Supporting Information

Magneto-Structural Properties and Theoretical Studies of a Family of Simple Heterodinuclear Phenoxide/alkoxide Bridged $Mn^{III}Ln^{III}$ Complexes: On the Nature of the Magnetic Exchange and Magnetic Anisotropy

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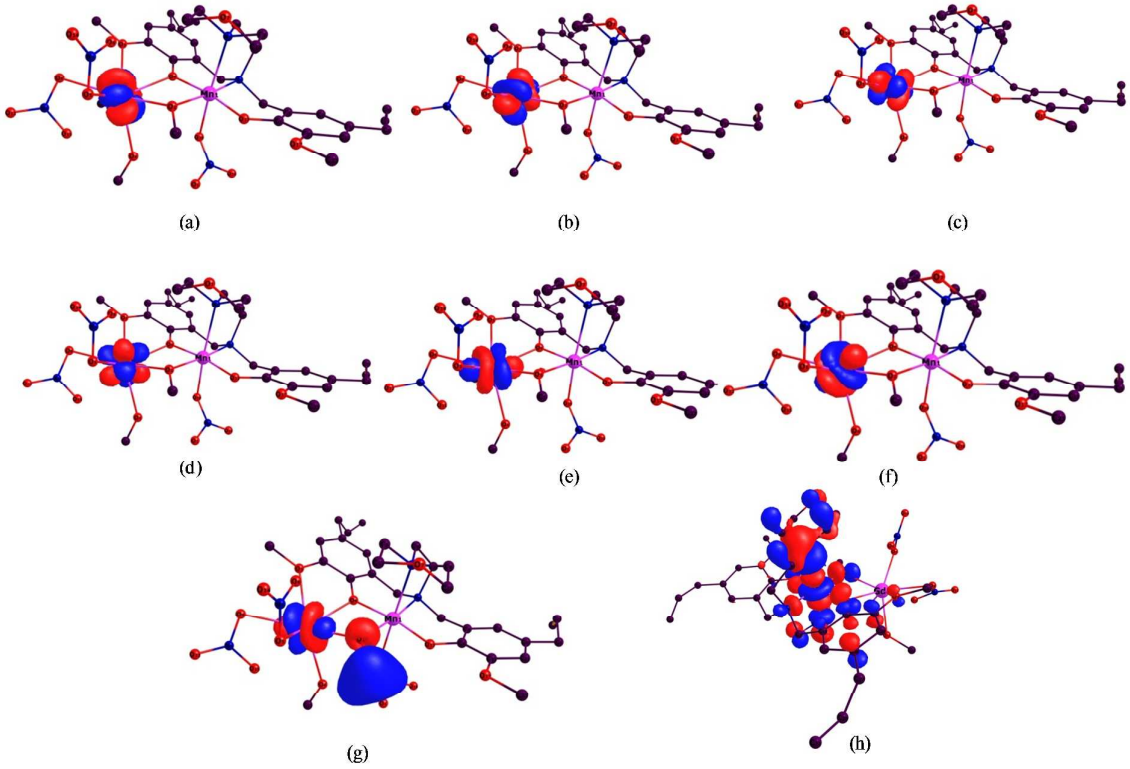

Figure **S1**. a)-g) The 4f orbitals of Gd(III) with the $3d_{xz}/3d_{yz}$ orbitals of Mn(III). Hydrogens are removed for clarity.

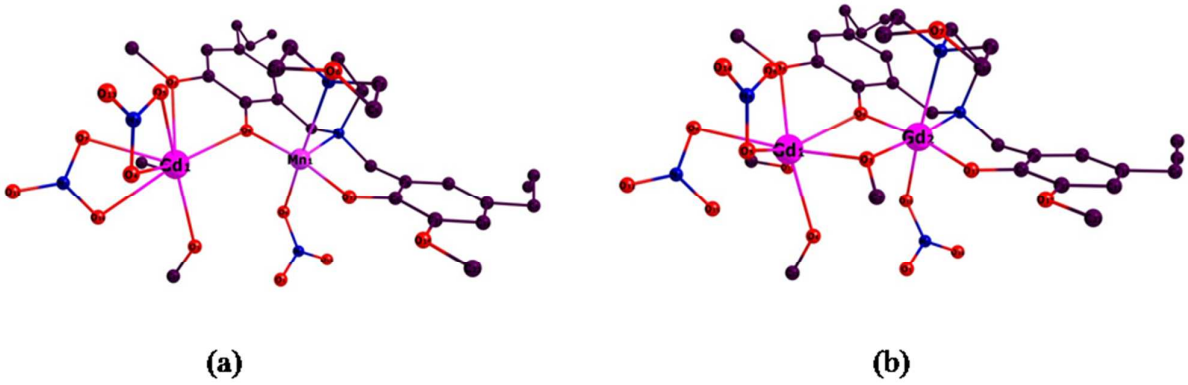

Figure **S2**. Model complex derived from complex **1.** (a) Removing –OMe group by taking into consideration of point charge of that group. (b) Replacing Mn(III) by Gd(III). In all the structures Hydrogens are removed for clarity.

