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Electronic supplementary information

Effect of Ligand Substitution on the SMM Properties of Three Isostructural Families of Double-Cubane Mn_4Ln_2

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1. Crystallographic supplementary data

Table S1. Crystal structure and structure refinement details for complexes **1-22.**

Complex	**1**	**2**	**3**	**4**	**5**	**6**
Formula	$C_{50}H_{98}N_6O_{28}La_2Mn_4$	$C_{50}H_{98}N_6O_{28}Ce_2Mn_4$	$C_{50}H_{98}N_6O_{28}Pr_2Mn_4$	$C_{50}H_{98}N_6O_{28}Nd_2Mn_4$	$C_{56}H_{107}N_9O_{28}Sm_2Mn_4$	$C_{50}H_{98}N_6O_{28}Eu_2Mn_4$
Formula weight	1728.92	1731.34	1732.92	1739.58	1874.97	1755.02
Crystal system	Monoclinic	Monoclinic	Monoclinic	Monoclinic	Monoclinic	Monoclinic
Space group	$P2_1/n$	$P2_1/n$	$P2_1/n$	$P2_1/n$	$C2/c$	$P2_1/n$
Temperature (K)	100(2)	100(2)	150(2)	100(2)	150(2)	100 (2)
a (Å)	12.5961(6)	12.6104(6)	12.6597(12)	12.6478(7)	24.8976(11)	12.7086 (7)
b (Å)	19.1851(9)	19.2016(9)	19.2686(14)	19.1917(10)	13.9166(6)	19.2548 (11)
c (Å)	14.3211(7)	14.2715(7)	14.2783(14)	14.1773(8)	22.3814(10)	14.1524 (8)
α (deg)	90	90	90	90	90	90
β (deg)	92.101(1)	92.147(1)	92.582(8)	92.331(1)	104.775(1)	92.764 (1)
γ (deg)	90	90	90	90	90	90
Volume (Å^3)	3458.5(3)	3453.3(3)	3479.4(5)	3438.4(3)	7498.5(6)	3459.1 (3)
Z	2	2	2	2	4	2
ρ_{calcd} (Mg m^{-3})	1.66	1.665	1.654	1.68	1.661	1.685
μ(Mo-$K\alpha$) (mm^{-1})	1.998	2.082	2.158	2.277	2.277	2.575
F(000)	1756	1760	1764	1768	3816	1780
Reflections collected	29022	22933	21749	17348	24104	18501
Unique data	8486	7665	7364	7708	8346	8495
R_{int}	0.0601	0.0157	0.0842	0.0347	0.021	0.037
Refl. with I>2σ(I)	7877	7318	5582	6155	7937	7234
Parameters/restraints	447 / 100	434 / 12	434 / 12	434 / 52	465 / 4	410 / 57
wR_2 (all data)	0.0904	0.0704	0.1850	0.0813	0.0608	0.1035
S on F^2	1.143	1.150	0.993	1.019	1.080	1.035
R_1 (I>2σ(I))	0.0402	0.0307	0.0703	0.0352	0.0246	0.0469
largest residuals (e Å^{-3})	+1.49 / -0.98	+1.17 / -1.06	+0.81 / -2.96	+1.07 / -0.78	+0.85 / -0.52	+1.51 / -0.82
CCDC	1560609	1560610	1560611	1560612	1560613	1560614

