Electronic Supplementary Information for:

Rational serendipity: ''undirected'' synthesis of a large {Mn$^{III}_{10}$Cu$^{II}_5$} complex from pre-formed Mn^{II} building blocks

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Experimental Section

General Considerations: All manipulations were performed under aerobic conditions using materials as received from commercial suppliers (Sigma Aldrich).

Synthesis of [Mn(H$_4$Edte)(NO$_3$)][NO$_3$] (1): A solution of H$_4$Edte (6.56 g, 23.76 mmol) in MeCN (100 ml) was added slowly to a previously prepared solution of Mn(NO$_3$)$_2$·4H$_2$O (7.14 g, 28.44 mmol) in the same solvent (100 ml). The reaction was stirred at room temperature for 17 hours, after which time a light pink precipitate formed. This was collected, air-dried and recrystallised by Et$_2$O diffusion of an ethanolic solution of the precipitate. The resulting IR data of the precipitate and the single-crystals were found to match closely. Selected IR data obtained for crystals of **1** (cm^{-1}): 3209 (br), 2976.26 (w), 2955.04 (w), 2916.47 (w), 2868.24 (w), 1656.91 (w), 1448.59 (m), 1417.73 (s), 1377.22 (m), 1361.79 (m), 1288.49 (s), 1261.49 (s), 1151.54 (w), 1112.96 (w), 1070.53 (s), 1058.96 (s), 1043.52 (s), 1030.02 (s), 1004.95 (m), 914.29 (m), 891.14 (w), 817.85 (m), 754.19 (m), 732.97 (m), 717.54 (w). Elemental analysis for [Mn(H$_4$Edte)(NO$_3$)][NO$_3$]·H$_2$O (%) calculated (found); C 27.72 (27.70), H 6.05 (6.08), N 12.93 (12.64).

Synthesis of [Mn$^{III}_{10}$Cu$^{II}_5$O$_8$(O$_2$CPh)$_8$(HEdte)$_4$(H$_2$O)$_4$][NO$_3$]$_4$·7MeOH·13H$_2$O (2):

A solution of Cu(OAc)$_2$·2H$_2$O (20 mg, 0.10 mmol), [Mn(H$_4$Edte)(NO$_3$)][NO$_3$]·H$_2$O (90 mg, 0.21 mmol) and NaO$_2$CPh (32 mg, 0.22 mmol) in MeOH (9 ml) was sonicated for several minutes, before being transferred to a Parr Instruments spring-loaded Teflon-lined steel digestion vessel (23 cm^3 capacity). The system was sealed and heated to 60 °C at 5 °C min^{-1} in a temperature controlled oven and kept at this temperature for 12 hours, before being cooled to room temperature at 0.1 °C min^{-1}. The resulting solution was filtered under gravity and left to evaporate. Small dark-brown block-like crystals suitable for single-crystal X-ray diffraction were obtained after approximately 6 weeks in 6% isolated yield. Selected IR data for **2** (cm^{-1}): 3350 (br), 2978.19 (w), 2916.47 (w), 2879.82 (w), 1593.25 (m), 1537.32 (m), 1492.95 (w), 1473.66 (w), 1444.73 (w), 1411.94 (m), 1386.86 (s), 1342.50 (m), 1263.42 (w), 1176.62 (w), 1153.47 (w), 1105.25 (w), 1080.17 (w), 1058.96 (m), 1022.31 (m), 929.72 (w), 916.22 (m), 896.93 (m), 827.49 (w), 721.40 (s), 669.32 (s). Elemental analysis for [Mn$^{III}_{10}$Cu$^{II}_5$O$_8$(O$_2$CPh)$_8$(HEdte)$_4$(H$_2$O)$_4$][NO$_3$]$_4$·13H$_2$O (%) calculated (found); C 33.41 (32.85), H 4.61 (3.97), N 4.87 (4.85).

