Electronic Supplementary Information

Cyanide vs azide "magnetic arm wrestling": Mn^{II}-Nb^{IV} and Mn^{II}-Mo^{IV} magnetic coordination polymers with mixed bridging.

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Experimental section

Preparation of compounds

Chemicals of analytical grade were purchased from commercial sources (Sigma-Aldrich and Avantor Materials) and used as received. $K_4[Nb(CN)_8]\cdot 2H_2O$ and $K_4[Mo(CN)_8]\cdot 2H_2O$ were synthesized according to the reported procedures.[S1] All operations were carried out under an ambient atmosphere. Caution! Sodium azide is highly toxic and can react with transition metals to form highly explosive compounds. Reaction with acids leads to highly volatile and toxic HN_3.

Synthesis of $\{(NH_4)[(H_2O)Mn^{II}\text{-}(\mu\text{-}N_3)\text{-}Mn^{II}(H_2O)][Nb^{IV}(CN)_8]\cdot 3H_2O\}_n$ (Mn_2NbN_3)

An equimolar aqueous solution (37.5 ml) of NaN_3 (1.595 g, 24.75 mmol) and NH_4Cl (1.325 g, 24.75 mmol) was prepared. Half of this solution was used to dissolve $K_4[Nb(CN)_8]\cdot 2H_2O$ (175 mg, 0.375 mmol) and the other half for $MnCl_2\cdot 4H_2O$ (150 mg, 0.75 mmol). Note that both NaN_3 and NH_4Cl are used in large excess to ensure complete insertion of the bridging anion. Both portions were mixed and left undisturbed for 7 days. Dark orange crystals (Yield 6 %) of **Mn_2NbN_3** were decanted, washed repeatedly with water, filtered and dried in air. Found C, 16.89; H, 2.674; N, 29.41. $C_8H_{14}Mn_2N_{12}NbO_5$ (561.06 g/mol) requires C, 17.13; H, 2.52; N, 29.96. IR (ν_{max}/cm^{-1}): 3607s, 3566s and 3262br ν(N-H) and ν(O-H), 2135vs ν(C≡N) and ν(N=N=N), 1609m δ(OH), 1431m and 1403m ν(NH_4^+).

Synthesis of $\{(NH_4)[(H_2O)Mn^{II}\text{-}(\mu\text{-}N_3)\text{-}Mn^{II}(H_2O)][Mo^{IV}(CN)_8]\cdot 3H_2O\}_n$ (Mn_2MoN_3)

An equimolar aqueous solution (15 ml) of NaN_3 (637.5 mg, 9.9 mmol) and NH_4Cl (529.8 mg, 9.9 mmol) was prepared. Half of this solution was used to dissolve $K_4[Mo(CN)_8]\cdot 2H_2O$ (70.0 mg, 0.14 mmol) and the other half for $MnCl_2\cdot 4H_2O$ (60.0 mg, 0.30 mmol). Both portions were mixed and left undisturbed for 5 days. Yellow crystals (Yield 26 %) of **Mn_2MoN_3** were decanted, washed repeatedly with water, filtered and dried in air. Found C, 16.67; H, 2.639; N, 29.71. $C_8H_{14}Mn_2N_{12}NbO_5$ (564.09 g/mol) requires C, 17.03; H, 2.50; N, 29.80. IR (ν_{max}/cm^{-1}): 3592s, 3554s and 3215br ν(N-H) and ν(O-H), 2132vs ν(C≡N) and ν(N=N=N), 1621m δ(OH), 1431m and 1403m ν(NH_4^+).

Physical measurements and calculations

Elemental analyses were performed using ELEMENTAR Vario Micro Cube CHNS analyser.

Magnetic Measurements

Magnetic measurements were performed using Quantum Design MPMS-3 Evercool magnetometer. Each sample was loaded into two plastic bags for safety. Samples were fixed to long quartz stick using small piece of kapton tape. The data of magnetic susceptibility were corrected for the diamagnetic contributions of the sample holders (foil and kapton) and diamagnetism of the samples themselves using Pascal constants[S2]. Value of the coupling constant J_{MnMn} through the additional bridging ligand N_3^- were obtained using PHI software[S3] by fitting the experimental $M(H)$ and $\chi(T)$ dependences for **Mn_2MoN_3**.