Complex	**7**	**8**	**9**	**10**	**11**
Formula	$C_{56}H_{107}N_9O_{28}Mn_4Tb_2$	$C_{56}H_{107}N_9O_{28}Dy_2Mn_4$	$C_{56}H_{107}N_9O_{28}Ho_2Mn_4$	$C_{56}H_{107}N_9O_{28}Er_2Mn_4$	$C_{56}H_{107}N_9O_{28}Tm_2Mn_4$
Formula weight	1892.10	1899.27	1904.12	1908.78	1912.13
Crystal system	Monoclinic	Monoclinic	Monoclinic	Monoclinic	Monoclinic
Space group	*C2/c*	*C2/c*	*C2/c*	*C2/c*	*C2/c*
Temperature (K)	200(2)	100(2)	100(2)	220(2)	200(2)
a (Å)	24.8658(12)	24.698(7)	24.650(4)	24.901(3)	24.768(2)
b (Å)	13.9234(10)	13.842(4)	13.825(2)	13.9253(11)	13.9171(13)
c (Å)	22.4690(11)	22.331(6)	22.304(3)	22.556(3)	22.513(2)
α (deg)	90	90	90	90	90
β (deg)	104.422(4)	104.571(4)	104.549(2)	103.852(14)	104.065(1)
γ (deg)	90	90	90	90	90
Volume (Å^3)	7534.0(8)	7388.0(3)	7357.2(19)	7594.0(15)	7527.5 (12)
Z	4	4	4	4	4
ρ_{calcd} (Mg m^{-3})	1.668	1.707	1.719	1.670	1.687
μ(Mo-*K*α) (mm^{-1})	2.584	2.744	2.875	2.912	3.065
F(000)	3840	3848	3856	3864	3872
Reflections collected	28387	23114	23782	24444	29641
Unique data	9006	8146	7736	7110	8700
R_{int}	0.0349	0.0437	0.0378	0.0801	0.0213
Refl. with I>2σ(I)	7529	6758	6773	5922	8003
Parameters/restraints	474 / 73	476 / 62	477 / 23	467 / 53	468 / 45
wR_2 (all data)	0.0608	0.1014	0.0983	0.1020	0.0575
S on F^2	1.022	1.070	1.075	1.034	1.031
R_1 (I>2σ(I))	0.0294	0.0428	0.0427	0.0380	0.0227
largest residuals (e Å^{-3})	+0.49 / -0.96	+1.27 / -2.68	+2.02 / -2.26	+0.79 / -1.39	+0.97 / -0.55
CCDC	1560615	1560616	1560617	1560618	1560619

Complex	**12**	**13**	**14**	**15**	**16**	**17**
Formula	$C_{56}H_{107}N_9O_{28}Yb_2Mn_4$	$C_{56}H_{107}N_9O_{28}Y_2Mn_4$	$C_{66}H_{80}N_8O_{28}Gd_2Mn_4$	$C_{66}H_{80}N_8O_{28}Tb_2Mn_4$	$C_{66}H_{80}N_8O_{28}Dy_2Mn_4$	$C_{68}H_{128}N_8O_{26}La_2Mn_4$
Formula weight	1920.35	1752.08	1967.64	1970.98	1978.14	1971.36
Crystal system	monoclinic	monoclinic	monoclinic	monoclinic	monoclinic	triclinic
Space group	*C2/c*	*C2/c*	$P2_1/n$	$P2_1/n$	$P2_1/n$	$P\bar{1}$
Temperature (K)	200(2)	100(2)	200(2)	150(2)	100(2)	150(2)
a (Å)	24.7488(18)	24.8255(17)	12.9107(12)	12.9252(11)	12.9182(4)	13.5179(7)
b (Å)	13.9263(10)	13.9078(9)	15.4585(10)	15.2245(8)	15.1094(4)	13.8472(8)
c (Å)	22.5440(16)	22.4894(15)	18.9297(17)	18.7403(15)	18.6730(6)	24.3303(13)
α (deg)	90	90	90	90	90	95.199(4)
β (deg)	103.921(1)	104.156(1)	99.040(11)	99.097(7)	99.213(1)	97.115(4)
γ (deg)	90	90	90	90	90	102.773(4)
Volume (Å^3)	7541.8(9)	7529.1(9)	3731.1(5)	3641.3(5)	3597.70(19)	4374.5(4)
Z	4	4	2	2	2	2
ρ_{calcd} (Mg m^{-3})	1.691	1.546	1.751	1.798	1.826	1.497
μ(Mo-*K*α) (mm^{-1})	3.186	2.257	2.496	2.678	2.822	1.588
F(000)	3880	3632	1968	1972	1976	2028
Reflections collected	24671	25782	22837	23049	23771	31070
Unique data	8563	8521	6556	7729	8163	17855
R_{int}	0.0191	0.0329	0.0745	0.0428	0.0203	0.0240
Data with I>2σ(I)	8129	7495	4225	6398	7330	14735
Parameters/restraints	471 / 42	485 / 89	494 / 2	494 / 2	494 / 2	989/4
wR_2 (all data)	0.0625	0.0897	0.0688	0.1168	0.0606	0.1026
S on F^2	1.070	1.057	0.949	1.003	1.050	0.964
R_1 (I>2σ(I))	0.0259	0.0389	0.0337	0.0458	0.0249	0.0393
largest residuals (e Å^{-3})	+0.97 / -0.63	+0.46/ -0.45	+0.71 / -0.44	+0.70 / -2.63	+1.67 / -0.51	+0.47 / -1.68
CCDC	1560620	1560621	1560622	1560623	1560624	1560625