Single Crystal X-ray Diffraction

A Nonius Kappa CCD diffractometer equipped with an Oxford Cryosystems Cryostream low-temperature device was used to collect unit cell and intensity data, using a Mo-Kα radiation source (λ = 0.71073 Å) and a graphite monochromator. The data reduction included a correction for Lorentz and polarization effects, with an applied multi-scan absorption correction (SADABS). The crystal structures of **1** and **2** were solved and refined using SUPERFLIP[1] and refined against full-matrix least-squares on F^2 using SHELXL[2] in OLEX2.[3]

In complex **1** all non-hydrogen atoms were refined with anisotropic atomic displacement parameters (adps). Hydrogen atoms were geometrically placed for all CH$_2$ groups and included as part of a riding model with constrained C-H distances, OH hydrogen atom coordinates were refined with suitable distance restraints applied and Uiso(H) was set to 1.5 Ueq(O/N).

For complex **2** some disorder was present. The OH group O40, 041,042 was modelled over 3 partially occupied sites with occupancies 0.3, 0.3 and 0.4, with the partially occupied sites were refined with isotropic adps. The nitrate anion also showed some disorder and was modelled with 2 of the O atoms over 2 approx. 0.5 occupied sites and with O12 common to both orientations. A molecule of MeOH was also included in the model (one per asymmetric unit, 4 per $\{Mn_{10}Cu_5\}$ complex). There was also a significant quantity of poorly defined and disordered solvent present in the crystal. SQUEEZE[4] was used to account for this lattice solvent and calculated solvent accessible voids of 534 $Å^3$ per complex containing 182 electrons. This is taken to correspond to 13 molecules of H_2O and 3 further molecules of MeOH per complex given the elemental analysis.

FT-IR data

IR spectra were recorded on a SHIMADZU FTIR-8400S spectrophotometer.

Elemental analysis

Elemental analysis was performed by the analytical service of the School of Chemistry at the University of Glasgow.