Table **S1.** Overlap integral values with variation in angle (Mn-O-Gd)

Mn-O-Gd angle(º)	104.1	107.2	110.7	114.6	119
103-dxy	-0.002	0.000	0.006	0.008	-0.008
103-dyz	-0.010	0.008	0.007	0.014	0.032
103-dxz	0.003	-0.010	-0.014	-0.017	-0.016
103-dz^2	-0.007	-0.004	-0.003	-0.003	-0.003

Mn-O-Gd angle(º)	104.1	107.2	110.7	114.6	119
104-dxy	-0.004	0.006	0.001	0.002	-0.003
104-dyz	0.041	0.004	0.004	0.003	-0.001
104-dxz	0.011	-0.015	-0.007	-0.003	-0.002
104-dz^2	0.014	0.008	0.003	0.001	0.001

Mn-O-Gd angle(º)	104.1	107.2	110.7	114.6	119
105-dxy	0.006	-0.001	0.006	-0.006	0.004
105-dyz	-0.021	-0.019	-0.003	-0.002	0.008
105-dxz	-0.023	-0.002	-0.023	-0.020	-0.015
105- dz^2	0.005	0.009	0.007	0.007	0.007

Mn-O-Gd angle(º)	104.1	107.2	110.7	114.6	119
106-dxy	0.003	0.003	0.007	-0.008	0.009
106-dyz	0.023	0.031	-0.009	-0.016	-0.043
106-dxz	0.017	-0.027	0.021	0.021	0.025
106-dz^2	0.006	-0.003	0.008	0.009	0.009

Mn-O-Gd angle(º)	104.1	107.2	110.7	114.6	119
107-dxy	0.005	-0.003	-0.005	0.008	-0.009
107-dyz	0.002	0.001	0.001	0.003	0.009
107-dxz	-0.001	0.001	0.001	-0.005	-0.010
107-dz^2	0.006	0.003	0.007	0.008	0.007

Mn-O-Gd angle(º)	104.1	107.2	110.7	114.6	119
108-dxy	0.008	0.008	0.009	-0.008	0.008
108-dyz	0.013	-0.016	0.005	0.009	-0.018
108-dxz	0.025	0.032	0.036	0.041	0.043
108-dz^2	0.003	0.008	0.008	0.008	0.008

Mn-O-Gd angle(º)	104.1	107.2	110.7	114.6	119
109-dxy	0.002	0.001	0.001	-0.002	-0.000
109-dyz	-0.020	-0.011	0.003	0.003	-0.002
109-dxz	-0.000	0.007	0.001	-0.003	-0.005
109-dz^2	-0.008	0.008	0.006	0.005	0.006

Table **S2.** Overlap integral values with variation in dihedral (Mn-O-Gd-O).

Mn-O-Gd-O dihedral(º)	0	4.7	8.4	15.7	19.7	23.7
103-dxy	0.005	0.004	0.001	-0.002	-0.004	0.000
103-dyz	0.047	0.030	0.004	0.002	-0.000	0.000
103-dxz	-0.003	-0.007	0.001	-0.010	-0.021	0.033
103-dz^2	-0.001	-0.002	0.006	-0.004	-0.005	-0.005

Mn-O-Gd-O dihedral(º)	0	4.7	8.4	15.7	19.7	23.7
104-dxy	-0.002	0.000	0.002	0.008	0.006	-0.004
104-dyz	-0.041	-0.029	0.013	0.019	0.018	-0.010
104-dxz	-0.004	-0.003	-0.009	-0.030	-0.038	0.020
104-dz^2	0.007	0.008	-0.003	0.004	0.003	-0.000

Mn-O-Gd-O dihedral(º)	0	4.7	8.4	15.7	19.7	23.7
105-dxy	0.006	0.005	-0.004	0.003	0.006	-0.006
105-dyz	-0.004	0.011	-0.023	0.003	0.002	0.006
105-dxz	0.017	0.009	0.002	-0.022	-0.026	-0.035
105-dz^2	0.002	-0.002	0.005	0.005	0.005	-0.004