Single crystal X-ray diffraction

The single crystal X-ray diffraction data were collected on a Bruker D8 Quest Eco Photon50 CMOS equipped with a Mo Kα sealed tube radiation source and a graphite monochromator. Data reduction and determination of the unit cell parameters were carried out using SAINT and SADABS, which are the part of Apex3 package. Reflections intensities were correct for each single crystal based on sample absorption using multi-scan method. Structures were determined by direct methods using Apex3 software (ShelXT). All non-hydrogen atoms were refined anisotropically. Least-squares refinement of parameters with approximation to the normal matrix were made by minimizing the function $\Sigma w(|F_o|-|F_c|)^2$, where F_o and F_c are the observed and calculated structure factors. Details of the measurements can be found in Table S1 and S2. Figure S1 presents the asymmetric units with atom labelling scheme. CCDC 1561250 (**Mn_2NbN_3**) and 1561249 (**Mn_2MoN_3**) contain the supplementary crystallographic data for this paper. These data can be obtained free of charge from the Cambridge Crystallographic Data Centre via www.ccdc.cam.ac.uk/data_request/cif.

Table S1. Sc-XRD measurements, solution and refinement parameters for **Mn_2NbN_3** and **Mn_2MoN_3**.

	Mn_2NbN_3	**Mn_2MoN_3**
Formula	$C_8H_{14}Mn_2N_{12}NbO_5$	$C_8H_{14}Mn_2MoN_{12}O_5$
Temperature, *K*	170(2)	120(2)
λ [Å]	0.71073 (Mo Kα)	0.71073 (Mo Kα)
Molecular weight, g/mol	560.87	564.09
Crystallographic system	Tetragonal	Tetragonal
Space group	*I*4/*m*	*I*4/*m*
Unit cell	a = 12.0837(3) Å c = 13.3147(3) Å	a = 11.9694(3) Å c = 13.1021(4) Å
Volume *V*, Å^3	1944.16(11)	1877.09
Z	16	4
Density ρ_{calc}, g/cm^3	1.828	1.989
F (000)	1036	2.032
θ, deg	27.632-3.060	1104
Abs. coeff. μ, mm^{-1}	1.886	3.404-28.252
Data/restrains/parameters	1190/0/71	1220/11/93
R [$F_o > 4\sigma(F_o)$]*	R_1 = 0.0365 (1134) wR_2 = 0.0844(1190)	R_1 = 0.0208 (1085) wR_2 = 0.0476 (1220)
GOF on F^2	1.120	1.033
max/min/resid. density, e·Å^{-3}	1.790/-1.867/0.116	0.641/-0.430/0.076
Reflections collected	9472	7342
Unique reflection	1190	1220
R_{int}	0.0240	0.0310
Completeness, %	99.8	99.1

Table S2. Selected bond lengths (Å) and angles (deg) in **Mn_2NbN_3** and **Mn_2MoN_3** (M1 = Nb1 or Mo1, respectively)

	Mn_2NbN_3	**Mn_2MoN_3**
bond lengths:		
M1-C1	2.247(3)	2.149(2)
M1-C2	2.247(3)	2.158(2)
Mn1-O1$_{aq}$	2.288(4)	2.267(2)
Mn1-N3$_{N3}$	2.115(7)	2.144(3)
Mn1-N1$_{CN}$	2.228(3)	2.236(2)
Mn1-N2$_{CN}$	2.195(3)	2.197(17)
angles:		
Mn1-N1-C1$_{CN}$	159.1(3)	158.42(15)
Mn1-N2-C2$_{CN}$	165.6(3)	164.26(16)
Mn1-N3-N4$_{N3}$	157.7(5)	155.6(2)

