Supplementary Information

New Members of Polynuclear Manganese Family: $Mn^{II}_2Mn^{III}_2$ Single-Molecule Magnets and $Mn^{II}_3Mn^{III}_8$ Antiferromagnetic Complex. Synthesis and Magnetostructural correlations

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Bond Valence Sum (BVS) Studies.
The BVS analysis was performed according to the following equation:[S1]

$$BVS = \sum_{i\,=\,1}^{n} e^{\frac{r_0 - r_i}{0.37}}$$

where r_i is the experimentally derived bond length for ligand i and r_0 is the reference bond length. The values used for r_0 include Mn(II)–O = 1.765, Mn(II)–N = 1.849, Mn(III)–O = 1.732, Mn(III)–N = 1.837 Å. With these data the following valences have been deducted: (**1**) Mn1: 2.936, Mn2: 1.939; (**2**) Mn1: 2.936, Mn2: 1.970; (**3**) Mn1: 3.020, Mn2: 2.995, Mn3: 3.008, Mn4: 2.829, Mn5: 2.006, Mn6: 2.645. In this way the positions Mn4 and Mn6 (in **3**) were considered as being mixed-valent. The total positive charge calculated using the Mn1–Mn6 valences is +29.98, what agrees with the total negative charge (–30) expected from the molecular structure of **3**. From BVS the numbers of divalent and trivalent manganese atoms in the structure of **3** appeared to be 3.06 and 7.94, respectively. Thus, the overall formula was fixed as $Mn^{II}_3Mn^{III}_8$.

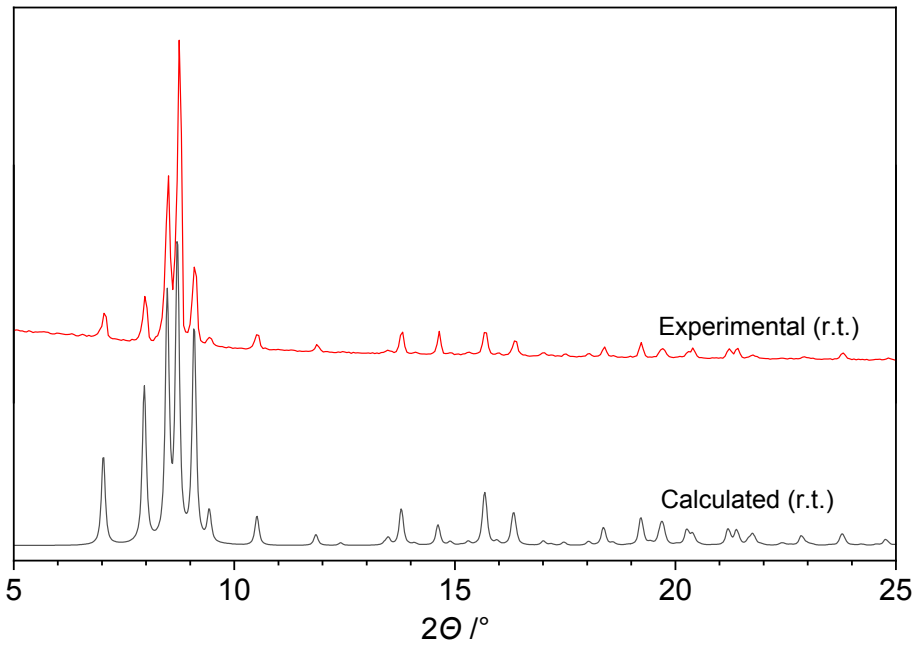


Fig. S1 Experimental and theoretical powder X-ray patterns for **1.**

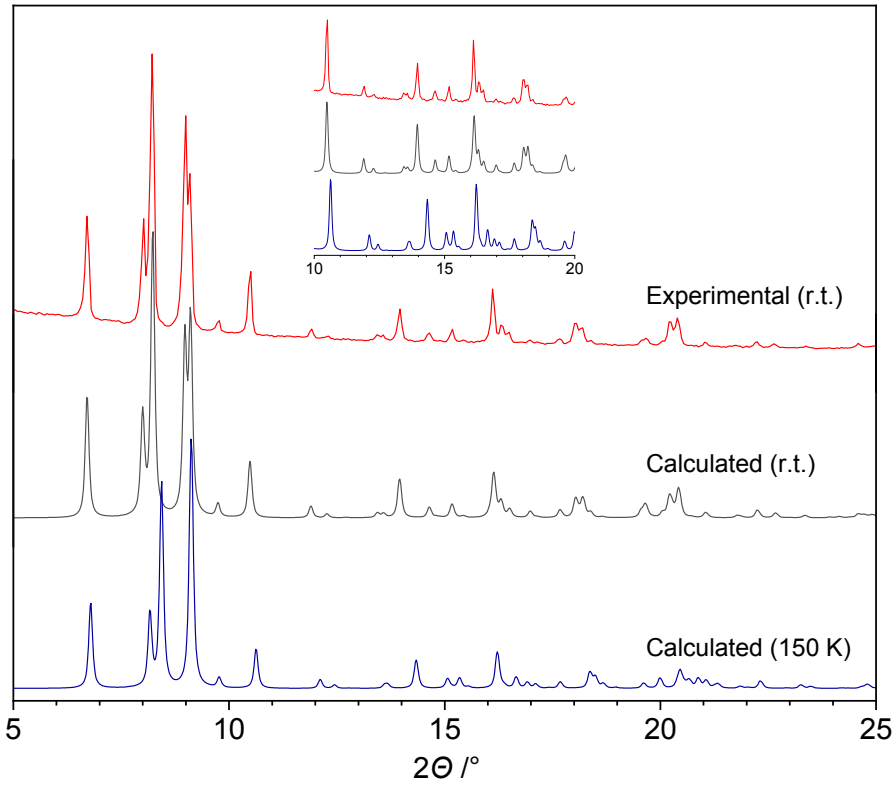


Fig. S2 Experimental (top) and theoretical powder X-ray patterns for **2rt** (middle) and **2** (bottom)**.** The inset shows the 10–20° region in detail.

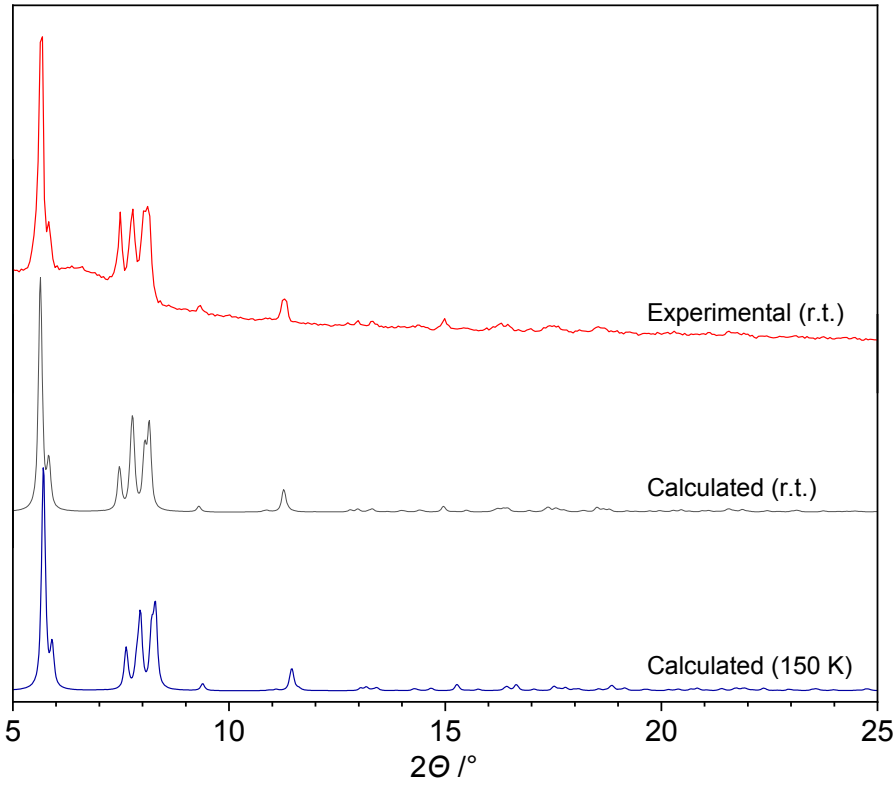


Fig. S3 Experimental and theoretical powder X-ray patterns for **3.**

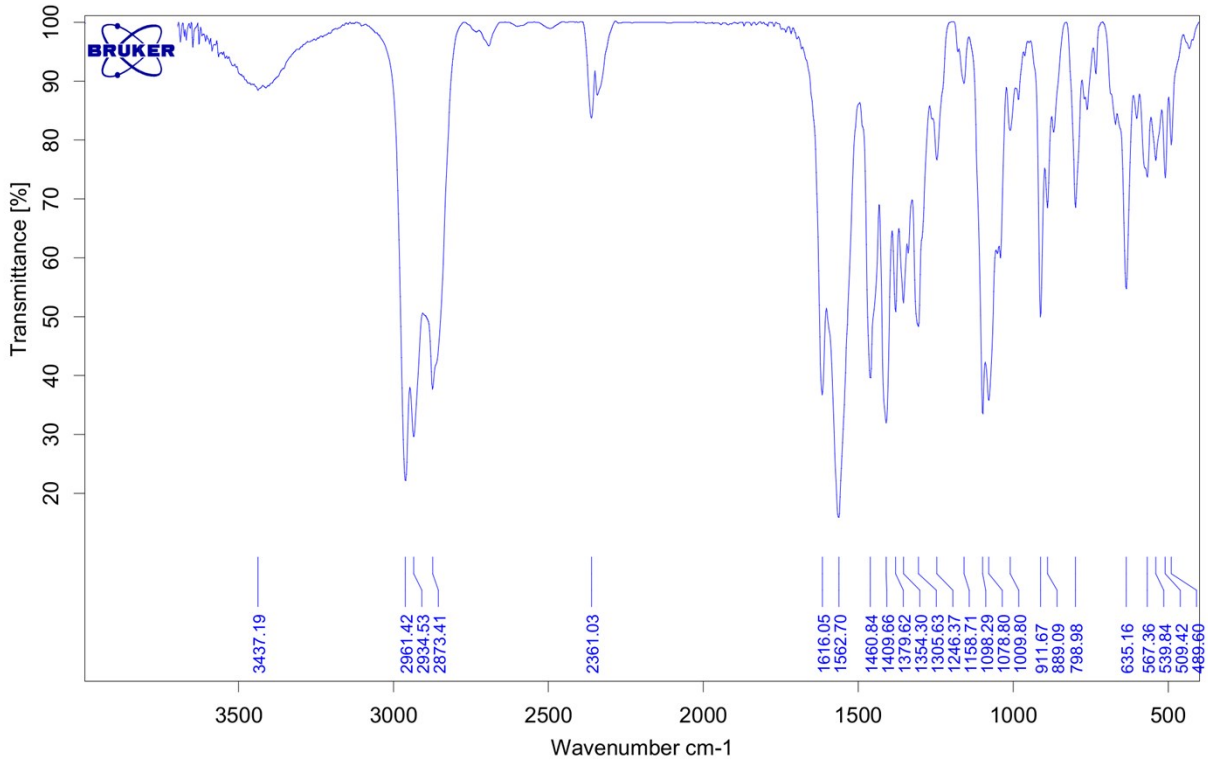


Fig. S4 IR spectrum of **1**.

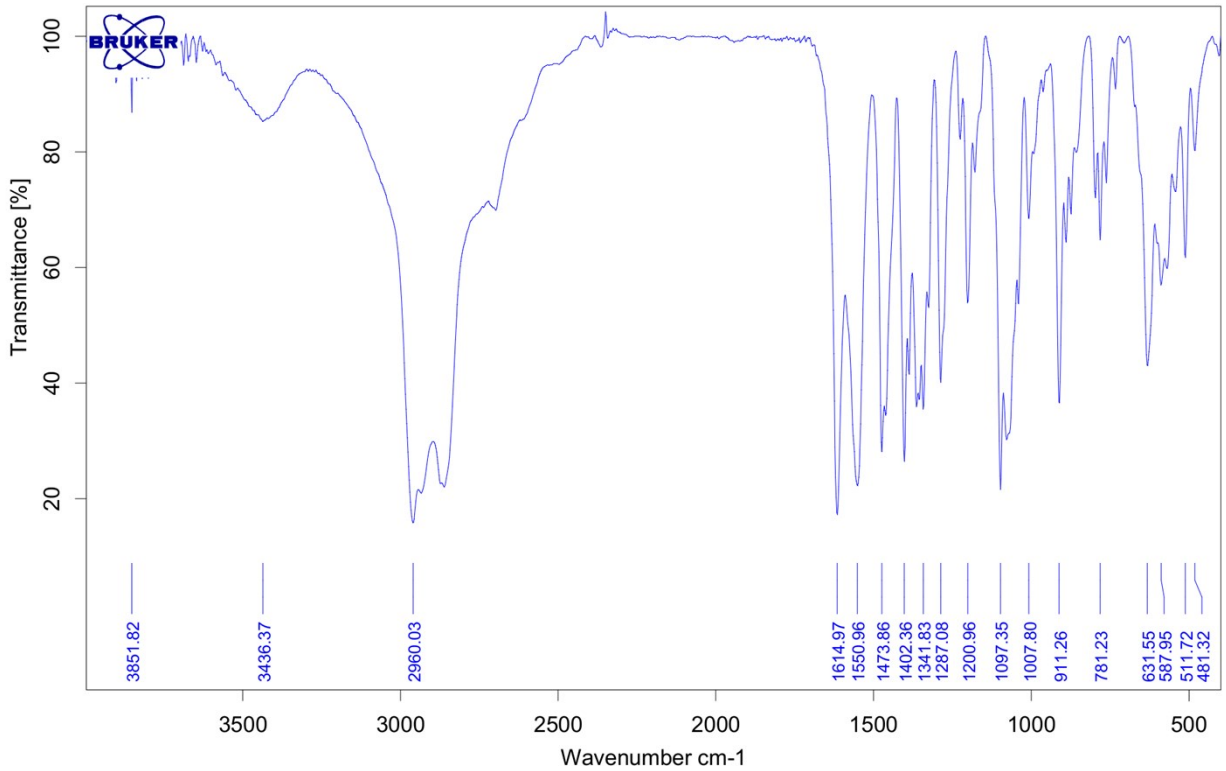


Fig. S5 IR spectrum of **2**.