Complex	**18**	**19**	**20**	**21**	**22**
Formula	$C_{71}H_{132}N_6O_{27}Pr_2Mn_4$	$C_{71}H_{132}N_6O_{27}Nd_2Mn_4$	$C_{71}H_{132}N_6O_{27}Sm_2Mn_4$	$C_{64.88}H_{124.44}N_{6.44}O_{26.56}Gd_2Mn_4$	$C_{71}H_{132}N_6O_{27}Tb_2Mn_4$
Formula weight	2003.40	2010.06	2022.28	1954.08	2039.42
Crystal system	Monoclinic	Monoclinic	Monoclinic	Triclinic	Monoclinic
Space group	*C2/c*	*C2/c*	*C2/c*	$P\bar{1}$	*C2/c*
Temperature (K)	100(2)	100(2)	100(2)	100(2)	100(2)
a (Å)	27.1710(7)	27.1777(17)	27.1856(10)	13.1507(5)	27.154(2)
b (Å)	14.5793(4)	14.5314(9)	14.5451(5)	13.7341(5)	14.4968(13)
c (Å)	22.0369(6)	21.9879(14)	21.9395(8)	13.8606(6)	21.8243(19)
α (deg)	90	90	90	64.935(1)	90
β (deg)	92.650(1)	92.649(1)	92.614(1)	66.609(1)	92.776(1)
γ (deg)	90	90	90	80.602(1)	90
Volume (Å^3)	8720.2 (4)	8674.4(9)	8666.2(5)	2081.26(14)	8581.1(13)
Z	4	4	4	1	4
ρ_{calcd} (Mg m^{-3})	1.526	1.539	1.550	1.559	1.579
μ(Mo-*K*α) (mm^{-1})	1.733	1.816	1.974	2.234	2.274
F(000)	4136	4144	4160	999	4184
Reflections collected	29942	23539	27447	17392	27332
Unique data	9868	9762	9738	8981	9762
R_{int}	0.0191	0.0284	0.0312	0.0177	0.0197
Data with I>2σ(I)	9026	8395	8227	8296	9053
Parameters/restraints	701 / 423	724 / 280	703 / 445	502 / 212	659 / 392
wR_2 (all data)	0.0645	0.0781	0.0715	0.0936	0.0736
S on F^2	1.074	1.033	1.047	1.119	1.059
R_1 (I>2σ(I))	0.0255	0.0319	0.0322	0.0396	0.0307
largest residuals (e Å^{-3})	+0.83 /-0.65	+0.84 / -0.57	+0.71 / -0.55	+1.65 / -1.33	+1.27 / -0.72
CCDC	1560626	1560627	1560628	1560629	1560630

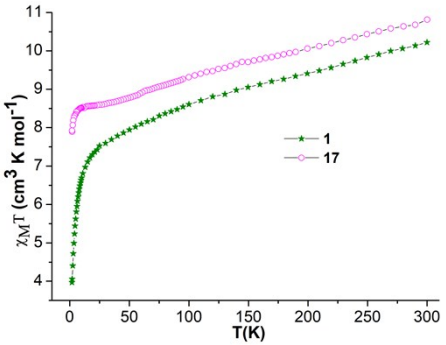
Table S2: Selected average bond distances in **1-22** (a, b, c, d, and e were used for averaged distances).