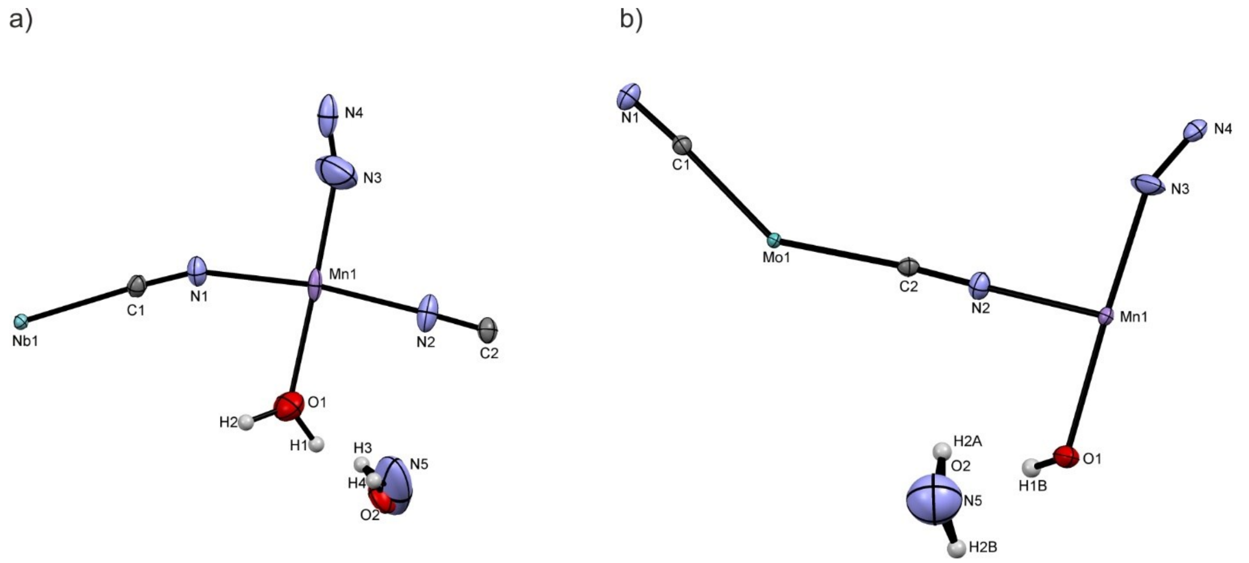

Figure S1. Asymmetric units of **Mn_2NbN_3** (a) and **Mn_2MoN_3** (b).