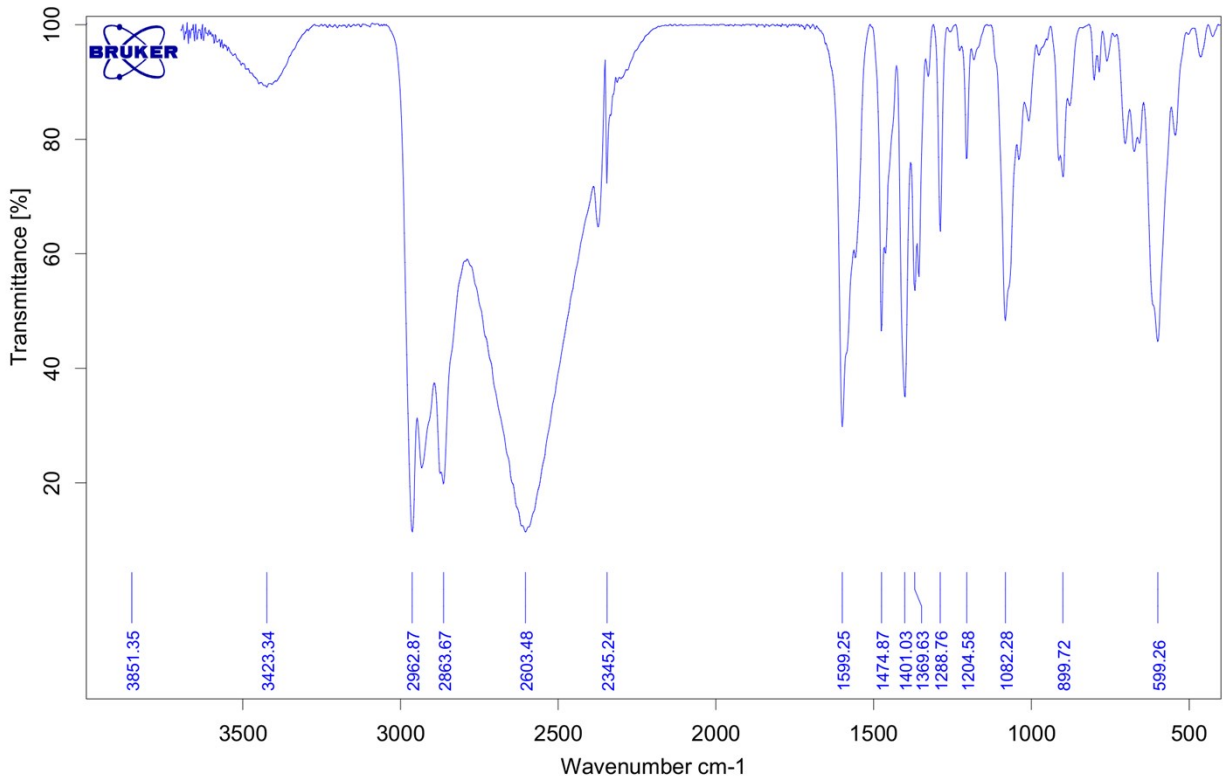


Fig. S6 IR spectrum of **3**.

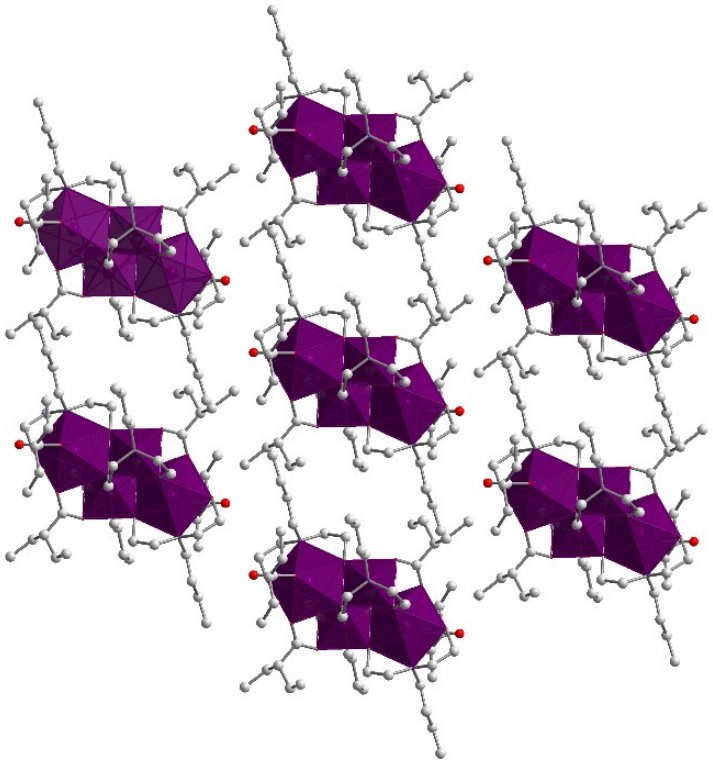


Fig. S7 Polyhedral representation of the packing of tetranuclear molecules in **1** viewed down the *a* axis.

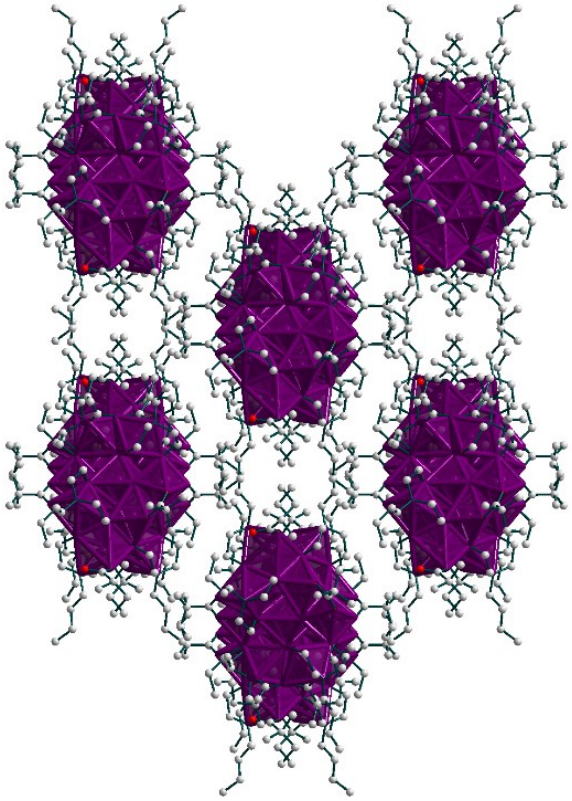


Fig. S8 Polyhedral representation of the packing of undecanuclear molecules in **3** viewed down the *c* axis.

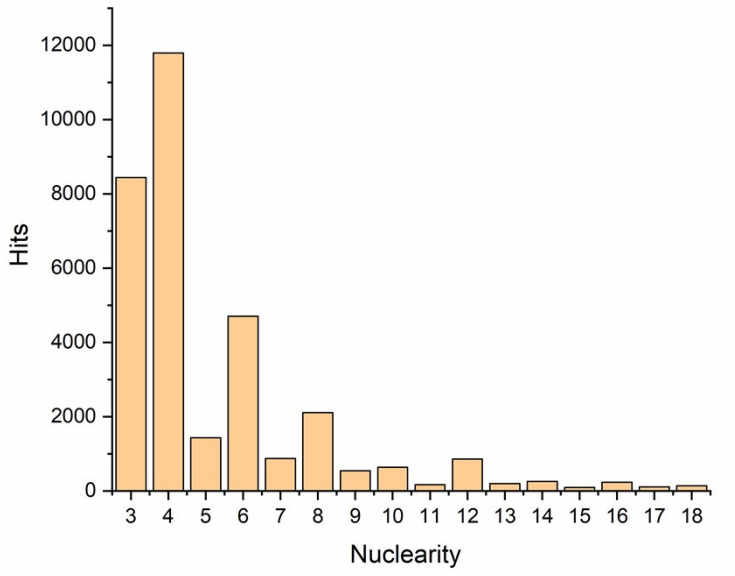


Fig. S9 The dependence of the number of complexes reported in the CSD (version 5.40, August 2019) on their nuclearity (for $3 < n < 18$). The search was provided only for non-polymeric compounds where all metal centers form a molecule.

Table S1 Selected geometrical parameters (distances/Å and angles/°) for **1**, **2** and **2rt**.

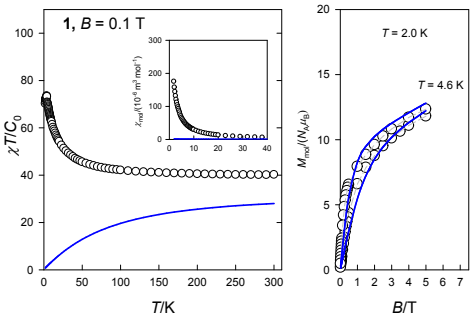
	1	**2**	**2rt**
Mn1–O1	1.912(2)	1.9183(19)	1.908(3)
Mn1–O2	1.951(2)	1.939(2)	1.945(3)
Mn1–O2^a	2.246(2)	2.220(2)	2.232(3)
Mn1–O3	1.878(2)	1.8809(18)	1.879(3)
Mn1–O5	1.931(2)	1.927(2)	1.922(3)
Mn1–N1	2.334(3)	2.338(3)	2.334(4)
Mn2–O1	2.137(2)	2.131(2)	2.132(3)
Mn2–O2^a	2.342(2)	2.3763(19)	2.360(3)
Mn2–O3^a	2.278(2)	2.293(2)	2.291(3)
Mn2–O4^a	2.336(3)	2.370(2)	2.364(4)
Mn2–O6	2.384(3)	2.303(2)	2.342(4)
Mn2–O7	2.104(3)	2.109(2)	2.115(3)
Mn2–N2^a	2.440(3)	2.385(3)	2.414(4)
O1–Mn1–O2	91.67(9)	91.85(8)	91.82(13)
O1–Mn1–O2^a	84.54(9)	85.26(8)	84.37(11)
O1–Mn1–O3	172.24(10)	171.16(8)	171.85(13)
O1–Mn1–O5	93.00(10)	93.04(8)	92.77(14)
O1–Mn1–N1	77.53(10)	76.87(8)	77.41(13)
O2–Mn1–O2^a	82.14(9)	82.11(8)	82.12(12)
O2–Mn1–O3	81.76(9)	81.24(8)	81.43(13)
O2–Mn1–O5	174.22(10)	173.25(9)	174.13(13)
O2–Mn1–N1	80.95(10)	81.28(8)	81.16(13)
O2–Mn1–N1^a	154.87(10)	155.09(8)	154.76(13)
O3–Mn1–O2^a	98.55(9)	99.14(8)	99.13(12)
O3–Mn1–O5	93.82(10)	94.31(8)	94.27(14)
O3–Mn1–N1	97.26(11)	96.53(8)	96.93(13)
O5–Mn1–O2^a	94.92(9)	93.67(8)	94.68(13)
O5–Mn1–N1	103.39(11)	104.36(9)	103.42(15)
O1–Mn2–O2^a	77.48(8)	76.96(7)	76.62(10)
O1–Mn2–O3^a	89.80(9)	89.45(7)	89.27(11)
O1–Mn2–O4^a	90.74(10)	90.59(8)	90.49(13)
O1–Mn2–O6	78.60(9)	80.01(8)	78.90(12)
O1–Mn2–O7	163.02(10)	165.34(8)	163.39(13)
O1–Mn2–N2^a	99.17(10)	96.49(8)	98.00(13)
O2^a–Mn2–O3^a	65.71(8)	64.34(7)	64.86(10)
O2^a–Mn2–O4^a	150.93(10)	150.59(8)	151.05(13)
O2^a–Mn2–N2^a	136.40(9)	135.84(8)	135.94(12)
O3^a–Mn2–O4^a	141.68(10)	143.15(8)	141.89(13)
O3^a–Mn2–N2^a	70.86(9)	72.07(8)	71.44(12)
O4^a–Mn2–N2^a	71.25(11)	71.32(8)	70.86(14)
O6–Mn2–O2^a	76.04(8)	75.79(7)	75.63(11)
O6–Mn2–O3^a	141.61(9)	140.10(7)	140.40(12)
O6–Mn2–O4^a	75.61(10)	75.86(8)	76.50(13)
O6–Mn2–O7	85.06(10)	85.59(8)	84.77(13)
O6–Mn2–N2^a	146.76(10)	146.96(9)	147.20(13)
O7–Mn2–O2^a	94.22(9)	96.97(7)	96.45(11)
O7–Mn2–O3^a	100.36(10)	100.01(8)	101.55(12)
O7–Mn2–O4^a	89.63(11)	88.48(8)	88.67(13)
O7–Mn2–N2^a	97.02(11)	97.06(8)	97.39(14)

Symmetry code: ^{a} 1–x, 1–y, 1–z.