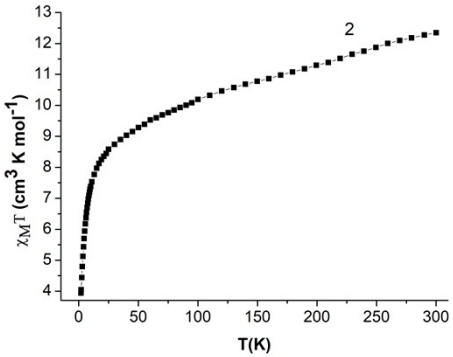
	LnO_a	LnO_b	Mn_1O_c	Mn_1O_d	Mn_2O_e	Mn_2O_d	Mn_2N
1	2.583	2.562	1.963	2.206	2.319	2.202	2.363
2	2.565	2.543	1.962	2.206	2.322	2.202	2.361
3	2.544	2.523	1.965	2.203	2.327	2.205	2.365
4	2.528	2.509	1.958	2.194	2.329	2.206	2.362
5	2.500	2.480	1.969	2.202	2.306	2.202	2.365
6	2.489	2.473	1.963	2.188	2.360	2.208	2.371
7	2.465	2.446	1.963	2.206	2.335	2.182	2.365
8	2.452	2.433	1.962	2.183	2.336	2.183	2.365
9	2.439	2.420	1.965	2.196	2.325	2.185	2.363
10	2.442	2.420	1.959	2.207	2.335	2.180	2.368
11	2.440	2.413	1.962	2.203	2.318	2.183	2.366
12	2.447	2.414	1.959	2.186	2.314	2.186	2.368
13	2.447	2.427	1.963	2.183	2.308	2.202	2.367
14	2.478	2.470	2.025	2.133	2.300	2.226	2.381
15	2.456	2.443	1.996	2.165	2.289	2.206	2.359
16	2.442	2.429	1.982	2.180	2.283	2.196	2.361
17	2.576	2.570	1.967	2.219	2.287	2.175	2.380
18	2.532	2.525	1.984	2.199	2.316	2.176	2.382
19	2.516	2.509	1.980	2.197	2.320	2.173	2.370
20	2.492	2.484	1.979	2.199	2.314	2.176	2.373
21	2.477	2.466	1.972	2.204	2.378	2.176	2.385
22	2.461	2.451	1.975	2.197	2.335	2.172	2.385

a = 7, 9, 10, 11, 12, 13, b = 1, 2, c = 6, 8, e = 3A, 5A, d = 2, 4

Table S3: Selected bond distances in **1-22**.

	Ln	LnLn	Mn_1Mn_1	Mn_2Mn_2	Mn_1Ln	Mn_2Ln (long)	Mn_2Ln (short)	Mn_1Mn_2	LnO_1	Mn_1O_1	Mn_2O_1
1	La	6.260	2.901	5.589	3.450	4.468	3.905	3.148	2.446	1.912	2.236
2	Ce	6.214	2.901	5.593	3.429	4.455	3.886	3.150	2.425	1.912	2.240
3	Pr	6.181	2.905	5.602	3.415	4.454	3.867	3.155	2.402	1.912	2.260
4	Nd	6.149	2.897	5.588	3.399	4.434	3.855	3.147	2.389	1.910	2.249
5	Sm	6.074	2.895	5.638	3.364	4.465	3.796	3.169	2.366	1.911	2.284
6	Eu	6.085	2.896	5.605	3.370	4.428	3.823	3.155	2.349	1.912	2.273
7	Tb	6.010	2.891	5.638	3.334	4.441	3.773	3.168	2.327	1.911	2.293
8	Dy	5.982	2.888	5.626	3.322	4.425	3.761	3.162	2.316	1.905	2.289
9	Ho	5.962	2.883	5.624	3.311	4.417	3.753	3.160	2.299	1.909	2.291
10	Er	5.955	2.890	5.637	3.310	4.422	3.750	3.168	2.289	1.913	2.306
11	Tm	5.927	2.887	5.635	3.296	4.412	3.739	3.166	2.277	1.910	2.307
12	Yb	5.904	2.886	5.639	3.286	4.409	3.727	3.167	2.267	1.913	2.308
13	Y	5.973	2.888	5.634	3.318	4.426	3.758	3.166	2.301	1.909	2.302
14	Gd	6.057	2.979	5.639	3.375	4.383	3.877	3.189	2.320	1.963	2.259
15	Tb	6.016	2.921	5.663	3.343	4.418	3.822	3.186	2.313	1.928	2.296
16	Dy	5.985	2.898	5.664	3.325	4.423	3.793	3.181	2.311	1.913	2.299
17	La	6.349	2.883	5.656	3.487	4.595	3.877	3.175	2.504	1.905	2.294
18	Pr	6.229	2.901	5.624	3.436	4.539	3.824	3.164	2.446	1.909	2.284
19	Nd	6.199	2.890	5.627	3.420	4.526	3.816	3.163	2.432	1.905	2.284
20	Sm	6.151	2.893	5.627	3.399	4.506	3.801	3.164	2.373	1.909	2.292
21	Gd	6.110	2.893	5.601	3.380	4.467	3.795	3.152	2.399	1.912	2.277
22	Tb	6.084	2.887	5.609	3.367	4.473	3.772	3.154	2.359	1.906	2.294
Max		6.349	2.979	5.664	3.487	4.595	3.905	3.189	2.504	1.963	2.308
Min		5.904	2.883	5.588	3.286	4.383	3.727	3.147	2.267	1.905	2.236