Magnetometery

Direct current (dc) magnetic susceptibility down to 1.9 K was measured on a crushed polycrystalline sample of **2** using a Quantum Design MPMS-XL5 SQUID magnetometer equipped with a 5 T dc magnet. The sample was set in eicosane to prevent torqueing of the crystallites. Alternating current (ac) magnetic susceptibility measurements were performed in the absence of a dc field under an oscillating ac field of 3.5 Oe and ac frequencies ranging up to 1300 Hz. Diamagnetic corrections were applied to the observed paramagnetic susceptibilities using Pascal's constants, with the diamagnetism of the sample holder and eicosane also corrected for.
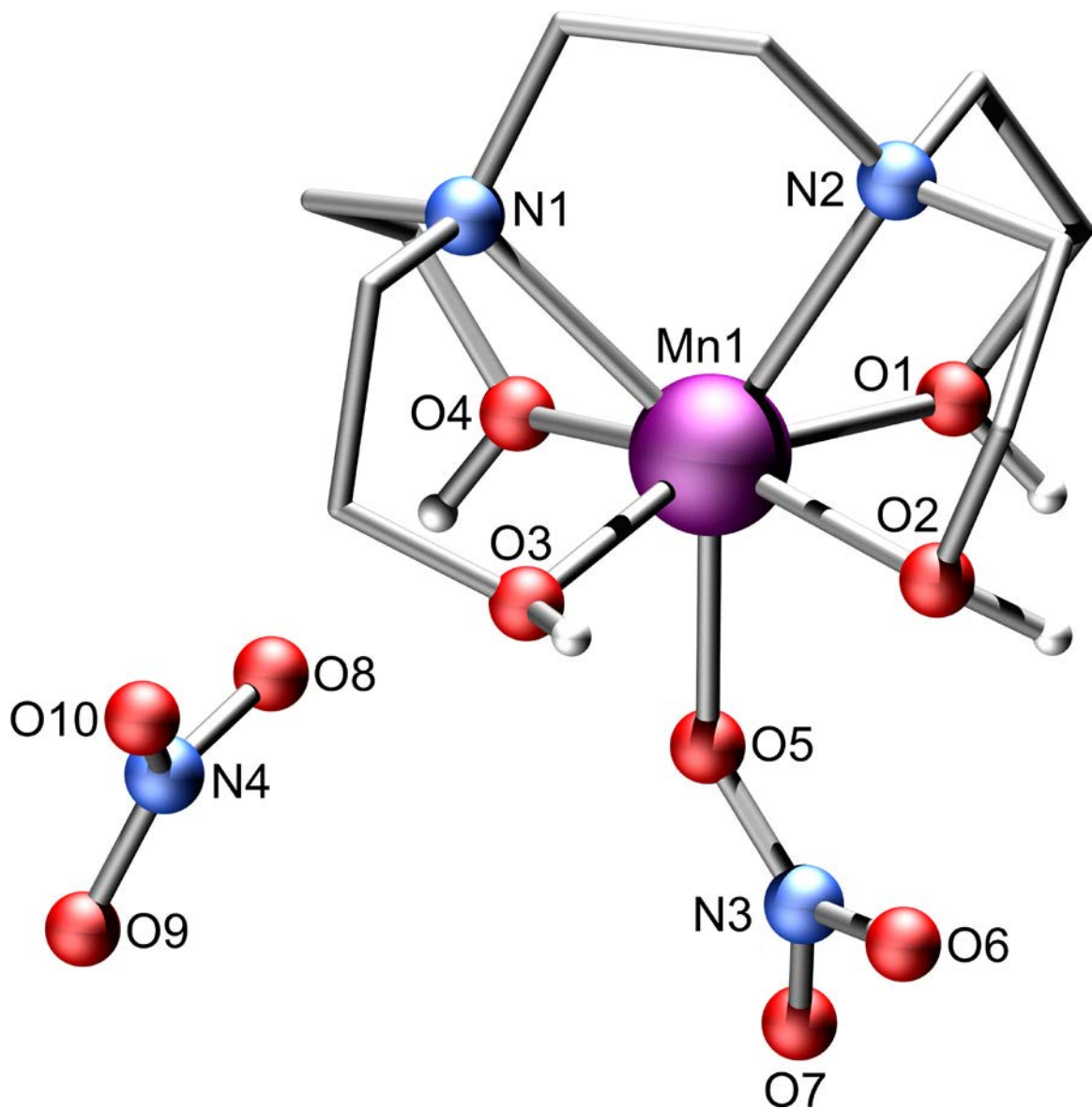
Fig. S1 Molecular structure of complex **1**. Colour code: Mn = purple, O = red, N = blue, C = silver, H = white. All hydrogen atoms except ligand OH groups are omitted for clarity

Table S1 Crystallographic data for complex **1**

Crystal Data

$C_{10}H_{24}MnN_3O_7 \cdot NO_3$	$D_x = 1.691$ Mg m^{-3}
$M_r = 415.27$	Mo $K\alpha$ radiation, $\lambda = 0.71073$ Å
Orthorhombic, *Pbca*	Cell parameters from 4178 reflections
$a = 13.4000\ (2)$ Å	$\theta = 1.0–27.5°$
$b = 13.8810\ (2)$ Å	$\mu = 0.87$ mm^{-1}
$c = 17.5344\ (3)$ Å	$T = 100$ K
$V = 3261.49\ (9)$ Å^3	Needle, pink
$Z = 8$	$0.43 \times 0.16 \times 0.14$ mm
$F(000) = 1736$	

Data Collection

Kappa CCD diffractometer	3196 reflections with $I > 2\sigma(I)$
Radiation source: fine focus sealed tube, Nonius FR590 Sealed Tube Generator	$R_{int} = 0.012$
Absorption correction: multi-scan *SADABS2006*/1 (Bruker, 2006) was used for absorption correction. R(int) was 0.0384 before and 0.0294 after correction. The Ratio of minimum to maximum transmission is 0.5809. The $\lambda/2$ correction factor is 0.0015.	$\theta_{max} = 27.5°$, $\theta_{min} = 2.3°$
$T_{min} = 0.250$, $T_{max} = 0.430$	
7038 measured reflections	
3731 independent reflections	

