_{14} + \hat{S}_2\hat{S}_6 + \hat{S}_{13}\hat{S}_{16}] \\
&-J_2[\hat{S}_2\hat{S}_5 + \hat{S}_{13}\hat{S}_{14} + \hat{S}_4\hat{S}_7 + \hat{S}_{11}\hat{S}_{15} + \hat{S}_3\hat{S}_6 + \hat{S}_{12}\hat{S}_{16}] \\
&-J_3[\hat{S}_3\hat{S}_4 + \hat{S}_{11}\hat{S}_{12} + \hat{S}_2\hat{S}_4 + \hat{S}_{11}\hat{S}_{13}] - J_4[\hat{S}_2\hat{S}_3 + \hat{S}_{12}\hat{S}_{13}] \\
&-J_5[\hat{S}_5\hat{S}_6 + \hat{S}_{14}\hat{S}_{16} + \hat{S}_5\hat{S}_7 + \hat{S}_{14}\hat{S}_{15} + \hat{S}_6\hat{S}_7 + \hat{S}_{15}\hat{S}_{16}] \\
&-J_6[\hat{S}_1\hat{S}_4 + \hat{S}_1\hat{S}_{11}] - J_7[\hat{S}_1\hat{S}_2 + \hat{S}_1\hat{S}_{13}] - J_8[\hat{S}_1\hat{S}_3 + \hat{S}_1\hat{S}_{12}] \\
&-J_9[\hat{S}_7\hat{S}_8 + \hat{S}_{15}\hat{S}_{17}] - J_{10}[\hat{S}_6\hat{S}_{10} + \hat{S}_{16}\hat{S}_{18} + \hat{S}_5\hat{S}_9 + \hat{S}_{14}\hat{S}_{19}] \\
&-J_{11}[\hat{S}_2\hat{S}_{10} + \hat{S}_{13}\hat{S}_{18} + \hat{S}_4\hat{S}_9 + \hat{S}_{11}\hat{S}_{19}] - J_{12}[\hat{S}_3\hat{S}_8 + \hat{S}_{12}\hat{S}_{17}] \\
&-J_{13}[\hat{S}_5\hat{S}_{10} + \hat{S}_{14}\hat{S}_{18}] - J_{14}[\hat{S}_7\hat{S}_9 + \hat{S}_{15}\hat{S}_{19} + \hat{S}_6\hat{S}_8 + \hat{S}_{16}\hat{S}_{17}]
\end{aligned}
$$

Hamiltonian used in the DFT calculations on **2** (c.f. ref. S5)

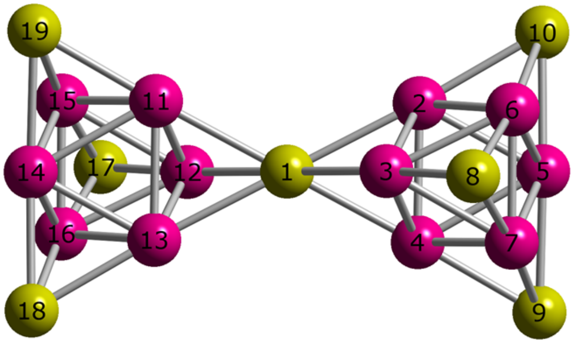

Fig. S5. Topology of the exchange interactions for the Mn_{19} complex (**2**). Purple and yellow spheres represent Mn^{III} and Mn^{II} cations respectively.

Here J_1-J_5 and J_6-J_{14} represent Mn^{III}-Mn^{III} and Mn^{III}-Mn^{II} interactions respectively. Regarding the complexity of such complex some considerations have been took in account to try to minimize the number of coupling constants: very similar Mn···Mn distances within the same exchange pathways, i.e. the same bridging ligands, are grouped into the same J constant, provided that difference of the angles will be smaller than 0.1°, if not, these J values were split into two groups. In the case of the presence of the μ_3-Cl bridging ligand this angle restriction is not considered because of the much longer Mn-Cl distance compared to Mn-O. In any case such considerations are totally subjective and can be as restrictive as one wants. However the ideal situation of treating all the exchange pathways separately entails the calculation at least of n+1 different spin distributions, where n is the number of J values. Therefore, it is important to find a good relation between the accuracy and the computational cost.

Some conclusions can be extracted from the calculated J values that are largely in agreement with previous calculations:[S5] i) all interactions are ferromagnetic with the exception of J_8 (-0.2 cm^{-1}) which is in concordance with a previous calculation of a Mn_{19} complex, where shorter Mn^{III}-Mn^{II} distances, being the Mn^{II} cation the one that is placed in the shared vertex of the two supertetrahedra, entails a less ferromagnetic coupling.[S6] This negative value, together with the presence of possible antiferromagnetic intermolecular coupling, could explain why the maximum value of the χT at low temperatures is smaller than the expected one for a total spin ground state $S = 83/2$, but higher than the expected for the spin inversion of one Mn^{III} or Mn^{II} cation, being the total spin ground state equal to $S = 75/2$ and $S = 73/2$ respectively; ii) the J_1-J_5 exchange interactions are, with the exception of J_4, the most ferromagnetic ones, being the J_5 exchange constant, that involves interactions through μ_4-O and μ_3-OMe bridging ligands, the strongest one; iii) the presence of the μ_3-Cl bridging ligand should give a ferromagnetic coupling between the Mn^{III} ions, since the nature of this ligand does not affect the character of those exchange interactions, indeed, the values are similar to those calculated for a Mn_{19} complex where μ_3-N_3 bridging ligands are present.[S5] However, for that latter compound a decrease of the Mn···Mn distance, as well as the Mn-X-Mn angles, involved an increase of the strength of the ferromagnetic coupling, meanwhile for the former it is the opposite, a decrease of the distance and the angles involves also a decrease of the ferromagnetic coupling; iv) the interactions of the central octacoordinate Mn^{II} atom (J_1-J_3) are weaker than the ones of the hexacoordinated Mn^{II} cations.