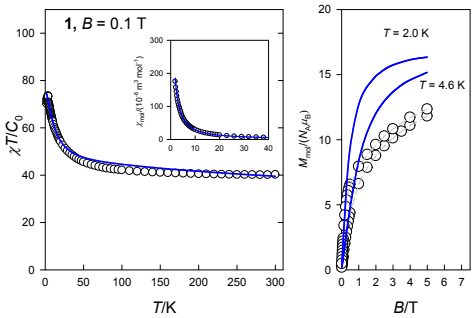
Table S2 Selected geometrical parameters (distances/Å and angles/°) for **3**.

Mn1–O6	1.83914	Mn4–O5	1.8829
Mn1–O1	1.87910	Mn4–O10	2.24810
Mn1–O4	1.91111	Mn4–O14	2.32710
Mn1–O2	2.3738	Mn4–O3	1.9069
Mn2–O1	1.9178	Mn4–N3	2.15116
Mn2–O7	1.8969	Mn5–O17	2.04115
Mn2–O3	1.9068	Mn5–O5	2.14911
Mn2–O9	1.9199	Mn5–O13	2.18614
Mn2–O11	2.17312	Mn5–O13[a]	2.18911
Mn2–O2	2.31110	Mn5–O14	2.38111
Mn3–O1	2.2949	Mn5–N2	2.35414
Mn3–O3	1.8789	Mn6–O6	1.9638
Mn3–O4	1.8844	Mn6–O15[a]	2.05215
Mn3–O14[a]	1.90310	Mn6–O8	2.07313
Mn3–O12	1.97310	Mn6–O16	2.11812
Mn3–O13	2.15711	Mn6–O7	2.19010
Mn4–O2	1.9129	Mn6–N1	2.23117
O6–Mn1–O1[a]	95.13	O5–Mn4–O3	95.54
O6–Mn1–O1	95.13	O5–Mn4–O2	174.74
O1[a]–Mn1–O1	169.85	O3–Mn4–O2	85.24
O6–Mn1–O4	180.0	O5–Mn4–N3	100.66
O1[a]–Mn1–O4	84.93	O3–Mn4–N3	160.26
O1–Mn1–O4	84.93	O2–Mn4–N3	79.95
O6–Mn1–O2	94.42	O5–Mn4–O10	90.84
O1[a]–Mn1–O2	95.83	O3–Mn4–O10	85.74
O1–Mn1–O2	83.43	O2–Mn4–O10	94.54
O4–Mn1–O2	85.62	N3–Mn4–O10	82.75
O6–Mn1–O2[a]	94.42	O5–Mn4–O14	76.24
O1[a]–Mn1–O2[a]	83.43	O3–Mn4–O14	116.04
O1–Mn1–O2[a]	95.83	O2–Mn4–O14	98.84
O4–Mn1–O2[a]	85.62	N3–Mn4–O14	79.35
O2–Mn1–O2[a]	171.15	O10–Mn4–O14	155.44
O7–Mn2–O3	168.85	O17–Mn5–O5	117.56
O7–Mn2–O1	90.24	O17–Mn5–O13	147.66
O3–Mn2–O1	86.54	O5–Mn5–O13	91.94
O7–Mn2–O9	90.44	O17–Mn5–O13[a]	88.65
O3–Mn2–O9	93.54	O5–Mn5–O13[a]	139.24
O1–Mn2–O9	177.15	O13–Mn5–O13[a]	75.84
O7–Mn2–O11	101.95	O17–Mn5–N2	94.56
O3–Mn2–O11	88.74	O5–Mn5–N2	76.95
O1–Mn2–O11	89.14	O13–Mn5–N2	78.25
O9–Mn2–O11	88.04	O13a–Mn5–N2	135.16
O7–Mn2–O2	94.14	O17–Mn5–O14	98.36
O3–Mn2–O2	74.93	O5–Mn5–O14	70.54
O1–Mn2–O2	84.44	O13–Mn5–O14	104.74
O9–Mn2–O2	98.44	O13[a]–Mn5–O14	75.34
O11–Mn2–O2	162.74	N2–Mn5–O14	147.35
O3–Mn3–O4	91.53	O6–Mn6–O15[a]	97.25
O3–Mn3–O14[a]	176.64	O6–Mn6–O8	93.74
O4–Mn3–O14[a]	85.33	O15[a]–Mn6–O8	169.16
O3–Mn3–O12	89.84	O6–Mn6–O16	97.25
O4–Mn3–O12	165.15	O15[a]–Mn6–O16	93.15
O14[a]–Mn3–O12	93.04	O8–Mn6–O16	86.15
O3–Mn3–O13	94.44	O6–Mn6–O7	101.44
O4–Mn3–O13	93.24	O15[a]–Mn6–O7	89.85
O14[a]–Mn3–O13	86.85	O8–Mn6–O7	87.54
O12–Mn3–O13	101.55	O16–Mn6–O7	160.65
O3–Mn3–O1	77.03	O6–Mn6–N1	173.86
O4–Mn3–O1	74.74	O15[a]–Mn6–N1	88.17
O14[a]–Mn3–O1	101.14	O8–Mn6–N1	81.06
O12–Mn3–O1	91.14	O16–Mn6–N1	85.75
O13–Mn3–O1	164.84	O7–Mn6–N1	75.25

Symmetry code: [a] –x, y, 0.5–z.



Good fit of the magnetization: $R(M) = 0.084$
$g_{\text{eff}} = 1.85$,
$J_1/hc = 37.0$ cm^{-1},
$J_2/hc = 15.0$ cm^{-1}, $J_3/hc = -9.7$ cm^{-1},
$\chi_{\text{TIM}} = -8 \times 10^{-9}$ m^3 mol^{-1},
$zj/hc = -2.0$ cm^{-1}



Good fit of the susceptibility: $R(\chi) = 0.031$
$g_{\text{eff}} = 1.85$,
$J_1/hc = 59.4$ cm^{-1},
$J_2/hc = 8.3$ cm^{-1}, $J_3/hc = -6.4$ cm^{-1},
$\chi_{\text{TIM}} = -10 \times 10^{-9}$ m^3 mol^{-1},

Fig. S10 Two fits of the DC magnetic data for **1**.

Table S3 Temperature dependence of AC susceptibility parameters for **1**:

a) at B_{DC} = 0 T

T/K	$R(\chi')$ /%	$R(\chi'')$ /%	χ_S	χ_T	α	τ /10^{-6} s
1.9	1.5	8.1	50.2(14)	175(1)	0.19(1)	2107(64)
2.1	1.2	4.9	47.8(13)	156(1)	0.15(1)	638(16)
2.3	0.91	3.2	47.8(14)	143(1)	0.11(1)	272(7)
2.5	0.58	1.7	51.1(16)	131(1)	0.06(1)	127(4)
2.7	0.47	0.96	55.8(26)	120(1)	0.02(1)	70(4)
2.9	0.31	1.3	52.6(54)	112(1)	0.01	37(4)
3.1	0.26	1.8	37(21)	104(1)	0.01	16(6)
3.3	0.36	3.0	37	97(1)	0.01	9.5(8)

b) at B_{DC} = 0.05 T

T/K	$R(\chi')$ /%	$R(\chi'')$ /%	χ_S	χ_T	α	τ /10^{-6} s
1.9	1.4	9.2	44.4(14)	166(1)	0.30(1)	3470(131)
2.1	1.2	6.5	43.7(14)	150(1)	0.24(1)	1030(34)
2.3	1.0	4.9	43.7(14)	138(1)	0.19(1)	433(14)
2.5	0.78	3.2	45.7(15)	127(1)	0.14(1)	196(6)
2.7	0.56	2.0	50.3(17)	117(1)	0.09(1)	107(4)
2.9	0.40	1.7	53.1(25)	109(1)	0.05(1)	63(4)
3.1	0.30	2.3	47.6(58)	102(1)	0.05(1)	32(5)
3.3	0.31	3.0	45(15)	95(1)	0.04(3)	19(7)
3.5	0.33	5.6	33	89(1)	0.05	9
3.7	0.40	9.0	33	85(1)	0.08(4)	4.8(9)

[a] Susceptibility χ_S and χ_T in units of 10^{-6} m^3 mol^{-1} (SI). Standard deviations in parentheses.

Table S4 Temperature dependence of AC susceptibility parameters for **2** at B_{DC} = 0.05 T.

T/K	$R(\chi')$ /%	$R(\chi'')$ /%	χ_S	χ_T	α	τ /10^{-6} s
1.9	0.69	3.6	44(3)	272(1)	0.14(1)	197(5)
2.1	0.21	1.7	31(4)	245(1)	0.13(1)	65(2)
2.3	0.19	4.8	0	226(1)	0.14(1)	23.6(4)
2.5	0.39	4.6	0	207(1)	0.11(1)	11.9(5)
2.7	0.40	7.2	0	190(1)	0.14(2)	5.2(5)
2.9	0.41	10	0	176(2)	0.21(4)	1.9(4)
3.1	0.44	14	0	164(2)	0.32(7)	0.45(27)

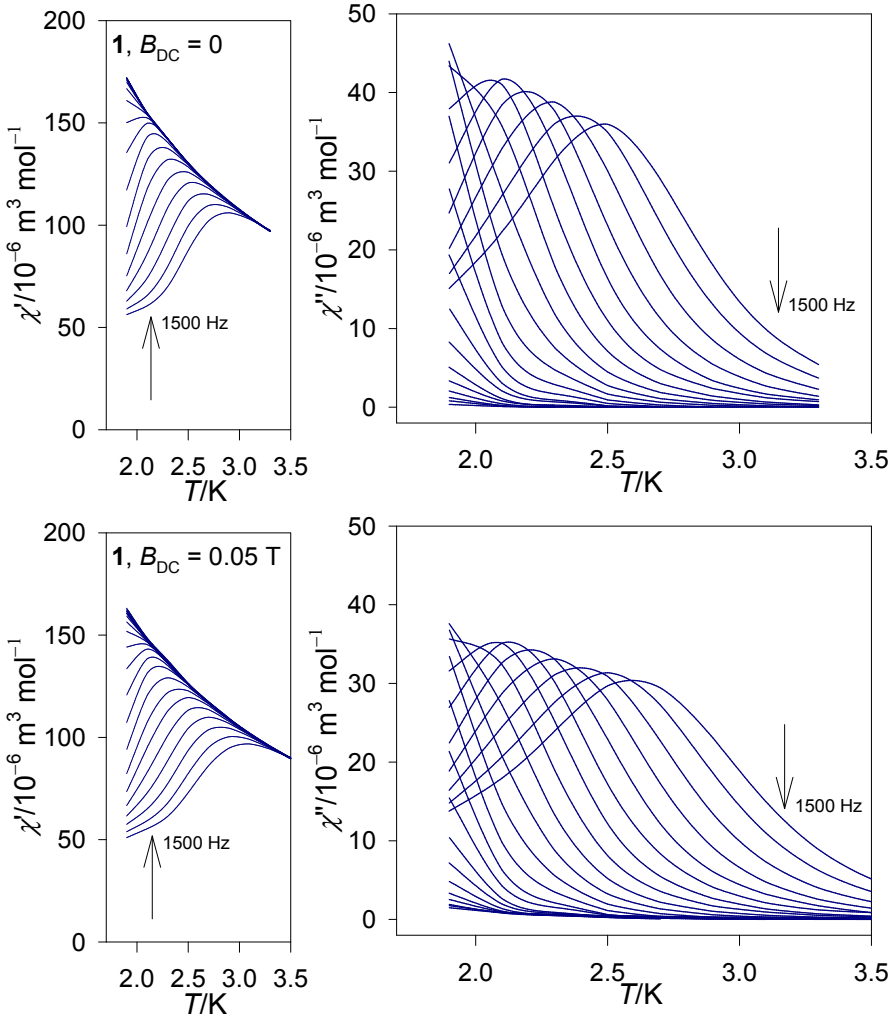


Fig. S11 Temperature evolution of the AC susceptibility components for **1** for different frequencies ranging between f = 0.1 to 1500 Hz.