Refinement

Refinement on F^2	12 restraints
Least-squares matrix: full	Hydrogen site location: mixed
$R[F^2 > 2\sigma(F^2)] = 0.027$	H atoms treated by a mixture of independent and constrained refinement
$wR(F^2) = 0.071$	$w = 1/[\sigma^2(F_o^2) + (0.0347P)^2 + 1.8497P]$ where $P = (F_o^2 + 2F_c^2)/3$
$S = 1.05$	$(\Delta/\sigma)_{max} = 0.002$
3731 reflections	$\Delta\rangle_{max} = 0.85$ e Å^{-3}
238 parameters	$\Delta\rangle_{min} = -0.22$ e Å^{-3}

Table S2 Pertinent bond lengths in complex **1**

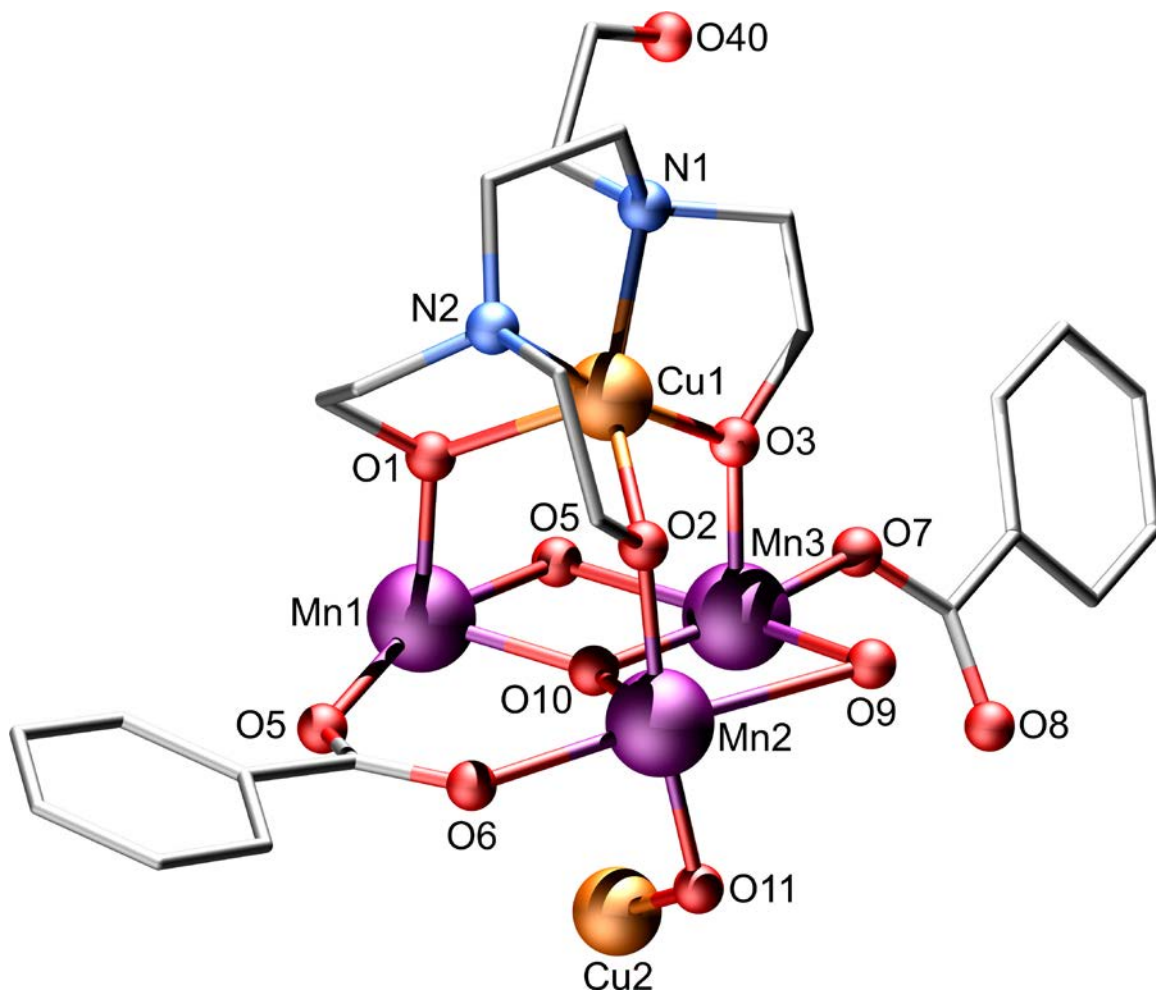|	
Mn1—O1	2.2647 (10)
Mn1—O2	2.2868 (11)
Mn1—O3	2.2448 (11)
Mn1—O4	2.2220 (10)
Mn1—O5	2.2897 (11)
Mn1—N1	2.3944 (12)
Mn1—N2	2.3724 (12)