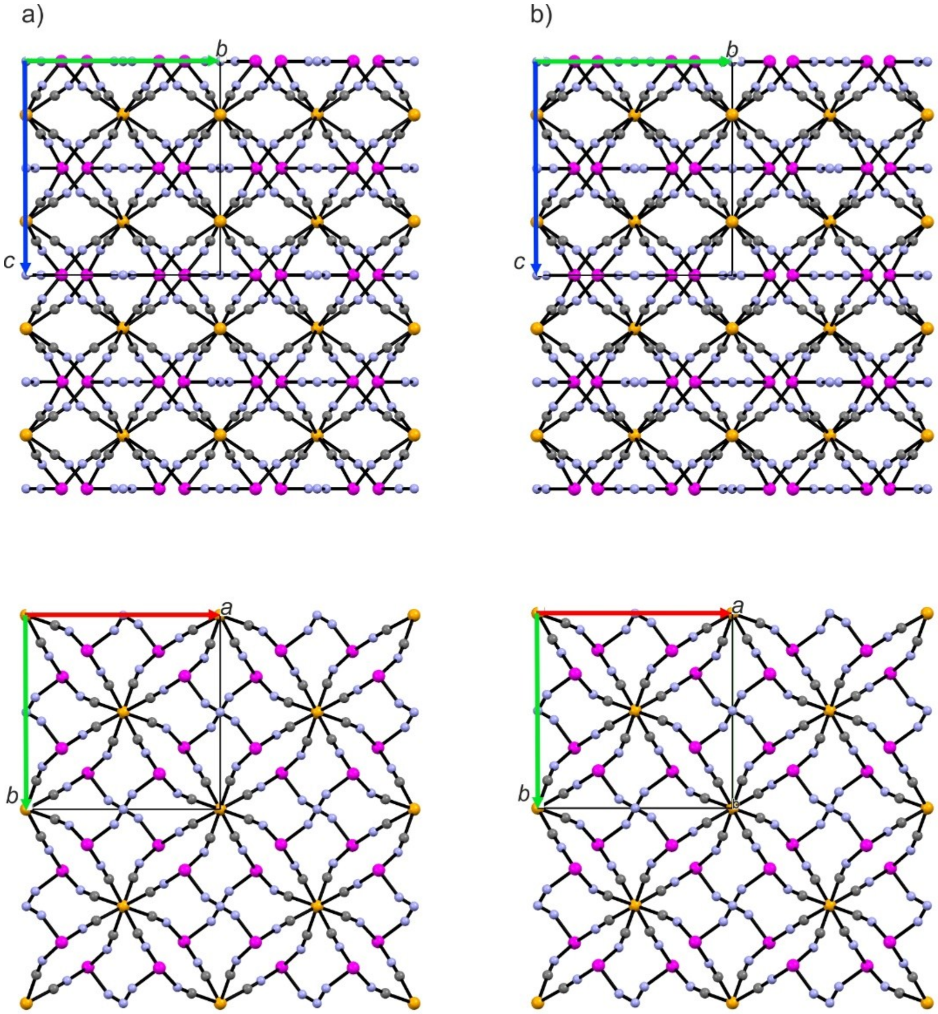

Figure S2. Structural diagrams showing the crystal packing of **Mn_2NbN_3** (a) and **Mn_2MoN_3** (b) along the *a* (top) and *c* (bottom) crystallographic directions. Nb/Mo – yellow, Mn – pink, C – gray, N – blue. O and H atoms omitted for the sake of clarity.

SHAPE calculations

Continuous Shape Measure Analysis for coordination spheres of Nb^{IV}, Mo^{IV} and Mn^{II} was performed using SHAPE software[S4] and results were summarised in Table S3.

Table S3. The analysis of the geometry of the coordination spheres of Mn^{II}, Nb^{IV} and Mo^{IV} ions in the parent frameworks $\{[Mn^{II}(H_2O)_2]_2[Nb^{IV}(CN)_8]\cdot 4H_2O\}_n$, $\{[Mn^{II}(H_2O)_2]_2[Mo^{IV}(CN)_8]\cdot 4H_2O\}_n$ and in **Mn_2NbN_3, Mn_2MoN_3**. S_{geometry} parameter indicate the agreement level with the reference geometry: OC – octahedral, SAPR – square antiprism. S_{geometry} = 0 indicate perfect match.

Compound	**S_{OC} (O_h) for Mn^{II}**	**S_{SAPR} (D_{4d}) for Nb^{IV}**	**Compound**	**S_{OC} (O_h) for Mn^{II}**	**S_{SAPR} (D_{4d}) for Mo^{IV}**
Nb-parent	0.217	0.131	**Mo-parent**	0.388	0.304
Mn_2NbN_3	0.122	0.085	**Mn_2MoN_3**	0.145	0.222

Powder X-Ray diffraction

The identity of the bulk samples of **Mn_2NbN_3** and **Mn_2MoN_3** was also confirmed by powder X-ray diffraction (Figure S3a and S3b, respectively). PXRD experiments were carried out using PANalytical X'Pert Pro MPD diffractometer (Cu Kα radiation and graphite monochromator) at ambient temperature for dry well-ground samples loaded into narrow diameter borosilicate-glass tubes (0.7 mm in diameter). Experimental PXRD diffraction patterns match almost perfectly the simulated ones from sc-XRD structural models obtained at ambient temperature which confirms the purity and homogeneity of the bulk samples.