$\chi_M T$ (cm^3 K mol^{-1})
T(K)
1
17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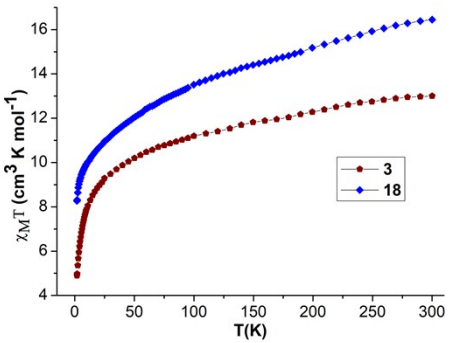
T(K)
2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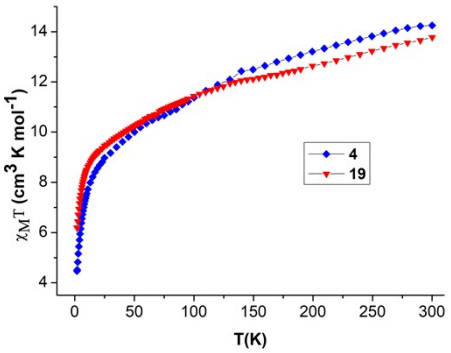
T(K)
3
18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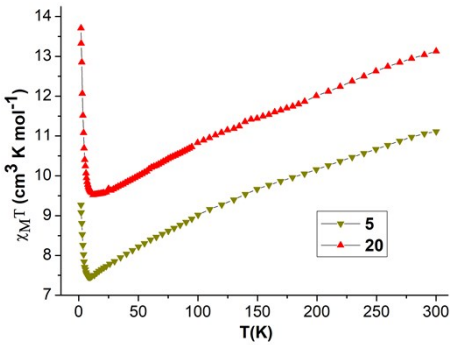
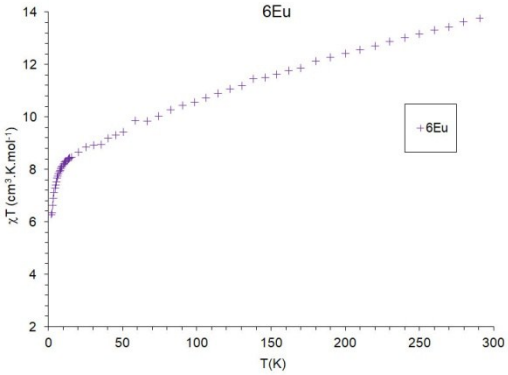
T(K)
4
19