Mn-O-Gd-O dihedral(º)	0	4.7	8.4	15.7	19.7	23.7
106-dxy	0.005	0.006	0.004	0.001	0.007	0.013
106-dyz	-0.020	0.018	0.026	-0.003	-0.016	0.003
106-dxz	0.004	-0.013	-0.024	0.018	0.017	-0.009
106-dz^2	0.009	0.004	0.001	0.016	0.066	-0.004

Mn-O-Gd-O dihedral(º)	0	4.7	8.4	15.7	19.7	23.7
107-dxy	-0.004	0.007	0.007	-0.004	-0.004	0.004
107-dyz	0.025	-0.027	-0.014	-0.002	-0.012	0.012
107-dxz	0.025	0.030	0.021	0.008	0.018	-0.024
107-dz^2	-0.006	0.008	0.004	0.006	0.013	0.015

Mn-O-Gd-O dihedral(º)	0	4.7	8.4	15.7	19.7	23.7
108-dxy	0.004	0.004	0.005	0.007	0.006	-0.003
108-dyz	-0.013	-0.015	-0.016	-0.009	-0.004	0.001
108-dxz	0.006	0.016	0.026	0.023	0.009	0.011
108-dz^2	0.010	0.010	0.009	0.004	0.002	0.002

Mn-O-Gd-O dihedral(º)	0	4.7	8.4	15.7	19.7	23.7
109-dxy	0.002	0.003	0.002	-0.004	0.013	0.024
109-dyz	-0.014	-0.018	-0.015	-0.005	-0.001	0.004
109-dxz	-0.016	-0.006	0.002	0.014	-0.014	0.002
109- dz^2	0.005	0.008	0.009	0.007	-0.006	-0.005

Table **S3**. Exchange of the model complexes

Complex	***J*/cm^{-1}**
1	-0.11
Model **1a**	1.60
Model **1b** ($Gd^{III}..Gd^{III}$)	0.24

Table **S4.**Overlap Integral values of the model complexes

	Model **1a**	Model **1b**
103-dxy	-0.002	0.000
103-dyz	0.001	0.000
103-dxz	0.000	0.001
103-dz^2	0.000	0.000

	Model **1a**	Model **1b**
104-dxy	0.000	0.000
104-dyz	0.000	0.001
104-dxz	0.000	0.002
104-dz^2	0.000	0.000

	Model **1a**	Model **1b**
105-dxy	0.000	0.000
105-dyz	0.000	0.000
105-dxz	0.000	0.000
105- dz^2	0.000	0.000

	Model **1a**	Model **1b**
106-dxy	-0.001	0.000
106-dyz	0.001	0.001
106-dxz	0.000	-0.001
106-dz^2	0.000	-0.001

	Model **1a**	Model **1b**
107-dxy	0.000	0.000
107-dyz	0.000	0.001
107-dxz	0.000	0.002
107-dz^2	0.000	0.000

	Model **1a**	Model **1b**
108-dxy	0.000	0.001
108-dyz	-0.001	-0.001
108-dxz	0.000	-0.001
108-dz^2	0.000	0.000

	Model **1a**	Model **1b**
109-dxy	0.000	0.000
109-dyz	0.000	0.000
109-dxz	0.000	-0.001
109-dz^2	0.000	0.000

Table **S5.** Spin density of all the atoms associated with metal centers

HS	BS
1 Gd 7.056900 1 Mn 3.834871 2 O 0.001017 2 N 0.044031 3 N -0.037843 4 O -0.002841 5 O -0.005709 6 O -0.005374 8 O -0.006275 9 O -0.005156 10 O 0.010811 11 O -0.005402 13 O 0.037330 15 O -0.005830	1 Gd 7.044931 1 Mn -3.833979 2 O -0.024950 2 N -0.044332 3 N 0.037896 4 O -0.002389 5 O -0.005912 6 O -0.005419 8 O -0.006207 9 O -0.008631 10 O -0.010346 11 O -0.006192 13 O -0.037625 15 O -0.006099

Table S6. Electron occupancies of 6s, 4f and the 5d orbitals of Gd^{III}

	Original structure
6s	0.12
4f	7.00
5d	0.47
6p	0.33

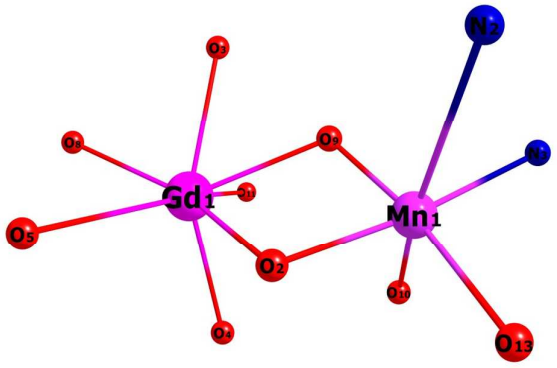

Figure S3. Model complex for showing the atom numbers followed for the spin density value given in Table S5.