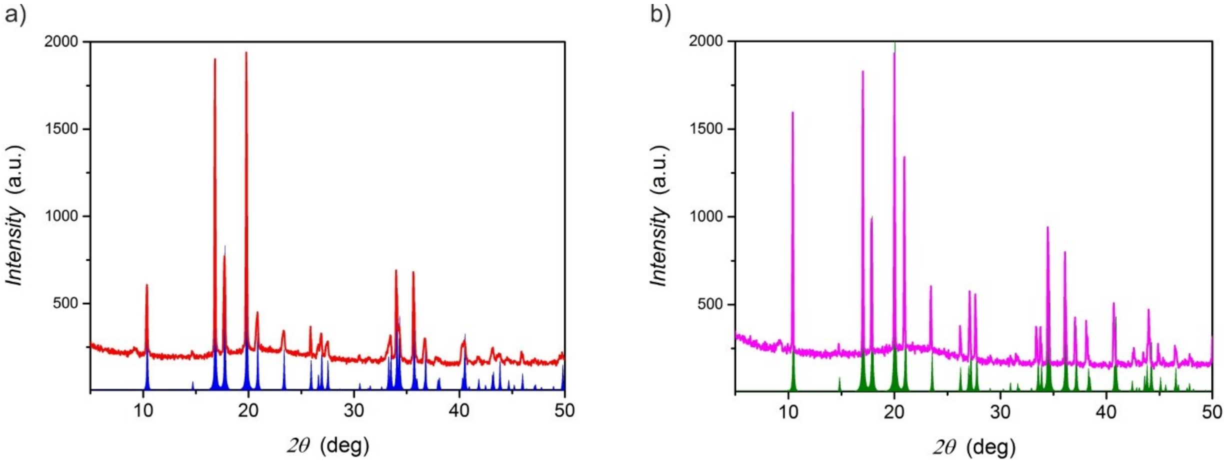

Figure S3. Experimental (red and magenta) and simulated from single crystal structural models (blue and green) powder X-ray diffraction patterns for **Mn_2NbN_3** (a) and **Mn_2MoN_3** (b).

Infrared spectra

Infrared spectra (Figure S4) were collected on Nicolet iS 5 FT-IR microscope in the 4000 - 650 cm^{-1} range. Compared to the parent frameworks (blue and green lines in Figure S4), **Mn$_2$NbN$_3$** (red line) and **Mn$_2$MoN$_3$** (magenta line) exhibit additional bands at around 3300 and 3225 cm^{-1} corresponding to *v*(N-H) of the ammonium cations, very strong bands around 2130 cm^{-1} corresponding to the stretching vibrations *v*(N=N=N) of azide (overlap with CN$^-$ stretching) and two new bands around 1400 cm^{-1} that correspond to the deformation vibrations of the ammonium cations. There are also bands connected to the presence of both crystallisation and coordination water molecules in the 3500-3000 cm^{-1} range and 1620-1600 cm^{-1}. IR spectra confirm the successful incorporation of both ammonium and azide ions into the frameworks of **Mn$_2$NbN$_3$** and **Mn$_2$MoN$_3$**.

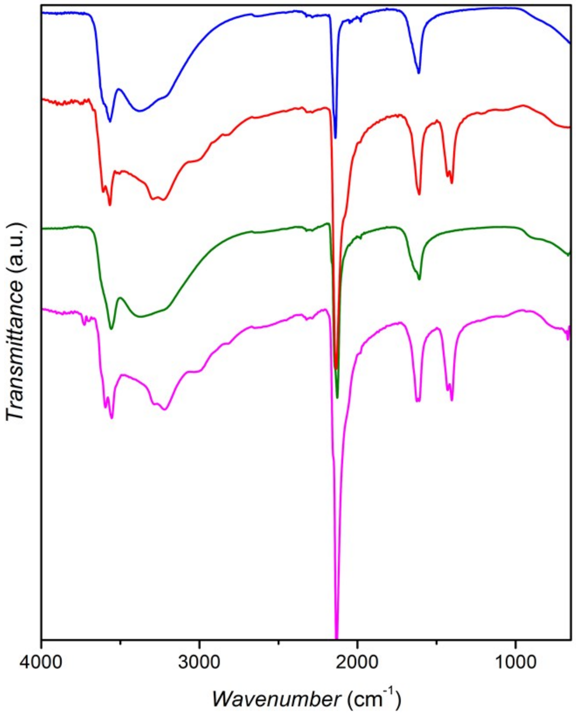

Figure S4. IR spectra of the parent {[Mn^{II}(H$_2$O)$_2$]$_2$[Nb^{IV}(CN)$_8$]·4H$_2$O}$_n$) (blue), **Mn$_2$NbN$_3$** (red), the parent {[Mn^{II}(H$_2$O)$_2$]$_2$[Mo^{IV}(CN)$_8$]·4H$_2$O}$_n$) (green), and **Mn$_2$MoN$_3$** (magenta). See the text "Infrared spectra" above for details.