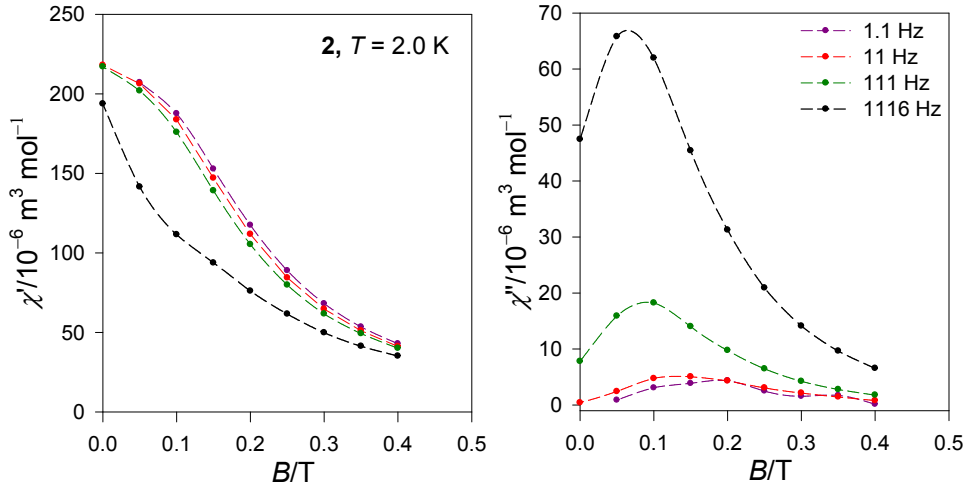


Fig. S12 AC susceptibility data for **2**: field dependence for a set of frequencies at T = 2.0 K.

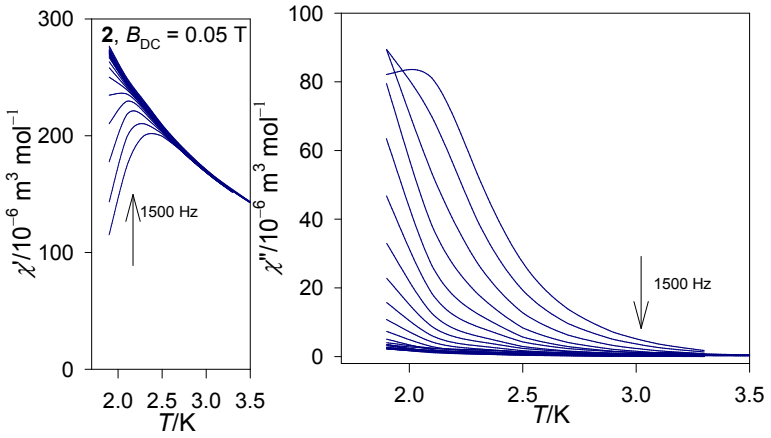


Fig. S13 Temperature evolution of the AC susceptibility components for **2** for different frequencies ranging between $f = 0.1$ to 1500 Hz.

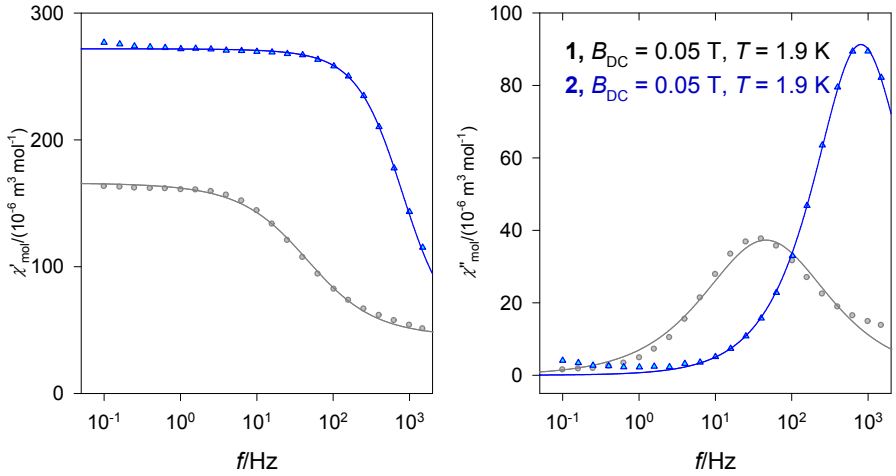


Fig. S14 A comparison of the AC susceptibility data for **1** and **2** at $B_{DC} = 0.05$ T and $T = 1.9$ K.

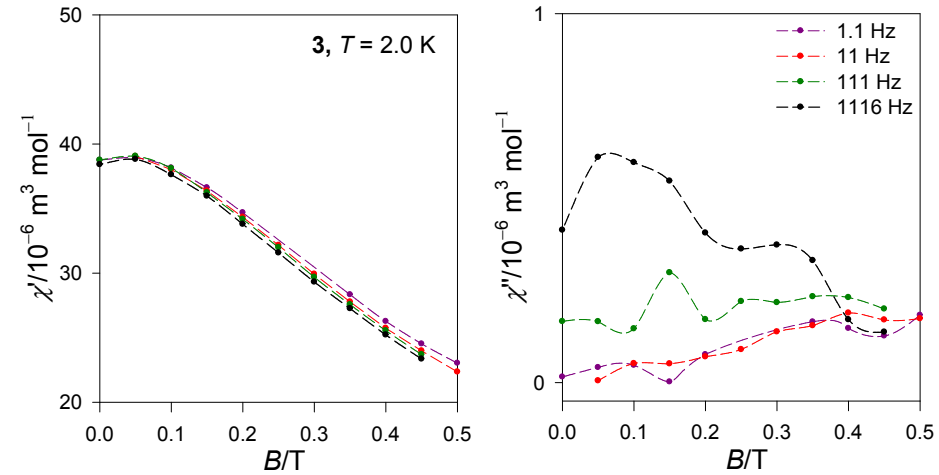


Fig. S15 AC susceptibility data for **3**: field dependence for a set of frequencies at $T = 2.0$ K.

Table S5 Exchange coupling constants and selected geometrical parameters of the literature reported complexes bearing a $\{Mn^{II}_2Mn^{III}_2(\mu_3\text{-}O)_2(\mu\text{-}O)_4\}$ core.[a]

					Jahn-Teller Mn^{III} geometry						Coefficients				
		A	**B**	**C**	**D**	**E**	**F**	**G**	**H**	**I**	**K**	**L**	**M**		
CSD refcode[b]	T / K[c]	$d(Mn_b\cdots Mn_b)$ / Å	$d(Mn_w\cdots Mn_w)$ / Å	$\angle(Mn_b\text{–}O\text{–}Mn_b)$ / °	$d(Mn_b\text{–}O)$ / Å	$d(Mn_b\text{–}X)$ / Å	$\angle(X\text{–}Mn_b\text{–}O)$ / °	$\angle(X\text{–}Mn_b\cdots Mn_b)$ / °	$d(Mn_b\text{–}O)$ / Å	$d(Mn_b\text{–}X)$ avg. / Å	Jahn-Teller d_{z2} distortion	Jahn-Teller axial elong.	$Mn_b\cdots Mn_w$ distortion / Å	J_{bb} / cm^{-1}	J_{wb} / cm^{-1}
1	293	3.170	5.803	97.86	2.246	2.333	154.89	123.00	1.951	1.918	0.963	1.194	0.137	–	–
2rt	293	3.156	5.847	97.86	2.233	2.334	154.76	123.03	1.945	1.913	0.957	1.194	0.153	12.85	1.55 / –0.47[d]
2	150	3.141	5.857	97.90	2.219	2.338	155.12	123.19	1.938	1.917	0.949	1.189	0.174		
GEFBEZ	93	3.210	5.816	98.91	2.246	2.199	157.73	132.06	1.973	1.943	1.021	1.144	0.059	6.81	1.12
VUGVOJ	93	3.206	5.881	99.44	2.118	2.127	160.85	131.51	2.085	1.987	0.996	1.068	0.019	6.38	0.88
XIYFER	100	3.211	5.819	99.73	2.179	2.209	159.06	136.20	2.018	1.959	0.986	1.120	0.039	4.52	1.3
CITZEL	100	3.211	5.846	99.48	2.262	2.207	159.82	141.68	1.936	1.921	1.025	1.163	0.051	6.97	0.4
IHETAR	100	3.135	5.869	96.89	2.227	2.322	153.87	123.20	1.956	1.919	0.959	1.185	0.099	2.3	0.18
IHETEV	100	3.143	5.835	97.40	2.207	2.275	155.56	122.52	1.972	1.925	0.970	1.164	0.148	2.4	0.44
PEKNEZ	100	3.162	5.837	98.31	2.218	2.376	153.87	121.98	1.956	1.923	0.934	1.194	0.158	4.66	0.28
PEKNID	100	3.174	5.720	98.46	2.229	2.285	154.48	122.70	1.955	1.916	0.975	1.178	0.077	7.65	0.9
UZUJAB	100	3.161	5.793	96.57	2.252	2.324	153.07	122.61	1.975	1.921	0.969	1.191	0.082	5.28	4.03 / –0.7[d]
BIGNUA01	105	3.253	5.783	100.28	2.264	2.319	161.03	138.84	1.967	1.919	0.976	1.194	0.067	8.1	0.4
AJISUH	108	3.202	5.731	99.38	2.091	2.138	160.61	133.26	2.108	1.996	0.978	1.059	0.026	5.3	0.78
VUGVID	113	3.284	5.770	100.51	2.280	2.22	161.19	140.23	1.984	1.950	1.027	1.154	0.067	8.52	0.87
NEPFET	113	3.192	5.798	98.35	2.256	2.217	157.99	137.47	1.955	1.942	1.018	1.152	0.129	8.79	0.93
GEFBID	118	3.238	5.915	100.58	2.239	2.222	159.88	136.07	1.964	1.944	1.008	1.147	0.041	8.8	0.8
BEXGES	120	3.267	5.665	100.64	2.255	2.309	161.52	139.82	1.984	1.942	0.977	1.175	0.092	3.2	0.28
ACINIK	123	3.149	5.754	97.39	2.236	2.391	154.93	122.87	1.948	1.919	0.935	1.206	0.157	7.0	0.06
EWIVEL	123	3.222	5.906	100.41	2.201	2.384	149.00	118.25	1.989	1.928	0.923	1.189	0.012	6.5	1.7
EWIVIP	123	3.165	5.792	97.03	2.255	2.316	154.13	123.78	1.961	1.914	0.974	1.194	0.107	6.6	0.4
EWIVOV	123	3.187	5.705	97.79	2.269	2.393	153.55	122.77	1.952	1.916	0.948	1.217	0.126	10.9	0.22
VASBAV	123	3.228	5.793	99.36	2.254	2.211	158.21	134.31	1.973	1.945	1.019	1.148	0.083	0.01	1.87
VASBEZ	123	3.259	5.866	100.15	2.290	2.229	158.41	142.00	1.951	1.946	1.027	1.161	0.116	–0.06	1.39
VASBID	123	3.195	5.742	99.28	2.227	2.361	152.89	121.53	1.959	1.919	0.943	1.195	0.144	2.32	0.66
VASBOJ	123	3.136	5.765	96.45	2.241	2.278	156.20	124.43	1.957	1.910	0.984	1.183	0.096	2.06	0.88
VASBUP	123	3.152	5.724	97.45	2.245	2.403	154.50	122.52	1.941	1.913	0.934	1.215	0.141	2.22	0.02
VASCAW	123	3.258	5.656	101.43	2.211	2.364	148.35	117.61	1.994	1.932	0.935	1.184	0.003	0.66	0.47
VASCEA	123	3.256	5.647	101.12	2.229	2.383	148.37	117.96	1.982	1.919	0.935	1.202	0.016	0.26	–0.42
VASCIE	123	3.217	5.961	100.10	2.231	2.419	148.92	118.94	1.959	1.929	0.922	1.205	0.003	0.27	–0.46
TEBZUW	150	3.239	5.602	100.16	2.235	2.216	161.02	135.79	1.983	1.946	1.009	1.144	0.084	5.97	0.49
XIYFIV	150	3.234	5.731	100.25	2.170	2.185	160.32	135.83	2.042	1.968	0.993	1.106	0.017	4.87	1.1
AJISIV	150	3.228	5.746	99.55	2.249	2.207	160.32	139.70	1.973	1.941	1.019	1.148	0.090	9.9	1.0
PEMSUW	150	3.174	5.801	97.62	2.255	2.325	154.17	124.10	1.955	1.910	0.970	1.199	0.098	8.55	1.801
QAQRAC	150	3.235	5.879	100.50	2.244	2.190	160.10	138.22	1.958	1.935	1.025	1.146	0.065	5.95	0.45
RAZMIP	150	3.281	5.734	97.88	2.410	2.213	165.64	142.48	1.920	1.901	1.089	1.216	0.224	7.71	3.42
RAZMOV	150	3.244	5.698	97.30	2.376	2.353	162.03	143.88	1.927	1.901	1.010	1.244	0.179	12.46	3.25
TECBAF	150	3.253	5.784	99.45	2.277	2.195	159.24	137.48	1.979	1.898	1.037	1.178	0.093	9.24	0.86
TECBIN	150	3.230	5.757	98.89	2.292	2.198	159.05	138.75	1.949	1.941	1.043	1.157	0.092	3.48	0.38
XIYFOB	150	3.218	5.875	99.55	2.241	2.196	160.42	137.43	1.968	1.942	1.020	1.142	0.078	5.56	0.54
XIYGAO	150	3.220	5.856	99.09	2.276	2.229	158.72	137.26	1.946	1.937	1.021	1.163	0.106	5.21	0.9
AJISOB	173	3.207	5.827	99.03	2.248	2.212	159.33	142.46	1.961	1.942	1.016	1.148	0.145	6.3	4.2