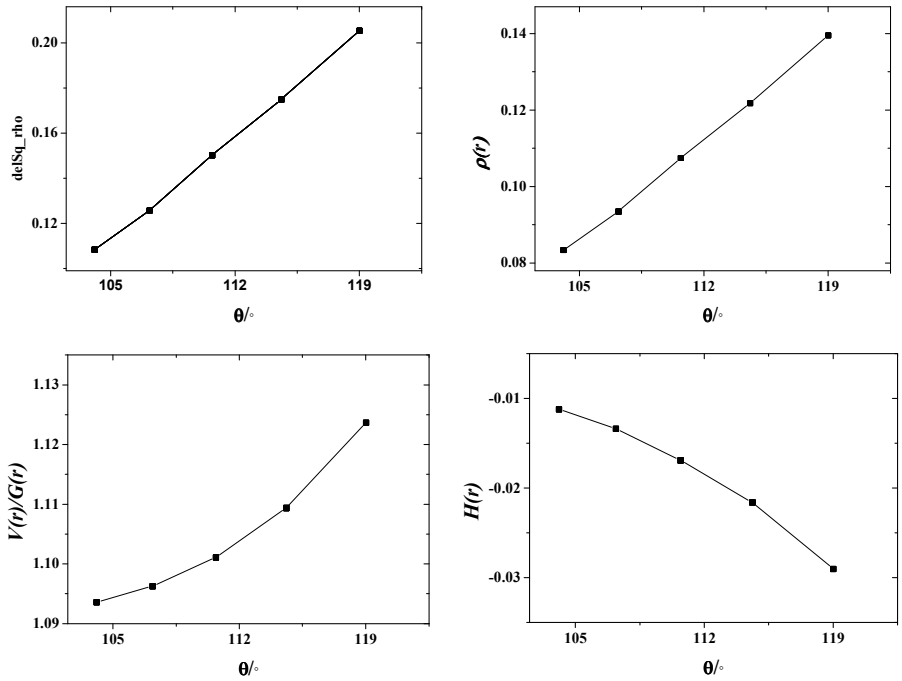

Figure S4. Correlations between the Mn-O(Ph) bonds QTAIM parameters and Mn-O-Gd angle.

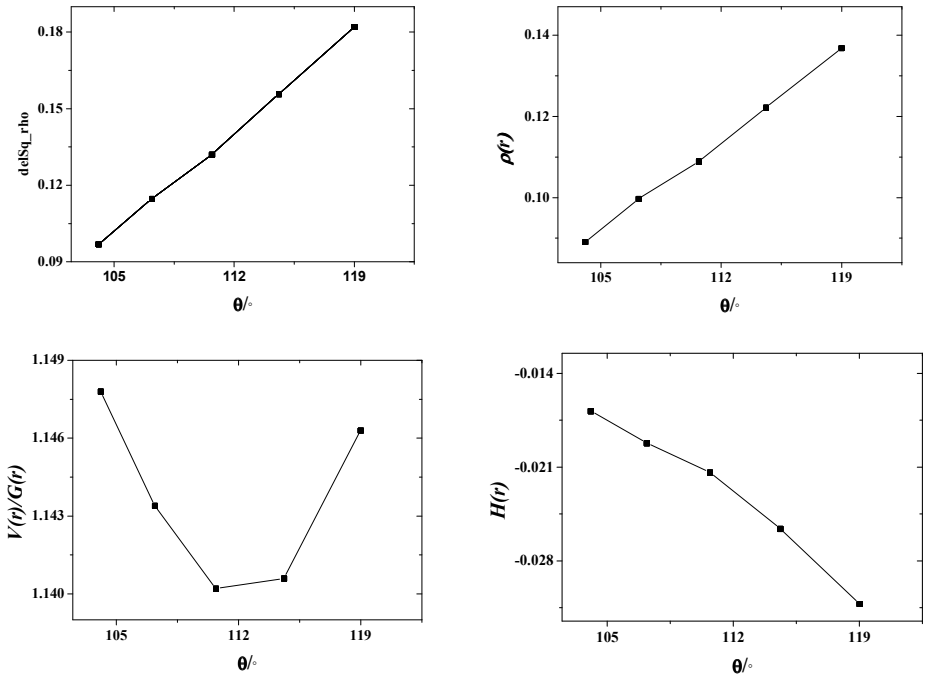

Figure S5. Correlations between the Mn-O(Me) bonds QTAIM parameters and Mn-O-Gd angle.