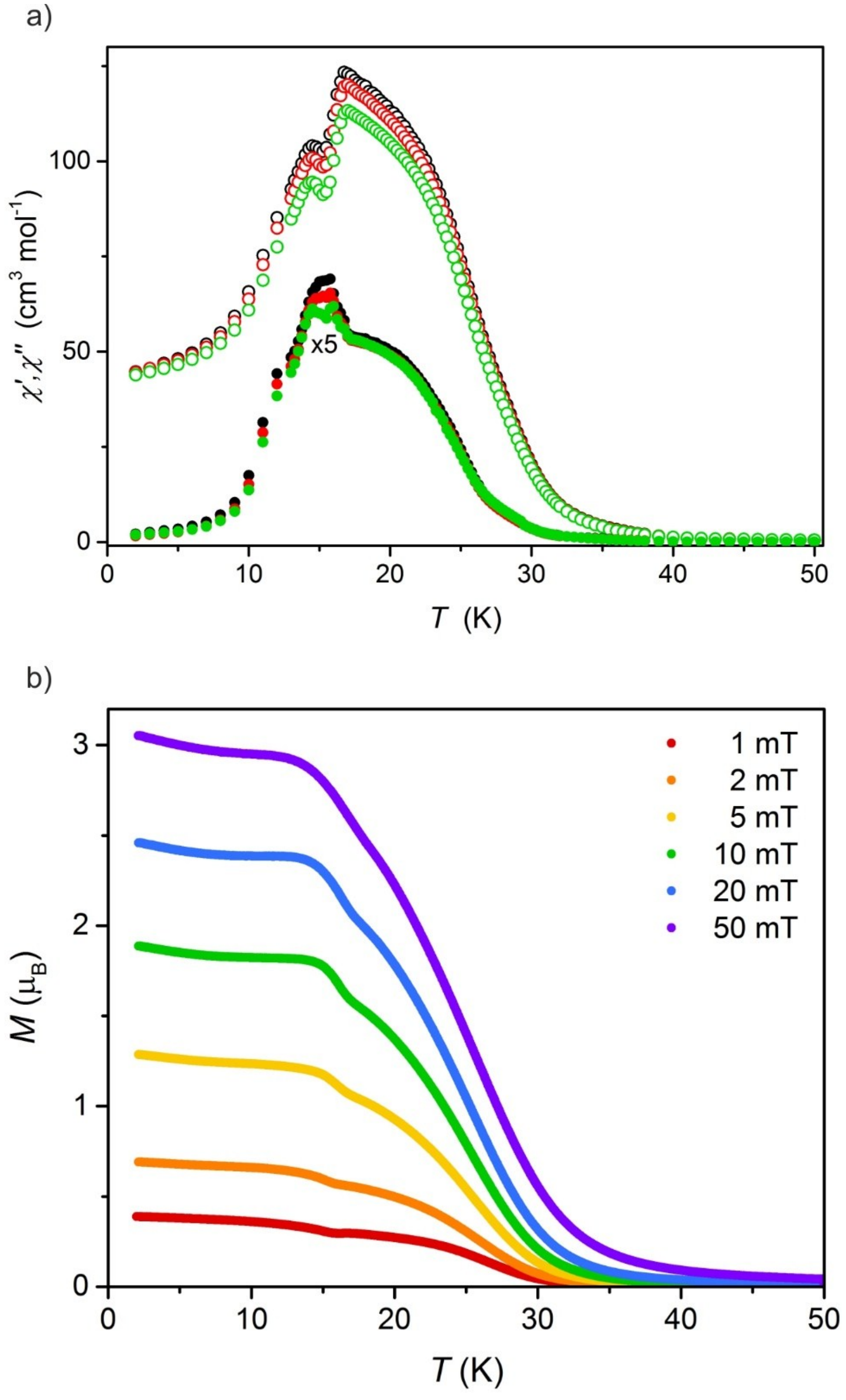

Figure S5. Temperature dependence of the in-phase and out-of-phase *ac* magnetic susceptibility at H_{ac} = 0.01 mT and ν_{ac} = 7 Hz (black), 70 Hz (red) and 700 Hz (green) (a) and temperature dependence of the magnetization at various magnetic fields in the 1-50 mT range (b) for **Mn_2NbN_3**. Both plots reveal a gradual increase of the susceptibility/magnetization and a "16 K" anomaly that disappear at higher magnetic fields.