[a] Mn_b refer to the Mn^{III} atoms that are at hexacoordinated "body" sites and Mn_w to the Mn^{II} at the remaining "wing" sites; the meaning of the parameters **A**–**M** are illustrated in Figure S16; *J* values refer to $H = -2JS_1S_2$ formalism; [b] the structures and references can be obtained free of charge at https://www.ccdc.cam.ac.uk/structures/ using the refcode; [c] temperature of the X-ray diffraction experiment; [d] two J_{bw} constants were reported; **I** is the averaged non-Jahn-Teller distances around the Mn_b atom; **M** = | $d(Mn_b\cdots Mn_w) - d(Mn_b\cdots Mn_w')$ |; **K** = **E**/**D**; **L** = (**E**+**D**)/2/**I**;

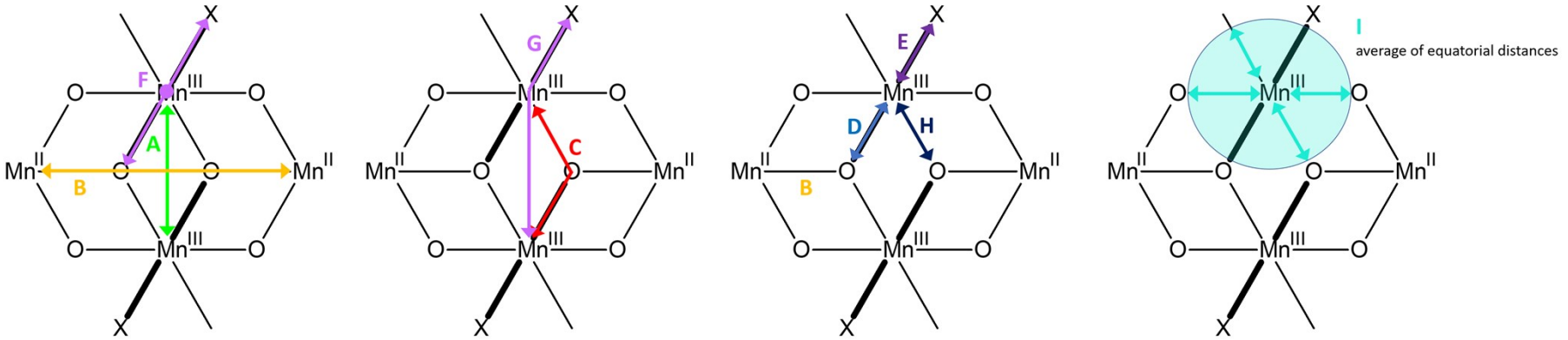


Fig. S16 Schematic illustration of the geometrical parameters **A**–**M** (Table S5).

Table S6 Experimental and calculated coupling constants of the reported complexes bearing $\{Mn^{III}_2\}$ and $\{Mn^{II}_2Mn^{III}_2(\mu_3\text{-}O)_2(\mu\text{-}O)_4\}$ cores.[a]

CSD refcode	Complex	Calculated J / cm^{-1}					
		Exp.[c] J / cm^{-1}	Form.[d] 1	Form.[d] 2	Type	Conditions[e]	Ref.
			Mn^{III}_2 dimers				
LEBQUF	$[Mn_2(HL^a)_2(bpy)_2](ClO_4)_2$	2.13	0.27	0.22	–	H atoms were added to –OH groups	[S2]
TEXBON	$[Mn_2(L^b)_2(CH_3O)_2(CH_3OH)_4]$	–10.33	–19.13	–15.31	–	–	[S3]
DILHEO	$[Mn_2O(L^{11})_2(bpy)_2Cl_{1.65}(H_2O)_{0.35}]Cl_{0.35}\cdot H_2O_{0.65}$	–5.1	–10.59	–8.57	–	–	[S4]
UBUWIA	$[Mn_2Ca_2(L^1)_6(H_2O)_4(CH_3CN)_2](ClO_4)_4$	1.52	0.01	0.01	–	–	[S5]
BASGIO	$[Mn_2(L^c)_2(N_3)_2]$	1.09	–1.41	–1.12	–	–	[S6]
			$Mn^{II}_2Mn^{III}_2$ tetramers				
1	$[Mn_4(HBuDea)_2(BuDea)_2(EBA)_4]$	–	5.21	4.17	J_{bb}	–	tw
		–	5.27	4.21	J_{bb}	Truncated ligands[f]	
		–	–1.1	–0.9	J_{bw1}	Truncated ligands	
		–	3.3	2.7	J_{bw2}	Truncated ligands	
		–	5.61	4.49	J_{bb}	Truncated ligands; terminal carboxylates, coordinated to Mn_w atoms, replaced with chlorides	
2	$[Mn_4(HBuDea)_2(BuDea)_2(DMBA)_4]$	12.85	6.01	4.81	J_{bb}	–	tw
		12.85	6.06	4.85	J_{bb}	Truncated ligands	
		–0.47	–1.49	–1.22	J_{bw1}	Truncated ligands	
		1.55	3.01	2.46	J_{bw2}	Truncated ligands	
		12.85	5.06	4.05	J_{bb}	Truncated ligands;	

						B3LYP-G functional, TZVP set	
		12.85	4.77	3.81	J_{bb}	Truncated ligands; B3LYP-G functional, SVP set	
2rt	$[Mn_4(HBuDea)_2(BuDea)_2(DMBA)_4]$	12.85	5.32	4.25	J_{bb}	Truncated ligands	tw
		–0.4 7	–1.04	–0.85	J_{bw1}	Truncated ligands	
		1.55	3.15	2.58	J_{bw2}	Truncated ligands	
PEKNEZ	$[Mn_4(BuDea)_2(HBuDea)_2(L^{11})_4]$	4.66	6.63	5.3	J_{bb}	–	[S7]
		4.66	6.63	5.3	J_{bb}	Truncated ligands	
		0.28	–1.05	–0.86	J_{bw1}	Truncated ligands	
		0.28	3.18	2.6	J_{bw2}	Truncated ligands	
PEMSUW	$[Mn_4(H_2L^9)_2(HL^9)_2(PhCO_2)_2](PhCO_2)_2{\cdot}0.7CH_3CN{\cdot}0.3EtOH$	8.55	3.78	3.03	J_{bb}	Truncated ligands	[S7]
		1.81	–0.83	–0.68	J_{bw1}	Truncated ligands	
		1.81	3.11	2.55	J_{bw2}	Truncated ligands	
VASBEZ	$[Mn_4(L^1)_6(NO_3)_2(L^5)_2]{\cdot}2CH_3CN$	-0.06	0.24	0.19	J_{bb}	Truncated *p*-tol groups	[S8]
VASCAW	$[Mn_4(L^7)_2(L^8)_2(H_2O)_2]{\cdot}6CH_3CN$	0.66	2.59	2.07	J_{bb}	–	[S8]
AJISUH	$[Mn_4(L^1)_4(L^6)_2(CH_3O)_2](ClO_4)_2{\cdot}2CH_3OH$	5.3	5.69	4.55	J_{bb}	–	[S9]
UZUJAB	$[Mn_4(HL^{12})_2(L^{12})_2(L^{15})_4](BPh_4)_4$	5.28	5.38	4.3	J_{bb}	–	[S9]
		0.7	0.99	0.81	J_{bw1}	–	
		4.03	3.62	2.96	J_{bw2}	–	
RAZMIP	$[Mn_4(HL^3)_4(CH_3OH)_4Cl_2]$	7.71	–0.78	–0.63	J_{bb}	–	[S10]
		3.42	2.66	2.17	J_{bw1}	–	
		3.42	–0.86	–0.71	J_{bw2}	–	
		3.42	2.61	2.13	J_{bw1}	Al^{III} as a trivalent diamagnetic metal	
		3.42	–0.9	–0.74	J_{bw2}	Al^{III} as a trivalent diamagnetic metal	
		7.71	–1.61	–1.29	J_{bb}	Terminal methanol molecules eliminated, structure optimized	
		7.71	0.49	0.39	J_{bb}	X-ray structure optimized	
RAZMOV	$[Mn_4(HL^3)_4(CH_3OH)_4Br_2]$	12.46	–1.75	–1.4	J_{bb}	–	[S10]
		3.25	3.06	2.5	J_{bw1}	–	
		3.25	–0.99	–0.81	J_{bw2}	–	
NEPFET	$[Mn_4(L^1)_6Br_2(H_2O)_2]Br_2{\cdot}4H_2O$	8.79	–0.88	–0.71	J_{bb}	–	[S11]
AJISIV	$[Mn_4(L^1)_6(NO_3)_2(CH_3CN)_2](ClO_4)_2{\cdot}2CH_3CN$	9.9	0.15	0.12	J_{bb}	H atoms added to CH_3CN ligands	[S12]
BIGNUA01	$[Mn_4(HL^4)_6(CH_3CO_2)_2](ClO_4)_2$	8.1/8.7	1.28	1.02	J_{bb}	H atoms added to OH groups	[S13]

[a] Mn_b refer to the Mn^{III} atoms that are at hexacoordinated "body" sites and Mn_w to the Mn^{II} at the remaining "wing" sites; [b] the original structures can be obtained free of charge at https://www.ccdc.cam.ac.uk/structures/ using the refcode; [c] exchange coupling determined through the fitting of experimental data; [d] formalism used to extract the J value: (Form. 1) $J_{AB} = -(E_{HS} - E_{BS}) / (S_A + S_B)^2$ and (Form. 2) $J_{AB} = -(E_{HS} - E_{BS}) / ((S_A + S_B)(S_A + S_B + 1))$. Both experimental and calculated J values refer to $H = -2JS_1S_2$ Hamiltonian; [e] unless stated otherwise, the atomic coordinates were taken from X-ray data without geometry optimization. All uncoordinated anions or solvent molecules, as well as disordered components, were eliminated. For other conditions see the main text; [f] to reduce the computational time, the hydrocarbon non-chelating groups of the ligands were transformed to methyl groups, e.g. benzoic O_2CPh and pivalic $O_2CC(CH_3)_3$ acids became acetic O_2CCH_3 one, *N*-butyl diethanolamine became *N*-methyl one.

H_3L^a = 1,1,1-tris(hydroxymethyl)ethane; bpy = 2,2′-bipyridine; H_2L^b = salicylic acid; H_2L^c = product of condensation of 1,1,2,2-tetramethylethylenediamine with 5-chlorosalicylaldehyde. All other ligands are described in Table 1 footnote.

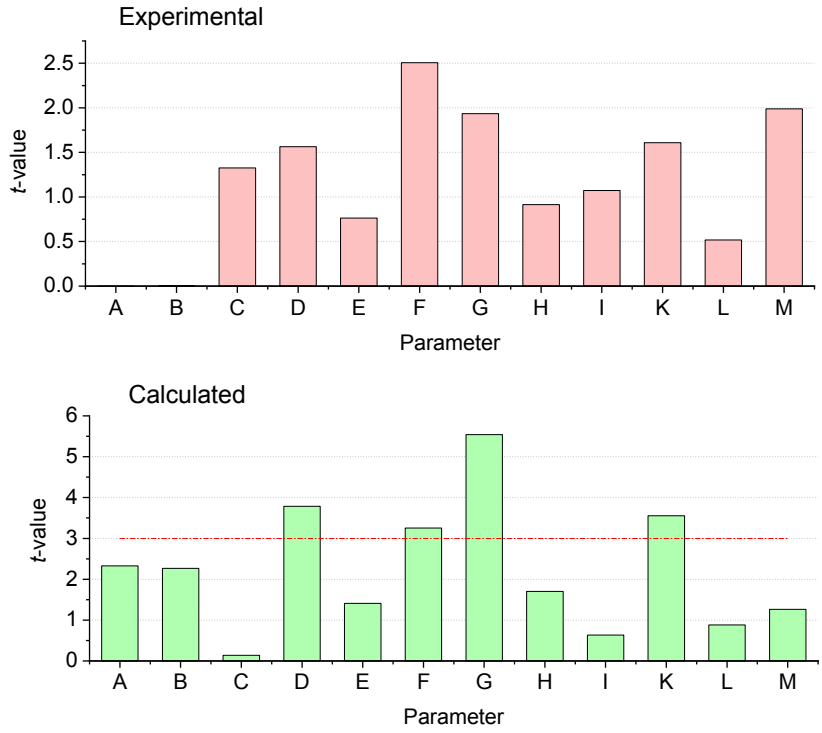


Fig. S17 The *t*-values, expressed as a slope/σ(slope) of the linear regressions of the dependences of experimental (top) and calculated (bottom) J_{bb} values on certain geometrical parameters **A**–**M** (Table S5). The red horizontal line indicates the 3σ threshold.