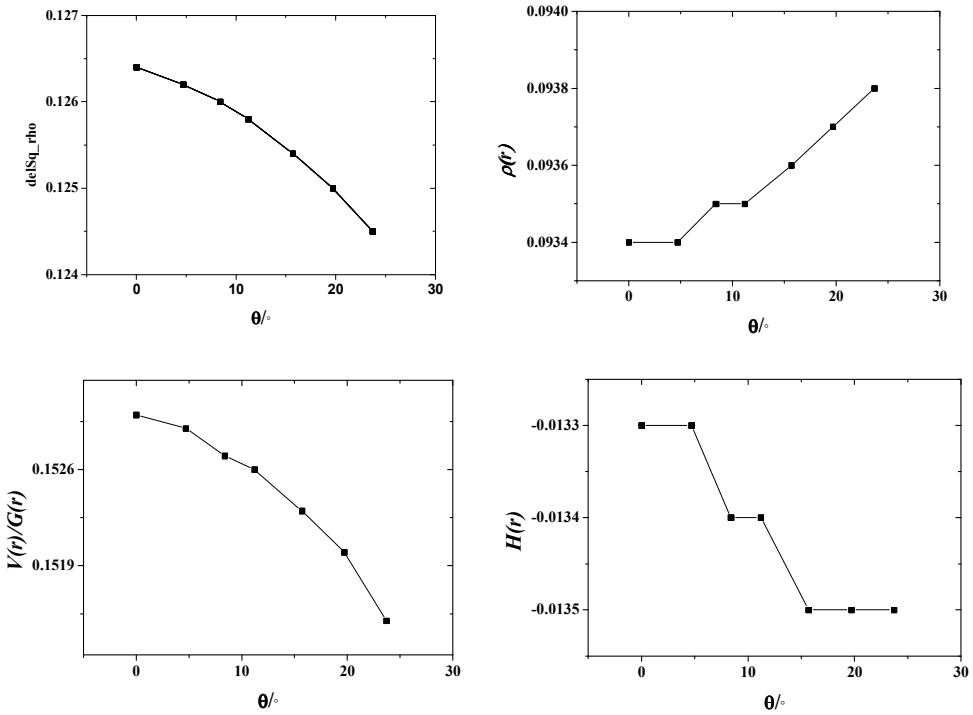

Figure S6. Correlations between the Mn-O(Ph) bonds QTAIM parameters and Mn-O-Gd-O dihedral.