$\chi_M T$ (cm^3 K mol^{-1})
T(K)
5
20


6Eu
χT (cm^3.K.mol^{-1})
T(K)
6Eu

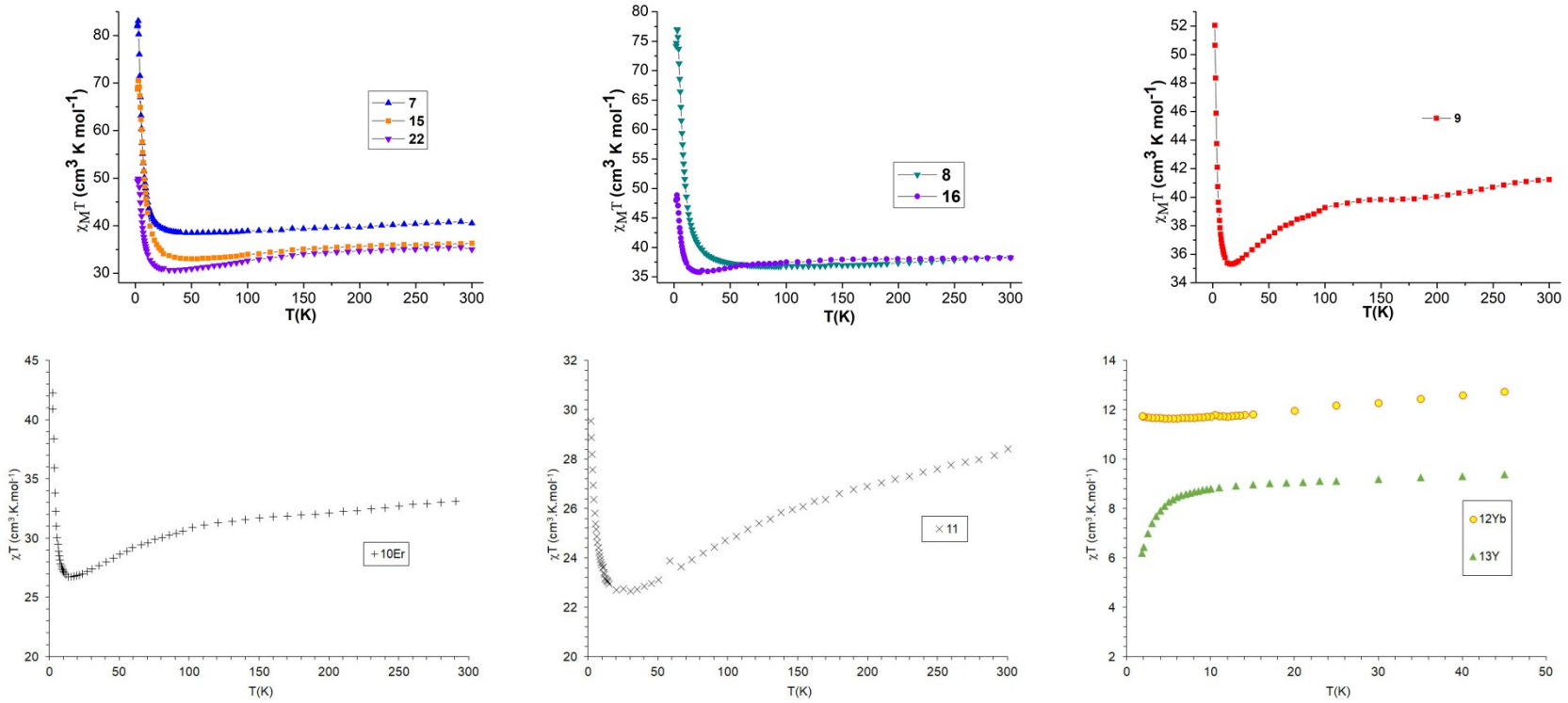


Figure S1. $\chi_M T$ versus T plots of complexes **1-22.**

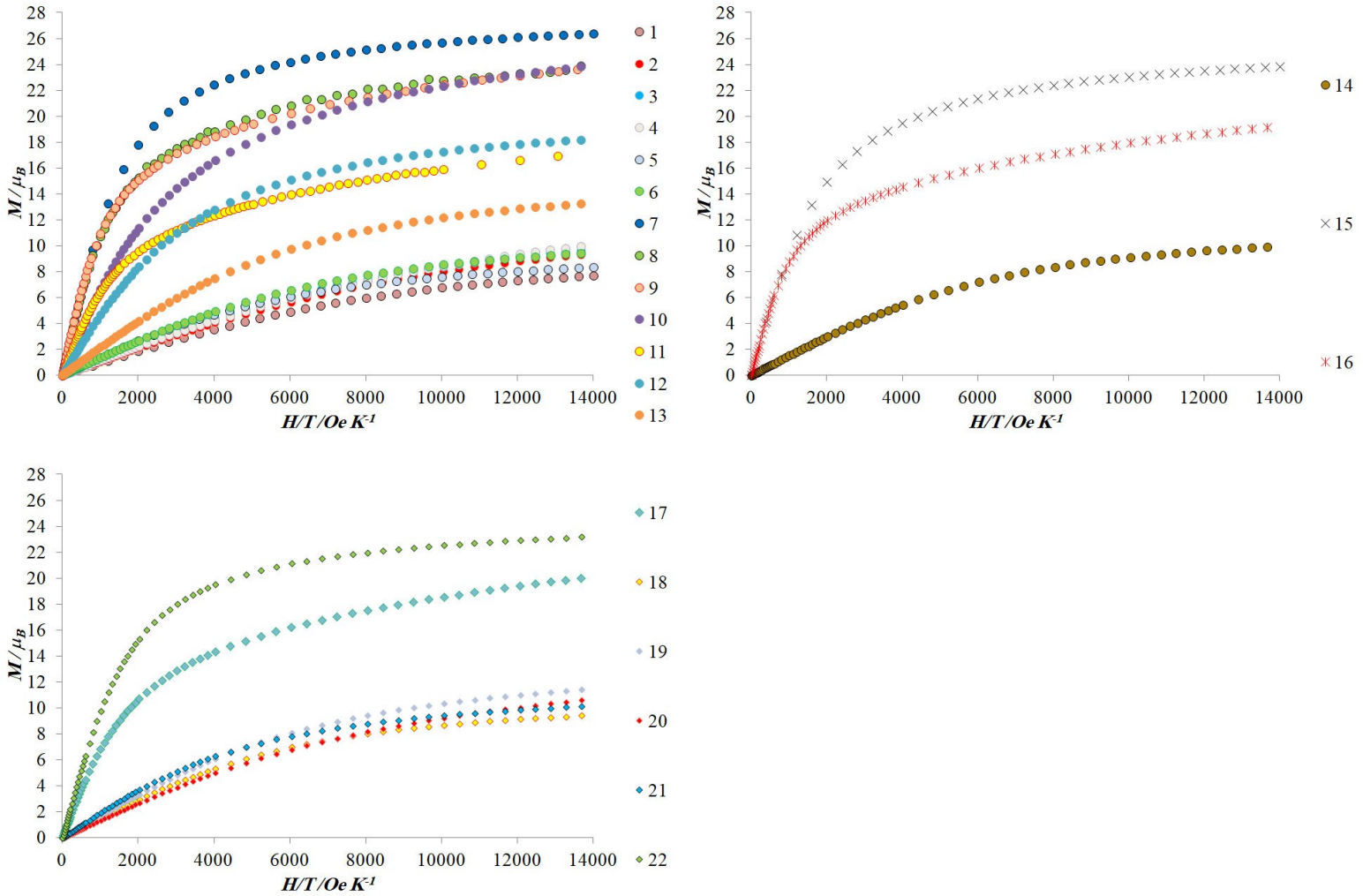


Figure S2. Reduced magnetization *vs.* applied field at 5 K for the three set of complexes **1**-**13, 14-16 and 17**-**22**, respectively.

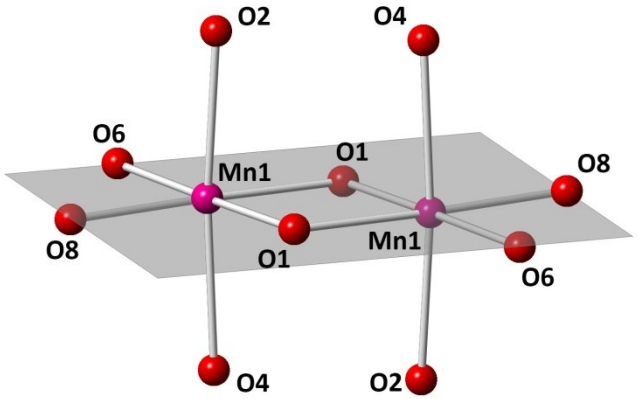


Figure S3 and Table S4. The fragment $Mn_2O_{10}^{14-}$. Best-fit plane ($Mn_1O_1Mn_1O_1$) of 0.001 Å.

Table S4. Bond distances in the fragment $Mn_2O_{10}^{14-}$ shown in Fig. S3

	Mn_1O_1	Mn_1O_6	Mn_1O_8	Mn_1O_2	Mn_1O_4	Mn_1Mn_1	O_1O_1	J_1
13	1.906	1.970	1.975	2.179	2.226	2.888	2.498	-36.3
17	1.899	1.984	1.989	2.178	2.259	2.887	2.485	-35.6
1	1.906	1.952	1.975	2.201	2.211	2.901	2.490	-34.0
21	1.911	1.971	1.974	2.179	2.211	2.893	2.500	-30.4
14	1.871	1.962	2.088	2.105	2.160	2.980	2.562	-27.3

In case with Dy-containing compounds (**8** and **16**), they also show frequency-dependent *ac* magnetic behaviour as seen in Figure S4a and S4b. However, the energy barriers for these compounds are clearly less than those for the corresponding Tb-containing compounds. This is unusual for lanthanide-containing SMMs, because Dy^{III} is usually regarded as the most anisotropic lanthanide ion, and several reported compounds follow this rule. An attempt to obtain the energy barrier for **16** by using the isothermal frequency-dependent *ac* susceptibility data was not successful. In contrary to Tb, the Dy complexes show that increasing the number of pivalate moieties will lead to decreasing of SMMs behaviour (ac-signal).