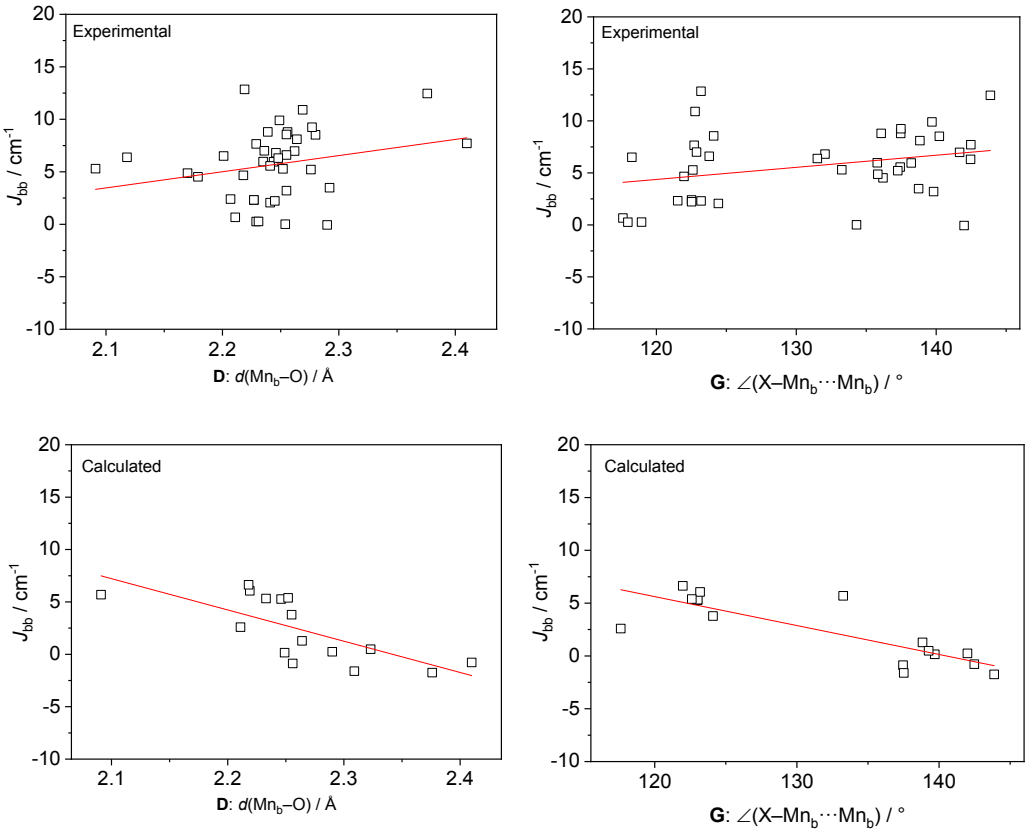


Fig. S18 The experimental and calculated J_{bb} values plotted as functions of **D** and **F** parameters (see Table S5 and S16).

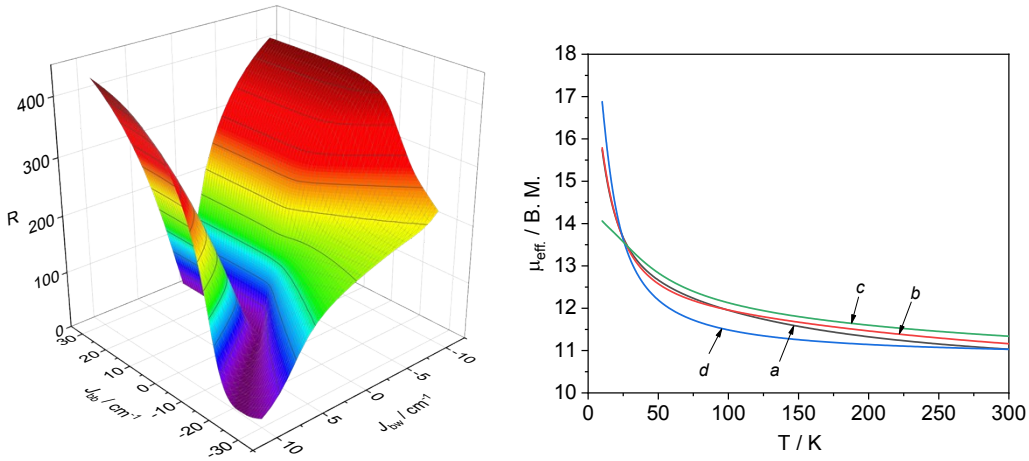


Fig. S19 Left: 3D map showing the discrepancy R factor between the calculated χT vs. T curves, where one curve was generated using the fitted parameters for **2** (parameters set *a*) and the other curve was obtained by varying J_{bb} and J_{bw} in a settled range with the step of 1 cm^{-1} (g_{eff} was varied from 1.85 to 2.0 with 0.01 step for every J_{bb}/J_{bw} pair and the solution with the lowest R was chosen). The use of smaller step of 0.1 and 0.5 cm^{-1} did not change the overall map shape, but influenced the distribution of best R solutions. Right: μ_{eff} vs. T curves calculated for particular solutions ($H = -2JS_1S_2$ formalism): *a*: g_{eff} = 1.90, J_{bb} = 12.9, J_{bw1} = 0.47, J_{bw2} = 1.6 cm^{-1}; *b*: g_{eff} = 1.86, J_{bb} = 30, J_{bw} = 0.6 cm^{-1}; *c*: g_{eff} = 1.99, J_{bb} = 0, J_{bw} = 0.9 cm^{-1}; *d*: g_{eff} = 1.91, J_{bb} = –21.9, J_{bw} = 10 cm^{-1}. The R factor was determined as $R = \sum_n \frac{(\chi T_{calcd} - \chi T_{exp})^2}{\chi T_{exp}^{\ 2}}$. The MAGPACK program was used to calculate the magnetic susceptibility for a given parameter set.[S14] The homemade software written by D.S.N. was used to screen the given parameters, generate MAGPACK input files and sort the output.

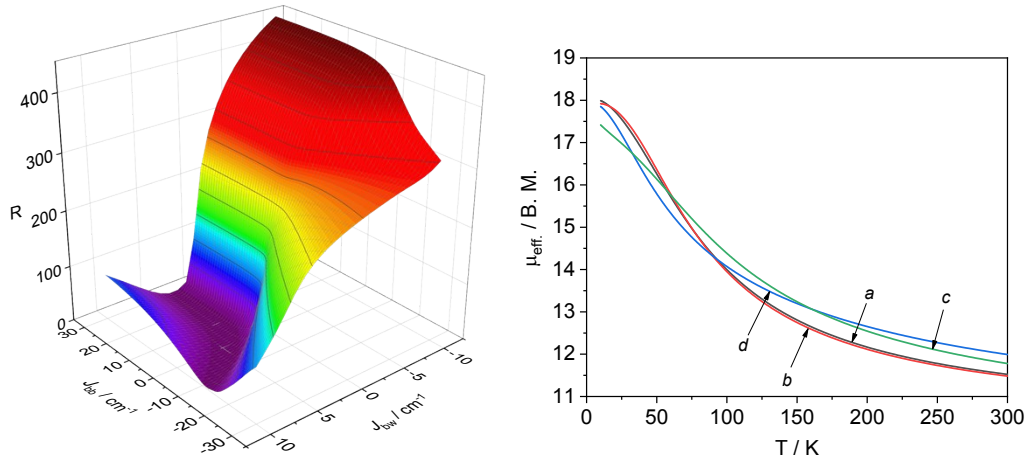


Fig. S20 Left: 3D map showing the discrepancy R factor between the calculated χT vs. T curves, where one curve was generated using the fitted parameters for RAZMIP (parameters set *a*) and the other curve was obtained by varying J_{bb} and J_{bw} in a settled range with the step of 1 cm^{-1} (the other conditions are described in Fig. S19 caption). Right: μ_{eff} vs. T curves calculated for particular solutions ($H = -2JS_1S_2$ formalism): *a*: g_{eff} = 1.89, J_{bb} = 7.71, J_{bw} = 3.42; *b*: g_{eff} = 1.89, J_{bb} = 0, J_{bw} = 5 cm^{-1}; *c*: g_{eff} = 1.89, J_{bb} = 30, J_{bw} = 2.7 cm^{-1}; *d*: g_{eff} = 1.85, J_{bb} = –10.4, J_{bw} = 10 cm^{-1}.

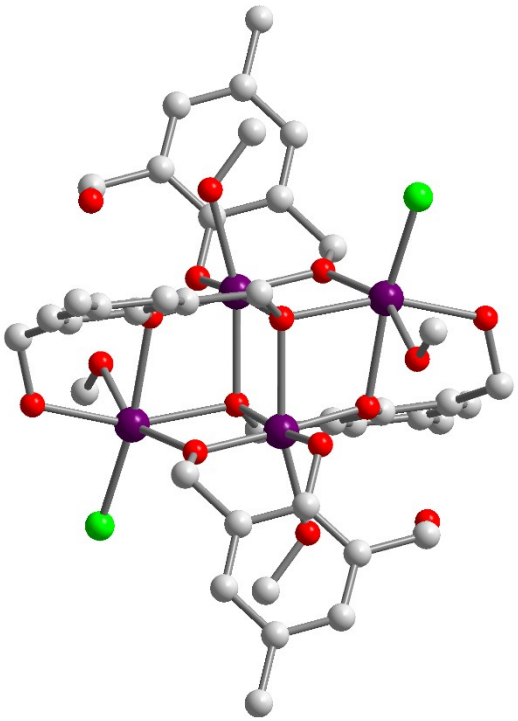


Fig. S21 DFT optimized structure RAZMIP.

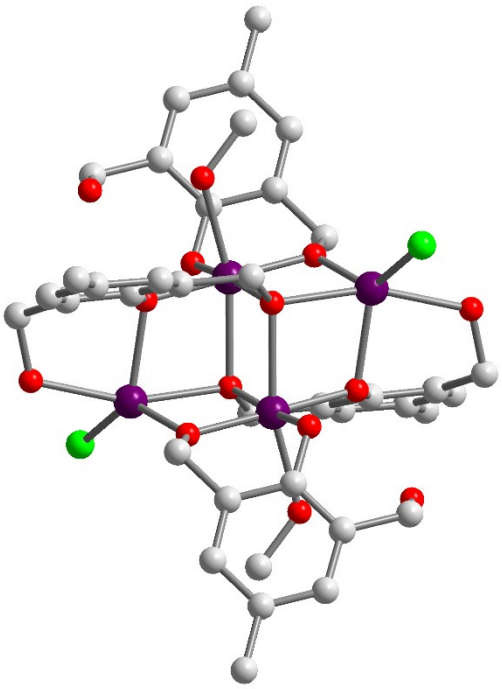


Fig. S22 DFT optimized structure RAZMIP with eliminated terminal methanol molecules.

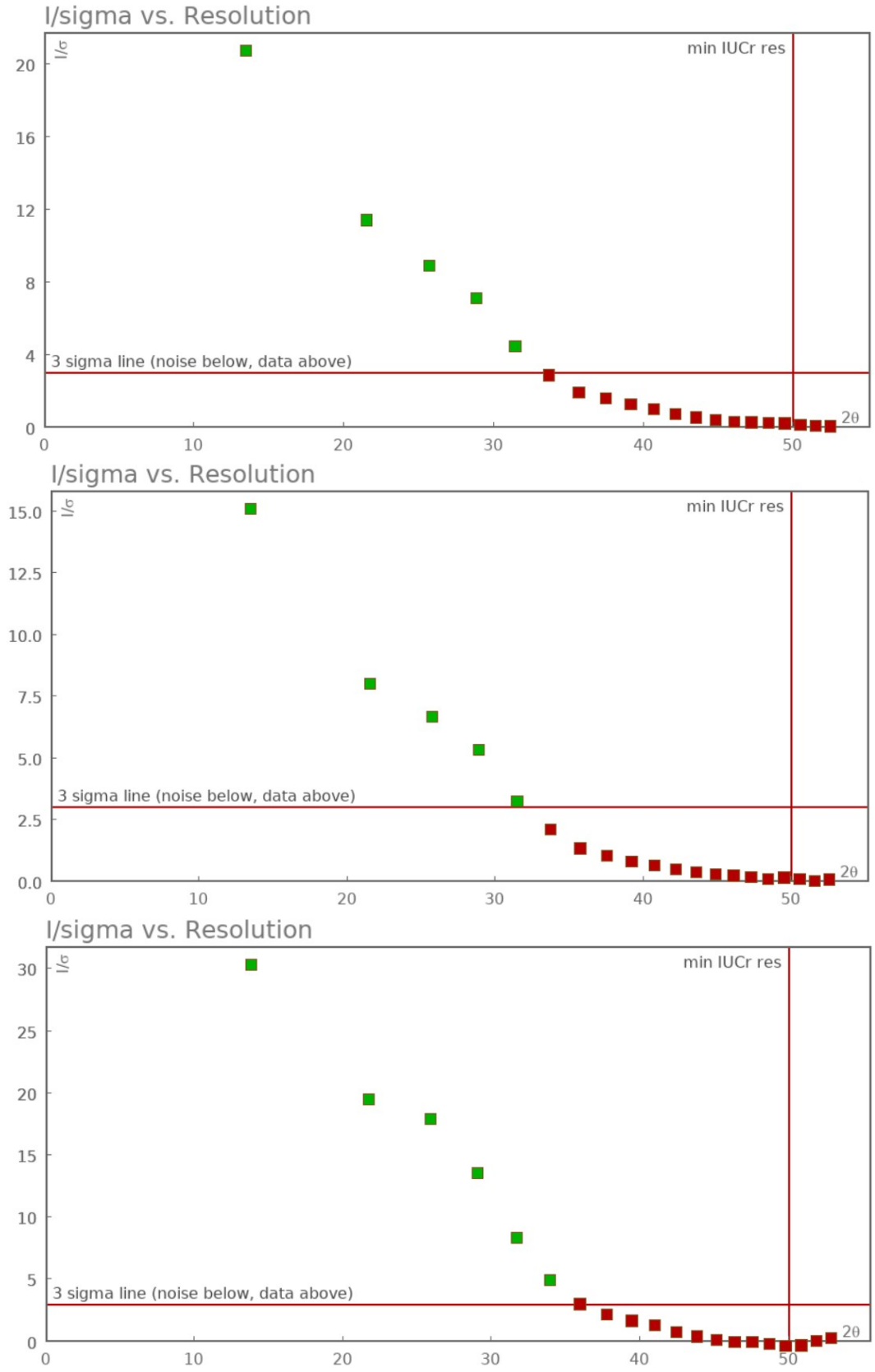


Fig. S23 Reflection intensity statistics for **3** for different experiments (exposure/temperature, top down): 19 s / 150 K, 19 s / 150 K, 60 s / room temperature.