Fig. S2 Asymmetric unit of **2** with H-atoms, NO$_3^-$ anions and MeOH/H$_2$O solvent molecules omitted for clarity. Colour code: Mn = purple, Cu = orange, O = red, N = blue, C = silver.

Table S3 Crystallographic data for complex **2**

Crystal Data

$C_{96}H_{128}Cu_5Mn_{10}N_8O_{44} \cdot 4(NO_3) \cdot 4(CH_4O)$	D_x = 1.581 Mg m^{-3}
M_r = 3341.36	Mo $K\alpha$ radiation, λ = 0.71073 Å
Tetragonal, $I4_1/a$	Cell parameters from 6445 reflections
a = 27.5814 (6) Å	θ = 2.0–25.4°
c = 18.4546 (4) Å	μ = 1.70 mm^{-1}
V = 14039.0 (7) Å^3	T = 100 K
Z = 4	Block, brown
$F(000)$ = 6812	0.42 × 0.38 × 0.33 mm

Data Collection

Kappa CCD diffractometer	6405 independent reflections
Radiation source: fine focus sealed tube, Nonius FR590 Sealed Tube Generator	5223 reflections with $I > 2\sigma(I)$
Horizontally mounted graphite crystal monochromator	θ_{max} = 25.4°, θ_{min} = 2.4°
Detector resolution: 9 pixels mm^{-1}	
Absorption correction: multi-scan *SADABS2006*/1 (Bruker, 2006) was used for absorption correction. R(int) was 0.0484 before and 0.0336 after correction. The Ratio of minimum to maximum transmission is 0.2833. The $\lambda/2$ correction factor is 0.0015.	
T_{min} = 0.121, T_{max} = 0.428	
6405 measured reflections	

Refinement

Refinement on F^2	119 restraints
Least-squares matrix: full	Hydrogen site location: mixed
$R[F^2 > 2\sigma(F^2)]$ = 0.043	H atoms treated by a mixture of independent and constrained refinement
$wR(F^2)$ = 0.128	$w = 1/[\sigma^2(F_o^2) + (0.0707P)^2 + 64.8638P]$ where $P = (F_o^2 + 2F_c^2)/3$
S = 1.02	$(\Delta/\sigma)_{max}$ = 0.001
6405 reflections	$\Delta\rangle_{max}$ = 0.87 e Å^{-3}
450 parameters	$\Delta\rangle_{min}$ = -2.52 e Å^{-3}

Table S4 Pertinent bond lengths (Å) and angles (°) in **2**.