Computational Details

We have used the SIESTA software[S7] with the GGA exchange-correlation functional proposed by Perdew, Burke and Erzernhof (PBE).[S8] Sixteen calculations have been performed in order to obtain the fourteen exchange coupling constants for the following spin-configurations: the high spin distribution ($S = 83/2$), an $S = 51/2$ configuration with negative spins at the following atoms {Mn4, Mn5, Mn13, Mn14}, and fourteen distributions with the following total spin and metal atoms with negative spins: S = 67/2 {Mn4, Mn5}{Mn5, Mn14}, S = 65/2 {Mn16, Mn17}, S = 57/2 {Mn1, Mn2, Mn7}, S = 51/2 {Mn3, Mn4, Mn5, Mn6}, S = 49/2 {Mn2, Mn5, Mn6, Mn10}, S = 47/2 {Mn4, Mn10, Mn14, Mn19}, S = 37/2 {Mn1, Mn2, Mn10, Mn13, Mn18, Mn19}, S = 35/2 {Mn2, Mn3, Mn4, Mn11, Mn12, Mn13}{Mn5, Mn6, Mn7, Mn14, Mn15, Mn16}{Mn2, Mn4, Mn5, Mn11, Mn13, Mn14}, S = 31/2 {Mn2, Mn7, Mn8, Mn11, Mn16}, S = 25/2 {Mn1, Mn2, Mn3, Mn4, Mn11, Mn12, Mn13}, S = 13/2 {Mn1, Mn8, Mn9, Mn10, Mn17, Mn18, Mn19}.

Electrospray ionization (ESI) Mass Spectrometry

Electrospray mass spectra of compound **1** were taken on a 7-Tesla Fourier transform ion cyclotron resonance (FT-ICR) mass spectrometer (APEX II, Bruker Daltonics, Billerica MA, USA) equipped with an electrospray ionization (ESI) source (Analytica of Branford) and for compound **4** on a quadrupole/o-time-of-flight mass spectrometer (SYNAPT G2-S HDMS, Waters Corp., Manchester, UK) employing a nanospray ion source.

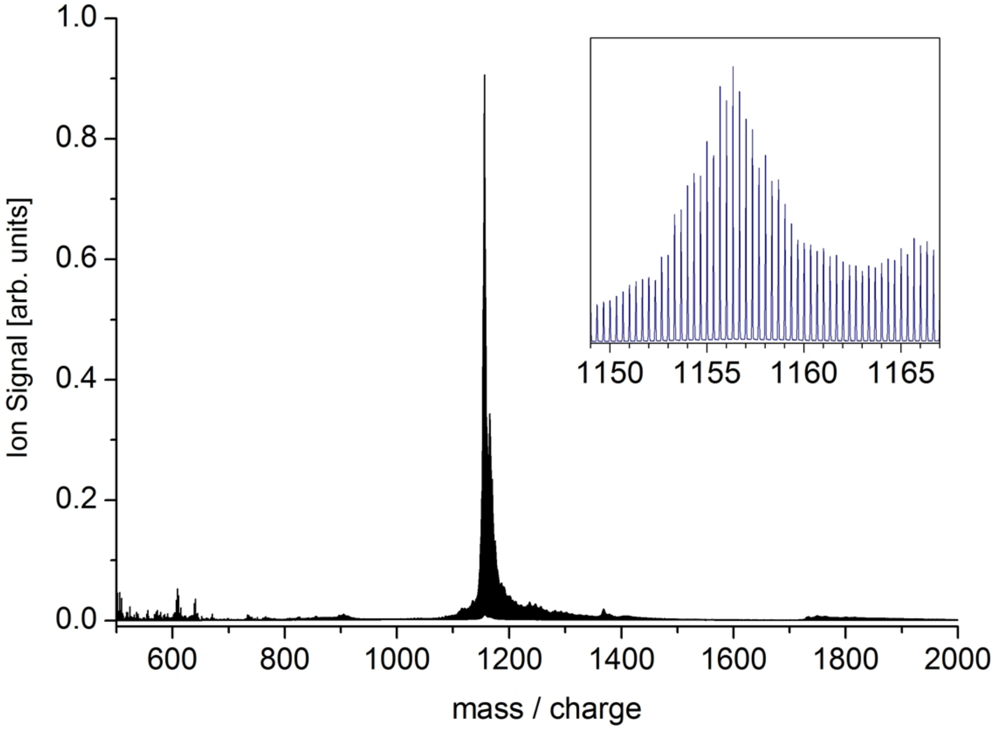

Figure S6: ESI-MS for $[Mn_{18}Y(O)_8(\mu_3\text{-}\eta^1\text{-}N_3)_8(HL^{Me})_{12}(MeCN)_6](NO_3)_3\cdot 11MeOH$

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