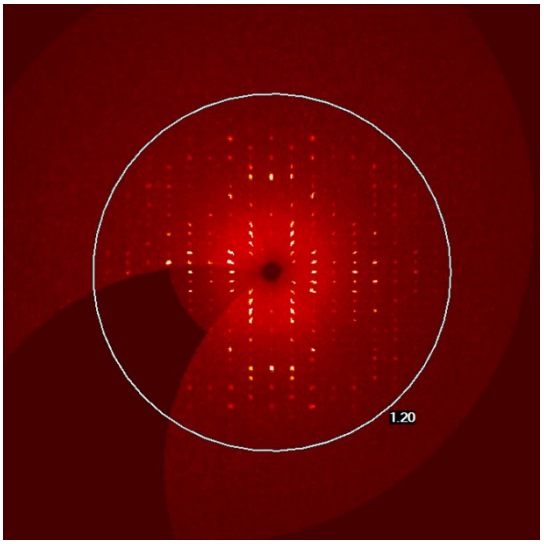


Fig. S24 Reconstructed precession image for **3** (60 s / room temperature) at 0.8 Å maximum resolution, showing absence of reflections in the 1.2–0.8 Å area.

Listing S1 Shortened example of the Orca input for "broken symmetry" calculation of an exchange coupling between Mn^{III} centres (only metal atoms are shown).

```
# Complex 2, truncated, Jbb constant
! uks tpssh def2-svp tightscf grid4 nofinalgrid rijcosx
%scf brokensym 4,4
end
* xyz 0 9
Mn    2.81854    7.87895    7.18779 newgto "def2-tzvp" end
Mn    4.42882   10.20673    5.82508 newgto "def2-tzvp" end
Zn    4.09710   10.05165    9.21481
Zn    3.15026    8.03403    3.79807
```

Listing S2 Selected output of the ORCA DFT calculations described in the Listing S1.

<u>High spin state:</u>

```
----------------
TOTAL SCF ENERGY
----------------

Total Energy       :        -8382.97726766 Eh         -228112.40846 eV

Components:
Nuclear Repulsion  :        14031.69277591 Eh          381821.77188 eV
Electronic Energy  :       -22414.67004357 Eh         -609934.18034 eV
One Electron Energy:       -39601.52007391 Eh        -1077612.14595 eV
Two Electron Energy:        17186.85003034 Eh          467677.96561 eV

Virial components:
Potential Energy   :       -16743.11406115 Eh         -455603.29603 eV
Kinetic Energy     :         8360.13679349 Eh          227490.88756 eV
Virial Ratio       :            2.00273207


DFT components:
N(Alpha)           :      250.000685709868 electrons
```

```
N(Beta)            :      242.000695477022 electrons
N(Total)           :      492.001381186890 electrons
E(X)               :     -513.687256868661 Eh
E(C)               :      -18.130420865545 Eh
E(XC)              :     -531.817677734206 Eh
DFET-embed. en.    :        0.000000000000 Eh


-----------------------------------------
MULLIKEN ATOMIC CHARGES AND SPIN POPULATIONS
-----------------------------------------
   0 Mn:    0.638024    3.839295
   1 Mn:    0.638021    3.839294
   2 Zn:    0.888141    0.008386
   3 Zn:    0.888136    0.008386
```

Low spin state:

```
---------------
TOTAL SCF ENERGY
---------------

Total Energy       :        -8382.97682576 Eh         -228112.39644 eV

Components:
Nuclear Repulsion  :        14031.69277591 Eh          381821.77188 eV
Electronic Energy  :       -22414.66960168 Eh         -609934.16832 eV
One Electron Energy:       -39601.50654311 Eh        -1077611.77776 eV
Two Electron Energy:        17186.83694143 Eh          467677.60945 eV

Virial components:
Potential Energy   :       -16743.11023201 Eh         -455603.19183 eV
Kinetic Energy     :         8360.13340625 Eh          227490.79539 eV
Virial Ratio       :            2.00273242


DFT components:
N(Alpha)           :      246.000689947738 electrons
N(Beta)            :      246.000689968849 electrons
N(Total)           :      492.001379916587 electrons
E(X)               :     -513.686387305042 Eh
E(C)               :      -18.130471161542 Eh
E(XC)              :     -531.816858466584 Eh
DFET-embed. en.    :        0.000000000000 Eh


-----------------------------------------
MULLIKEN ATOMIC CHARGES AND SPIN POPULATIONS
-----------------------------------------
   0 Mn:    0.638753    3.838021
   1 Mn:    0.638751   -3.838020
   2 Zn:    0.888166   -0.005604
   3 Zn:    0.888162    0.005604


-----------------------------------------
BROKEN SYMMETRY MAGNETIC COUPLING ANALYSIS
-----------------------------------------

S(High-Spin)      =   4.0
<S**2>(High-Spin) =  20.0643
<S**2>(BrokenSym) =   4.0575
E(High-Spin)      = -8382.977268 Eh
E(BrokenSym)      = -8382.976826 Eh
E(High-Spin)-E(BrokenSym)= -0.0120 eV    -96.975 cm**-1 (FERROMAGNETIC coupling)

          ---------------------------------------------------------
          | Spin-Hamiltonian Analysis based on H(HDvV)= -2J*SA*SB |
    -------                                                         -----------
    | J(1) =       6.06 cm**-1    (from -(E[HS]-E[BS])/Smax**2)              |
    | J(2) =       4.85 cm**-1    (from -(E[HS]-E[BS])/(Smax*(Smax+1))       |
    | J(3) =       6.06 cm**-1    (from -(E[HS]-E[BS])/(<S**2>HS-<S**2>BS)) |
    -------------------------------------------------------------------------
```

```
  J(1): (a) A.P. Ginsberg J. Am. Chem. Soc. 102 (1980), 111
        (b) L. Noodleman J. Chem. Phys. 74 (1981), 5737
        (c) L. Noodleman E.R. Davidson Chem. Phys. 109 (1986), 131
  J(2)  (d) A. Bencini D. Gatteschi J. Am. Chem. Soc. 108 (1980), 5763
  J(3)  (e) K. Yamaguchi Y. Takahara T. Fueno in: V.H. Smith (Ed.)
            Applied Quantum Chemistry. Reidel, Dordrecht (1986), pp 155
        (f) T.Soda et al. Chem. Phys. Lett., 319, (2000), 223
```

Listing S3 Shortened example of the Orca input geometry optimization (only metal atoms are shown).

```
# RAZMIP, X-ray structure optimization,
! RI BP86 def2-SVP def2/J D3BJ TIGHTSCF Opt Grid3 FinalGrid5
* xyz 0 19
Mn     -4.409441    5.653581    7.843303 newgto "def2-tzvp" end
Mn     -5.344142    2.886245    9.122344 newgto "def2-tzvp" end
Mn     -6.534917    5.846319   10.335214 newgto "def2-tzvp" end
Mn     -5.600216    8.613655    9.056174 newgto "def2-tzvp" end
```

Listing S4 Selected output of the ORCA DFT calculations described in the Listing S3.

```
                        .--------------------.
  ----------------------|Geometry convergence|--------------------------
  Item                value                   Tolerance       Converged
  ---------------------------------------------------------------------
  Energy change      -0.0000045109            0.0000050000      YES
  RMS gradient        0.0000307532            0.0001000000      YES
  MAX gradient        0.0002160359            0.0003000000      YES
  RMS step            0.0016824988            0.0020000000      YES
  MAX step            0.0119827072            0.0040000000      NO
  ................................................
  Max(Bonds)      0.0006      Max(Angles)    0.06
  Max(Dihed)        0.69      Max(Improp)    0.00
  ---------------------------------------------------------------------

       The energies and gradients are converged
       and the convergence on bond distances, angles, dihedrals and impropers
       is acceptable.
       Convergence will therefore be signaled now


                ******************************************************
                *** FINAL ENERGY EVALUATION AT THE STATIONARY POINT ***
                ***               (AFTER   50 CYCLES)                ***
                ******************************************************

----------------
TOTAL SCF ENERGY
----------------

Total Energy       :        -8285.17527297 Eh         -225451.08089 eV

Components:
Nuclear Repulsion  :        16717.74747161 Eh          454913.03603 eV
Electronic Energy  :       -25002.92274459 Eh         -680364.11692 eV
One Electron Energy:       -44763.09926726 Eh        -1218065.85633 eV
Two Electron Energy:        19760.17652268 Eh          537701.73941 eV

Virial components:
Potential Energy   :       -16530.35439915 Eh         -449813.81129 eV
Kinetic Energy     :         8245.17912618 Eh          224362.73040 eV
Virial Ratio       :            2.00485085


DFT components:
N(Alpha)           :      288.000109530604 electrons
N(Beta)            :      270.000113408799 electrons
N(Total)           :      558.000222939404 electrons
E(X)               :     -618.797621681450 Eh
E(C)               :      -22.262142985094 Eh
```

```
E(XC)              :     -641.059764666543 Eh
DFET-embed. en.    :        0.000000000000 Eh


-----------------------------------------
MULLIKEN ATOMIC CHARGES AND SPIN POPULATIONS
-----------------------------------------
   0 Mn:    0.515120    3.836839
   1 Mn:    0.393686    4.766871
   2 Mn:    0.514746    3.836801
   3 Mn:    0.393213    4.766783
```

Listing S5 Cartesian coordinates for DFT optimized structure RAZMIP.

```
  Mn  -4.29300718175490      5.67552486367432      8.06970794743486
  Mn  -5.25877922423304      2.87732319443740      9.16045651322295
  Mn  -6.65153503641551      5.82319883658339     10.10874777573369
  Mn  -5.68574409159810      8.62177103946940      9.01735376957693
  Cl  -5.04015374891351      1.23975173984244      7.52732491638608
  O   -3.54397686845586      4.13920107949689      8.88869563880580
  O   -2.66621783088743      6.65090318758413      8.27291243782339
  O   -2.93643015301554      7.58440774886511      5.50218269152781
  H   -3.55716424201324      7.70479331067607      6.26514693480507
  O   -5.96099594193863      4.73859093114104      8.17355338523489
  O   -5.18762174223965      7.21246148697746      7.24333766430665
  O   -4.72513312318497      1.50639239640028     10.82933569314555
  H   -5.20703328674000      0.68162407138327     10.61726606432613
  O   -3.92693006006335      5.09763193785252      5.92400775230473
  H   -3.48166680909163      5.89862173808324      5.52223615795675
  O   -7.43081071128597      2.42694715066961      9.55972050310502
  H   -7.89111922298027      3.31131403514774      9.72272577588342
  C   -1.27938074475357      4.70164403754030      8.19378105452648
  C   -1.62075404633995      5.99162528203567      7.71545413319665
  C   -0.98699964392722      6.53555916022137      6.57445561625437
  C    0.08112870872766      5.82639069869185      5.99698689742875
  H    0.57709845907472      6.24449385535432      5.10471839326830
  C    0.50951012204587      4.58256622607885      6.50691646436473
  C   -0.20894437852777      4.02564162520926      7.58872128098971
  H    0.05458202145047      3.01761267722091      7.94977661192009
  C   -2.16308197816627      4.08659042197095      9.25946945461992
  H   -1.88478266615243      3.02342857667845      9.41644587740383
  H   -2.03394461046397      4.61781578142552     10.23072553981143
  C   -1.58092217235760      7.78433415183568      5.95857382729999
  H   -1.56124710620632      8.63304326586224      6.67685351451436
  H   -0.98963376366564      8.08409158065892      5.07021746048020
  C    1.68269481641196      3.85158078891901      5.89825724606673
  H    1.53824724686366      2.75271787656912      5.92664384312314
  H    2.62377204584556      4.06927741718687      6.44940414560174
  H    1.84624860748677      4.14845781014705      4.84304742421811
  C   -7.05859057978583      5.93699203593086      6.30228745511137
  C   -6.27536031736839      7.11197381039205      6.43419782012081
  C   -6.67773550772159      8.28962957857052      5.74130089836561
  C   -7.81097123536892      8.27465868827804      4.91626133511475
  H   -8.10552842198012      9.20611495865409      4.40531179537273
  C   -8.58139514921298      7.10938212251759      4.74112891373059
  C   -8.18709242347193      5.96806673060570      5.46042512612798
  H   -8.79434672632053      5.05063665500733      5.37608092657550
  C   -6.77636552380248      4.63240978962333      7.01624516475127
  H   -7.74942218154971      4.20542668610625      7.34243617370618
  H   -6.31059489452449      3.89991485350361      6.31830692651918
  C   -5.02018485895499      1.93410548068360     12.18903791934155
  H   -4.68809754093205      1.14742349376638     12.89788369084641
  H   -6.11540784843472      2.08396089562618     12.30473585868426
  C   -9.77880849341641      7.08962323256167      3.82174814645985
  H  -10.47376159796085      6.26455968640158      4.07510785805592
  H   -9.47261754481349      6.94770210576890      2.76221536725269
  H  -10.34625132265437      8.04132273293886      3.86915136965289
  C   -3.29301585380302      3.88759981906084      5.49371260928248
  H   -3.47783625180173      3.72063178543835      4.41065147795333
  H   -3.73686287536528      3.05166869029691      6.06922687764455
  H   -2.19943636738478      3.91373929290592      5.68103519552951
  C   -8.24859843738061      1.61354168048429      8.71702526171082
```