Cu1—O1	2.097 (3)
Cu1—O2	1.992 (3)
Cu1—O3	1.942 (3)
Cu1—N1	2.020 (4)
Cu1—N2	1.993 (3)
Cu2—O11	1.953 (2)
Mn1—Mn3	3.1950 (7)
Mn1—O1	1.872 (3)
Mn1—O5	2.280 (2)
Mn1—O10	1.961 (2)
Mn2—Mn3	3.0855 (8)
Mn2—O2	1.906 (3)
Mn2—O6	2.180 (3)
Mn2—O8^{i}	1.962 (3)
Mn2—O9	2.451 (3)
Mn2—O10	1.896 (2)
Mn2—O11^{i}	1.880 (2)
Mn3—O3	1.918 (3)
Mn3—O5^{iii}	2.345 (3)
Mn3—O7	1.943 (3)
Mn3—O9	2.246 (3)
Mn3—O10	1.889 (2)
Mn3—O11	1.882 (2)
Mn2—O2—Cu1	120.58 (13)
C6—O2—Cu1	112.9 (2)
C6—O2—Mn2	121.2 (2)
Mn3—O3—Cu1	121.03 (13)
C8—O3—Cu1	112.6 (2)
C8—O3—Mn3	125.7 (2)
Mn1—O5—Mn3^{iii}	87.37 (9)
Mn3—O9—Mn2	82.00 (9)
Mn2—O10—Mn1	136.42 (13)
Mn3—O10—Mn1	112.18 (12)
Mn3—O10—Mn2	109.23 (12)
Mn2^{ii}—O11—Cu2	112.63 (12)
Mn2^{ii}—O11—Mn3	129.07 (13)
Mn3—O11—Cu2	114.25 (12)

Symmetry codes: (i) -y+5/4, x+1/4, -z+5/4; (ii) y-1/4, -x+5/4, -z+5/4; (iii) -x+1, -y+3/2, z.

Table S5 The results of BVS calculations for **2** obtained in respect of Mn1-3.

Atom	Mn^{II}	Mn^{III}
Mn1	3.38	**3.12**
Mn2	3.41	**3.15**
Mn3	3.29	**3.03**

Table S6 The results of BVS calculations for **2** obtained in respect of Cu2.