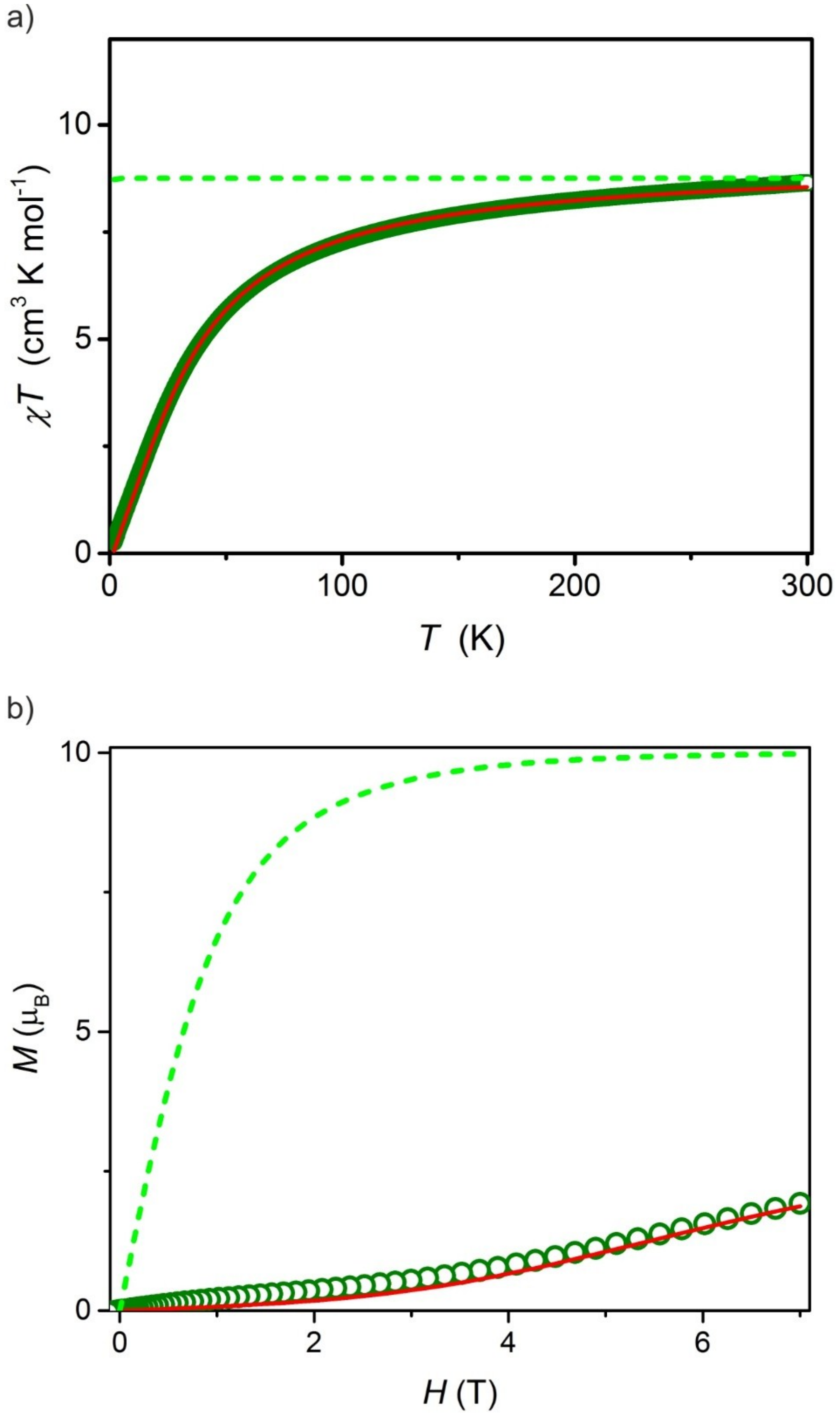

Figure S6. Experimental $\chi(T)$ at 0.1 T (a) and $M(H)$ (b) at 1.8 K for **Mn_2MoN_3** (dark green points) together with the best simultanous fit using the Hamiltonian $\hat{H} = -2 \cdot J_{MnMn} \cdot S_{Mn} \cdot S_{Mn}$ (red solid line) leading to $J_{MnMn} = -2.4(1)$ cm^{-1} and $g_{Mn} = 2.04(1)$. Dashed green lines represent the $\chi(T)$ at 0.1 T (a) and $M(H)$ (b) at 1.8 K for the Mo-parent compound without additional azide bridges.

References in the ESI

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[S4] M. Llunell, D. Casanova, J. Cirera, P. Alemany, S. Alvarez, *SHAPE* v. 2.0; University of Barcelona, Barcelona, Spain, 2010.