H	-9.09425393953538	1.17181320847074	9.28893934863043
H	-7.60949398031175	0.81144628595372	8.30168560774434
H	-8.65885760841926	2.19484017414000	7.86273436076811
Cl	-5.90611337012315	10.26054057909161	10.64910982363111
O	-7.40032519845597	7.35992403482691	9.29036339033711
O	-8.27913758233821	4.84834719621171	9.90568422029774
O	-8.00565258046288	3.92373394933524	12.68006702392723
H	-7.38452123728757	3.80500494036075	11.91723379137385
O	-4.98387246825464	6.76041935293861	10.00491835509178
O	-5.75685152239432	4.28599577490336	10.93460393234294
O	-6.21975692940327	9.99183561837217	7.34854198088554
H	-5.73876208379457	10.81709940041830	7.56081109692748
O	-7.01870036789219	6.39931371251001	12.25413630813976
H	-7.46208773426681	5.59807063840899	12.65726603812077
O	-3.51415877283121	9.07298360346760	8.61681681040158
H	-3.05426125927246	8.18791672664377	8.45626026166089
C	-9.66523822268796	6.79836076192579	9.98442085016614
C	-9.32424132844992	5.50841446675661	10.46294119888946
C	-9.95710517472228	4.96560243405340	11.60495099797679
C	-11.02497266641337	5.67516148125909	12.18239047158543
H	-11.51976977864202	5.25839012315162	13.07593166060495
C	-11.45310702179310	6.91901699925306	11.67222096461692
C	-10.73503106943259	7.47511094807573	10.58972644506047
H	-10.99812704442670	8.48322327639242	10.22859187270008
C	-8.78105300764169	7.41288296653634	8.91878212353196
H	-9.05894938399848	8.47608392297654	8.76140477934456
H	-8.90972897723421	6.88143184275856	7.94761617304900
C	-9.36044272245935	3.71945337940181	12.22367688470215
H	-9.37801380094690	2.86931755282992	11.50701630966428
H	-9.95137432893641	3.41993448351532	13.11236149671666
C	-12.62608241066356	7.65034667204428	12.28082319369538
H	-12.48162149278414	8.74918806348603	12.25179551970384
H	-13.56733736624833	7.43236344464259	11.73008866731054
H	-12.78934652306631	7.35408247712152	13.33625071019758
C	-3.88630674748896	5.56183581375087	11.87605065783203
C	-4.66921281334852	4.38666060723626	11.74384676506159
C	-4.26647452981715	3.20888099609998	12.43626558752710
C	-3.13297037398564	3.22378243144708	13.26099100379074
H	-2.83810775073302	2.29223092353602	13.77158878640155
C	-2.36263659910952	4.38910204209191	13.43614850706193
C	-2.75745600578243	5.53062067065996	12.71743906771914
H	-2.15037453467839	6.44814100702296	12.80201973779556
C	-4.16958865151242	6.86668115186012	11.16309948847490
H	-3.19689071428667	7.29542405909197	10.83810537265211
H	-4.63692174617314	7.59789928808945	11.86130099816925
C	-5.92413418069598	9.56449400857939	5.98881869658805
H	-6.25627454249055	10.35114730603045	5.27997623545886
H	-4.82885882330540	9.41494720525877	5.87351601811470
C	-1.16474834655761	4.40874591477104	14.35491015984968
H	-0.47018554041507	5.23415875299723	14.10162074880846
H	-1.47037152523058	4.55000155814422	15.41469637118324
H	-0.59701416929609	3.45726017879885	14.30668861652815
C	-7.65343259435409	7.60861957060011	12.68577722509577
H	-7.46975731391008	7.77385967450502	13.76923455274378
H	-7.20993948562572	8.44570089116774	12.11174330615781
H	-8.74685279286831	7.58151077003929	12.49760753666067
C	-2.69692439193241	9.88804292633898	9.45834273326397
H	-1.85173500955569	10.32981342508517	8.88577804790982
H	-3.33647536168920	10.69027728701803	9.87279116537815
H	-2.28610718808981	9.30819626052990	10.31334736939517

Listing S6 Cartesian coordinates for DFT optimized structure RAZMIP, where terminal methanol molecules were eliminated.

Mn	-4.24771801114839	5.73619534913295	8.07239773872393
Mn	-5.17727583141411	2.98858822211688	9.16940135935311
Mn	-6.69738029422083	5.76288012327661	10.10502731361007
Mn	-5.76807310890673	8.51033418302585	9.00822946516719
Cl	-4.60789740267172	10.19731651365164	10.04748810758349
Cl	-6.33835124127098	1.30195967138109	8.13025393832402
O	-3.48832823431560	4.11720426353260	8.78722727665051
O	-2.63882207045482	6.66527042333342	8.25399211839460
O	-2.85394150018583	7.72928164543818	5.62082969251755

H	-3.42175011922169	7.79332379825459	6.42807447468097
O	-5.92524523649020	4.79368478574511	8.15728716018864
O	-5.17476395510420	7.29375852514961	7.28908374465203
O	-4.78517748878718	1.46308450352224	10.74863206659964
H	-5.45737808602392	0.82520655633874	10.41079844683292
O	-3.89241660391362	5.25188300661375	5.88411774328395
H	-3.42983375325228	6.07420320048846	5.54138147136003
C	-1.22234309367163	4.72462812469583	8.18483188017523
C	-1.58177494949768	6.01820074243102	7.72307237951255
C	-0.91220912143799	6.59438350824234	6.61475737294472
C	0.17700409763727	5.91053874390441	6.04949887291383
H	0.69475078255254	6.35753658165007	5.18386116448821
C	0.60532882518993	4.65743076218444	6.53855052711436
C	-0.12996288165397	4.07226330295267	7.59300461671918
H	0.14225141367347	3.06310406369630	7.94506869608303
C	-2.11852321481157	4.08490263542666	9.21827241572580
H	-1.82393530536537	3.02764362205169	9.38490125431582
H	-2.04371031017553	4.61493633131015	10.19461937051390
C	-1.47815714307485	7.87388849115589	6.04137549750534
H	-1.41089463320626	8.69734280089890	6.78558362255348
H	-0.90363077714024	8.17723358044020	5.14355095752409
C	1.80300037151188	3.95618638474214	5.94283870047480
H	1.70444687131374	2.85380113535655	6.00517888166580
H	2.73854617269305	4.22928311930384	6.47870424046178
H	1.94808859636032	4.22756925233567	4.87786949298071
C	-7.03725849061415	6.01778108108970	6.31708352325276
C	-6.26002239555775	7.19567879611541	6.46353396456885
C	-6.66021267235950	8.38167629347391	5.78617346666183
C	-7.79471338651897	8.37558559420265	4.96195816395143
H	-8.09040846445393	9.31267113330657	4.46248930481371
C	-8.56455686008795	7.21187126830155	4.77639423150738
C	-8.16755546772546	6.05954806111795	5.47803946270817
H	-8.77268446247579	5.14215529162507	5.38261864801654
C	-6.73570149074889	4.69673638167415	6.99159763729860
H	-7.68917580464169	4.21588572257412	7.29553181951727
H	-6.24311755496316	4.01034302866707	6.26679027424971
C	-5.04802204707534	1.85022193878382	12.12515634681109
H	-4.70830786394007	1.04081863905926	12.80431708462663
H	-6.13832339929677	2.00828974282220	12.27255746854649
C	-9.76590291652394	7.19739498606455	3.86204042652961
H	-10.54625489667495	6.49884457514381	4.22483372972870
H	-9.48752742971589	6.86964005350235	2.83654770135389
H	-10.22143592060173	8.20350329766054	3.77068666070780
C	-3.23855208556430	4.06834676421680	5.42785543694834
H	-3.38903800174237	3.93256920327367	4.33505367917946
H	-3.69445765388304	3.20979370224155	5.95774651361514
H	-2.15174788340695	4.08294483641356	5.65362809212655
O	-7.45661381449924	7.38169874594443	9.38956179286792
O	-8.30648675569461	4.83434021420129	9.92376981346745
O	-8.08871465864758	3.77206168251911	12.55773840407689
H	-7.52090841996980	3.70713902220223	11.75047835434968
O	-5.01970930659733	6.70516059112946	10.01997259214187
O	-5.77057756809795	4.20530719564202	10.88797779084742
O	-6.16221922163611	10.03587831413660	7.42944677267394
H	-5.49098444903656	10.67491136496863	7.76693704968966
O	-7.05080967751289	6.24741000416549	12.29287072970572
H	-7.51242952375004	5.42481630317609	12.63708775459151
C	-9.72219376729625	6.77580064609353	9.99355862925418
C	-9.36264517702777	5.48232371474284	10.45551266426761
C	-10.03100797621009	4.90715782318697	11.56504424498375
C	-11.11909254245712	5.59173266614929	12.13163191198264
H	-11.63583610950274	5.14543451990849	12.99821567565472
C	-11.54757956640749	6.84469198966467	11.64238184404759
C	-10.81346998525694	7.42892111203837	10.58653628182328
H	-11.08573649045202	8.43798821752121	10.23425643327211
C	-8.82659196558240	7.41456548733816	8.95896092151438
H	-9.12067530423864	8.47189035240105	8.79192369522845
H	-8.90202533618413	6.88409344995990	7.98294054325615
C	-9.46500579505136	3.62779190049414	12.13854866370932
H	-9.53299750603739	2.80364658852235	11.39521912953322
H	-10.03875747911075	3.32517604455381	13.03713370308927
C	-12.74394976664035	7.54700954098033	12.23943901781290
H	-12.64441817570394	8.64931285965506	12.17714104510516
H	-13.68029119642289	7.27489159820000	11.70446536321844
H	-12.88821013929889	7.27561559453775	13.30451118239755
C	-3.90774575391871	5.48082631033932	11.86011769857144
C	-4.68539819076830	4.30322395515603	11.71386863664057

C	-4.28607709403921	3.11724028513783	12.39177775248029
C	-3.15186276836817	3.12308211410448	13.21637564158597
H	-2.85671198725152	2.18605486946476	13.71626587569741
C	-2.38163460001695	4.28656902932099	13.40187288100503
C	-2.77785300746005	5.43883044561747	12.69971700326301
H	-2.17227825390254	6.35594070248761	12.79504621855587
C	-4.20813947373482	6.80181137645010	11.18486240205044
H	-3.25420687725659	7.28094666092506	10.87962785726237
H	-4.69906887436195	7.48940367081311	11.90963191742742
C	-5.89880171213883	9.64895822056652	6.05299607079216
H	-6.23874925742023	10.45810929203726	5.37361948323922
H	-4.80836589608054	9.49144168483363	5.90589147891951
C	-1.18072217730913	4.30083812065833	14.31679570449421
H	-0.40023327096288	4.99953754666523	13.95459251037624
H	-1.45961231449445	4.62826773694533	15.34225295357141
H	-0.72517751290048	3.29472721671907	14.40807788173416
C	-7.70431675331549	7.43124714554339	12.74890140404768
H	-7.55208620481886	7.56803096127128	13.84131604521020
H	-7.24952414249970	8.28952260803071	12.21760781249802
H	-8.79141181759768	7.41596415776636	12.52456706769613

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