Atom	Cu^{II}	Mn^{II}
Cu2	**1.949**	2.631
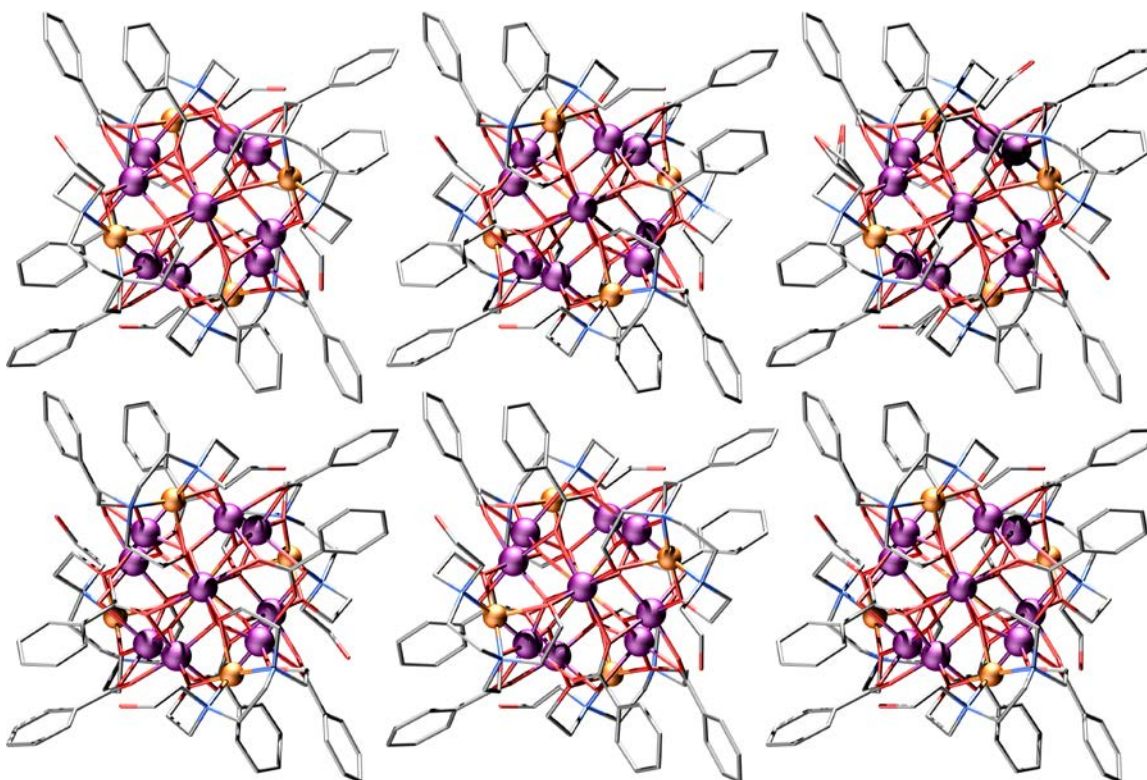
Fig. S3 Crystal packing of **2** as viewed along the *c*-axis. H-atoms, NO_3^- anions and MeOH/H_2O solvent molecules omitted for clarity. Colour code: Mn = purple, Cu = orange, O = red, N = blue, C = silver.
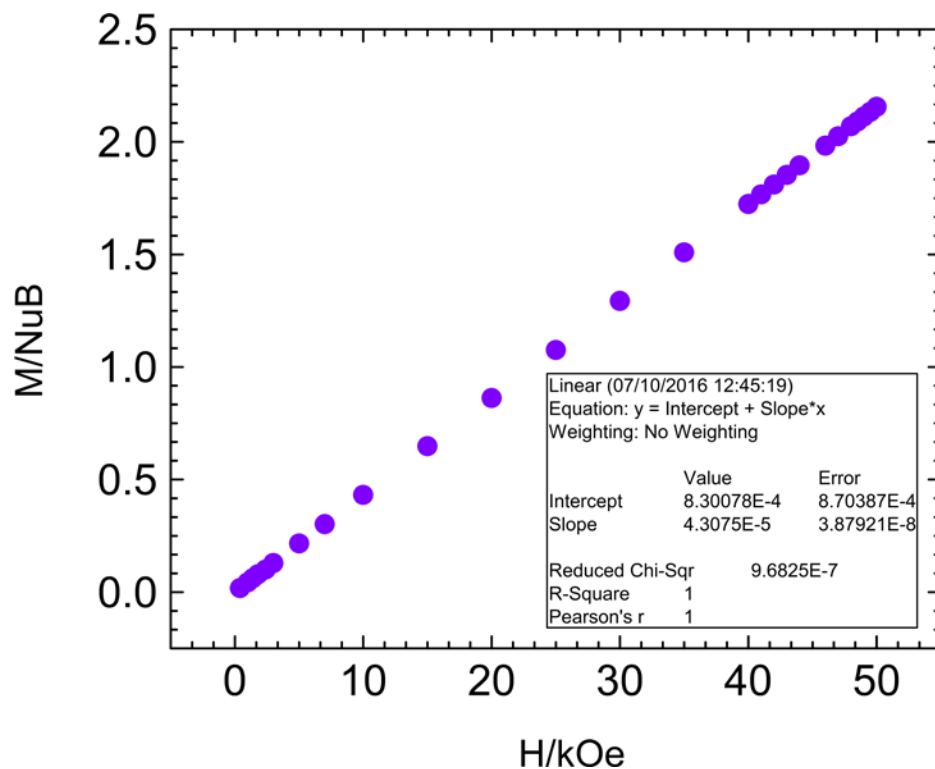
Fig. S4 *M vs. H* at 100 K for **2**. The linear trend of the data indicates an absence of ferromagnetic impurities.
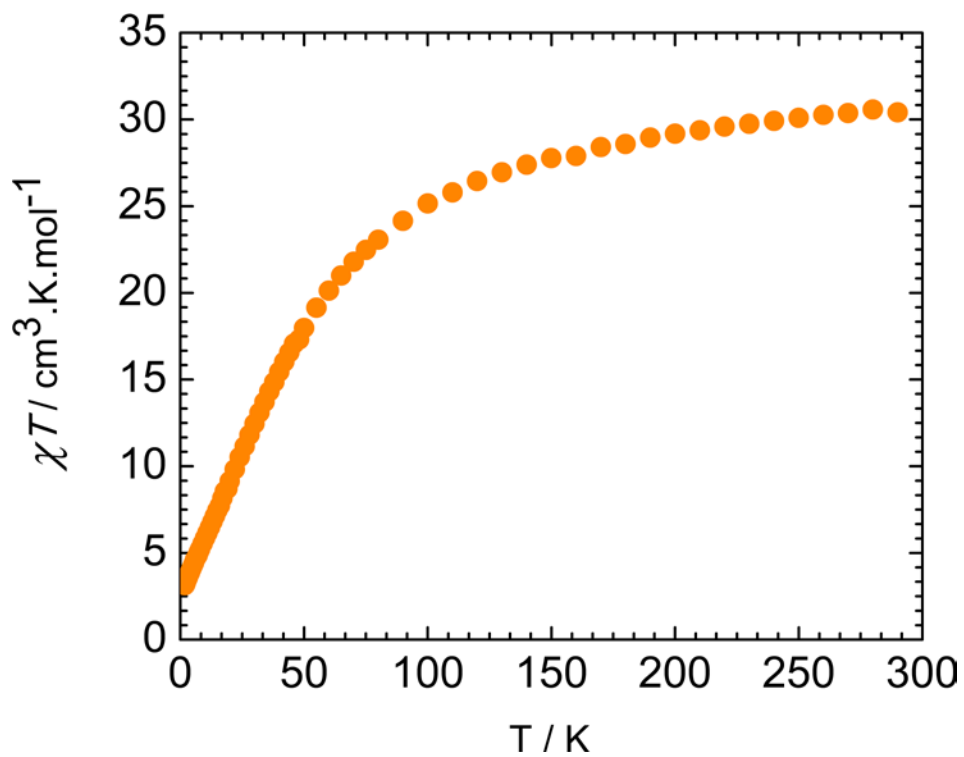