From the ac, several compounds present a signal but they have blocking temperatures below 2 K, and only a slope is visible at very low temperatures (Figure S4c). Since the first reported SIMs[1] only few complexes with samarium where reported which are $[SmCu_4(L)_2(OH)_4(H_2O)_8(NO_3)](ClO_4)_2$,[2] $[Fe_{12}Sm_4O_{10}(OH)_4(PhCO_2)_{24}]$ [3] and $[Mn_4Sm_4(nBudea)_4(HCOO)_4(OMe)_4(OOCEt)_8(MeOH)_4]$.[4] Although the $J_z = 5/2$ of Sm^{3+} is small comparable to Dy^{III} and Tb^{III}, the ground state in Sm^{3+} is $^6H_{5/2}$ and the first excited state $^6H_{7/2}$ is low-lying with 1100 cm^{-1}.[5] This may be a reason of the SMM behavior in **20**. Furthermore, there are many characterizations of the Samarium as its nuclear spin isotopes and the crystal and ligand fields. These parameters are needed to be taken into account to explain such a behaviour which is not always easy to do and the answer why **5** does not behave as SMM is not straightforward. In case of **20** in which Ln is Sm^{III} there also ac-signal (Fig. 9). The in-phase and out-of-phase are both weak, a maximum reachable χ'' is equal to 0.31 $cm^3.mol^{-1}$ and so it is not safe to say whether it

is SMM or not. However, it is important to have such a behaviour with manganese and samarium cluster due to their scarcity and to enrich the library of possible SMMs complexes. A literature survey shows that there are a few published examples like Ni_2Sm [6], Mn_4Sm_4 [3], $Fe_{12}Sm_4$ [2], Cu_4Sm [1].

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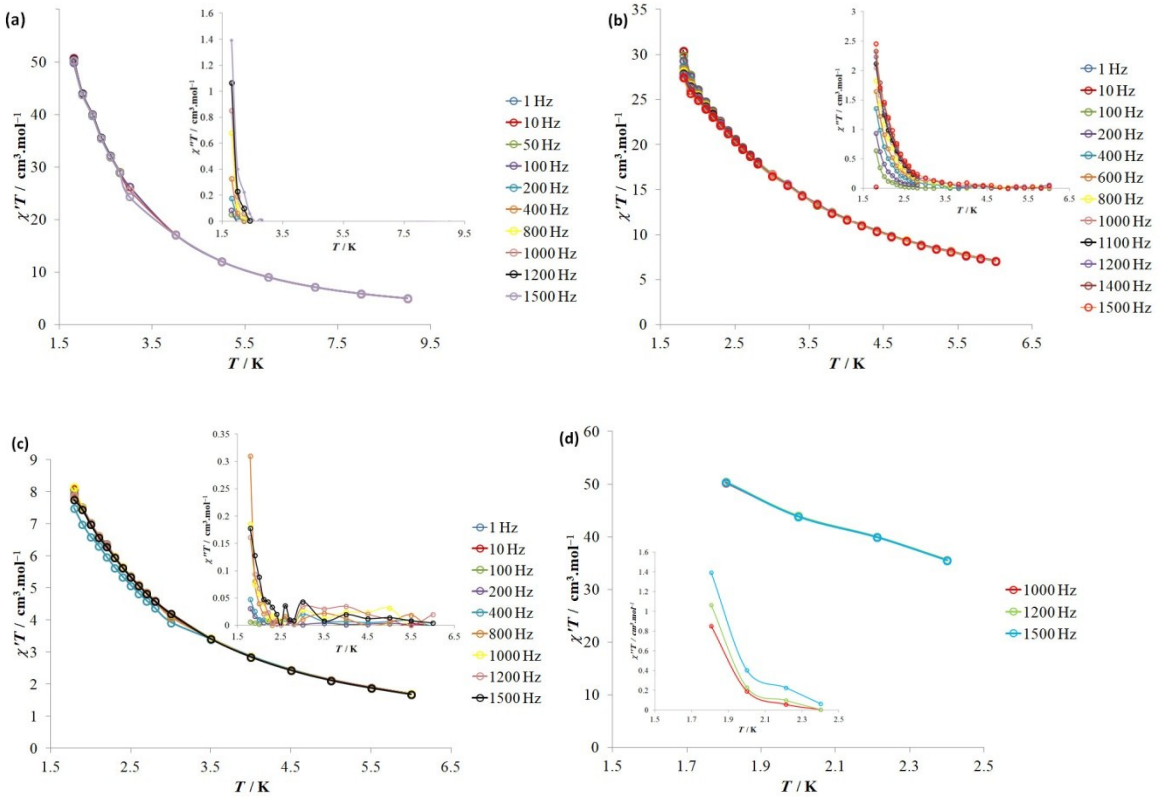

Figure S4. Temperature-dependence of *ac* susceptibilities for in-phase and out-of-phase (inset) (a), (b), (c) and (d) for **8**, **16, 20** and **9**, respectively.