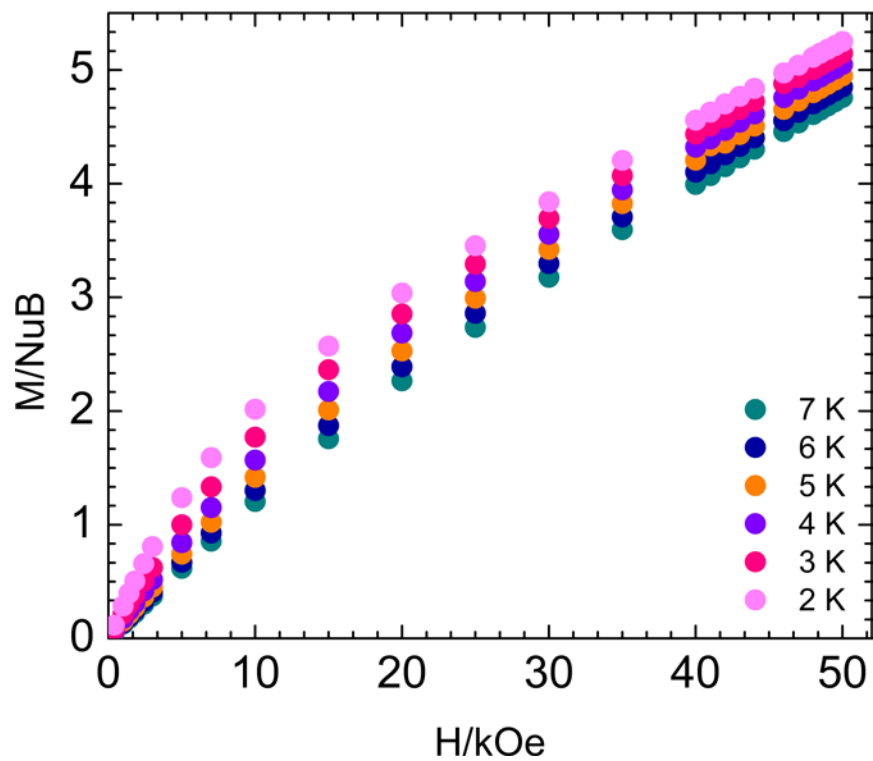**Fig. S5** $X_M T$ *vs. T* plot for complex **2** at *B* = 0.1 Tesla.

Fig. S6 *M vs. H* for **2** at the indicated temperatures.

References

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