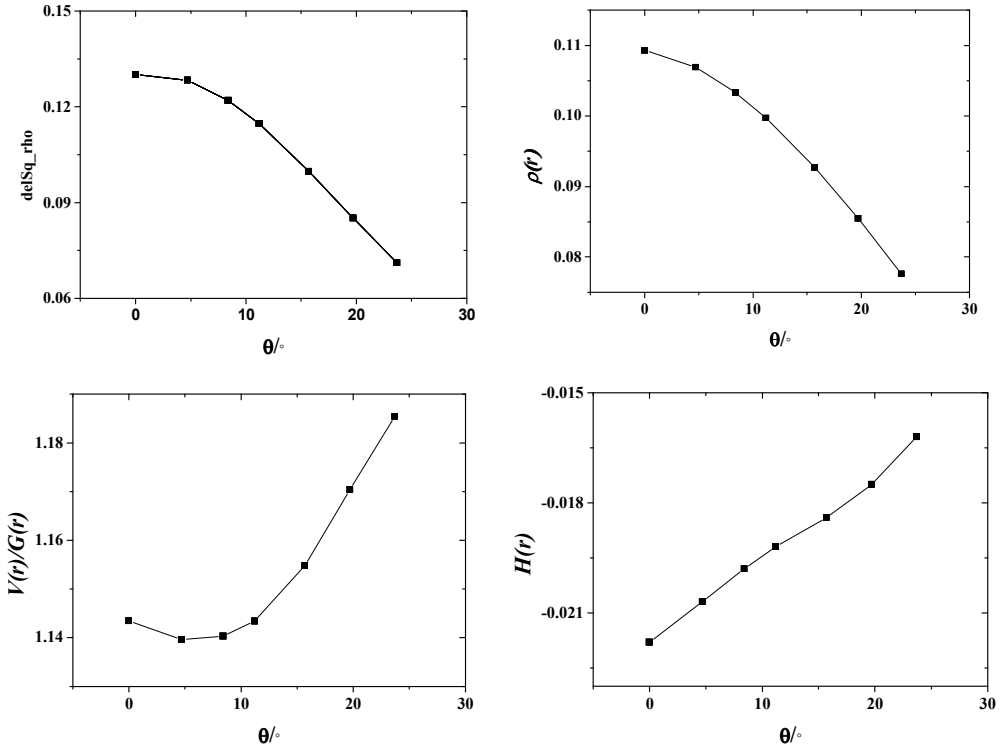

Figure S7. Correlations between the Mn-O(Me) bonds QTAIM parameters and Mn-O-Gd-O dihedral.

Table S7. Topological parameters at BCPs in the Mn^{III}-Gd^{III} complexes. All parameters are in a.u. ρ(r) in units of eÅ^{-3}, G(r), V(r), H(r) in units of a.u.

	ρ(r)	∇^2_ρ	H(r)	G(r)	ε	V(r)	|V(r)|/G(r)
Gd1-O11	0.0524	0.0537	-0.0031	0.0568	0.1081	0.0599	1.0546
M2n-O11	0.0942	0.1265	-0.0133	0.1399	0.0390	0.1532	1.0951
Gd1-O4	0.0576	0.0565	-0.0055	0.0619	0.0411	0.0673	1.0872
Mn2-O4	0.1002	0.1157	-0.0189	0.1346	0.0667	0.1535	1.1404
Gd1-O10	0.0419	0.0391	-0.0018	0.0409	0.0516	0.0426	1.0416
Gd1-O34	0.0408	0.0380	-0.0014	0.0394	0.0541	0.0408	1.0355
Gd1-O5	0.0273	0.0307	0.0023	0.0283	0.1028	0.0260	0.9187

Gd1-O14	0.0511	0.0549	-0.0019	0.0568	0.1266	0.0586	1.0317
Gd1-O6	0.0496	0.0507	-0.0019	0.0527	0.1371	0.0546	1.0361
Gd1-O7	0.0462	0.0422	-0.0029	0.0451	0.0537	0.0480	1.0643
Gd1-O8	0.0456	0.0423	0.0025	0.0450	0.0501	0.0473	1.0511
Mn2-N17	0.0400	0.0296	-0.0050	0.0346	0.0075	0.0396	1.1445
Mn2-O13	0.0414	0.0424	-0.0040	0.0465	0.0857	0.0504	1.0839
Mn2-O19	0.1220	0.1595	-0.0236	0.1831	0.0465	0.2067	1.1289
Mn2-N118	0.0791	0.0694	-0.0157	0.0851	0.0448	0.1008	1.1845

Table S8. Summary of crystallographic data for complexes **1-4** at 123K.

Compound	**1**	**2**	**3**	**4**
Formula	$C_{31}H_{47}GdMnN_5O_{17}$	$C_{31}H_{47}DyMnN_5O_{17}$	$C_{31}H_{47}HoMnN_5O_{17}$	$C_{31}H_{47}ErMnN_5O_{17}$
M_r	973.93	979.18	981.61	983.94
Crystal system	Monoclinic	Monoclinic	Monoclinic	Monoclinic
Space group	Pn	Pn	Pn	Pn
a/Å	11.4050(2)	11.3710(2)	11.3626(3)	11.3696(2)
b/Å	10.8550(2)	10.8550(2)	10.8847(3)	10.8857(2)
c/Å	15.5823(3)	15.5461(3)	15.5017(3)	15.4958(3)
α/°	90	90	90	90
β/°	99.7360(10)	99.6990(10)	99.576(2)	99.594(1)
γ/°	90	90	90	90
V/Å^3	1901.32(6)	1891.46(6)	1890.51(8)	1891.03(6)
Z	2	2	2	2
ρ_c(g/cm^3)	1.701	1.719	1.724	1.728
μ/mm^{-1}	2.141	2.374	2.492	2.618
F(000)	986	990	992	994
Reflections collected	17336	17790	13929	17962
Independent reflections	5966	5939	5545	5836
R_{int}	0.0466	0.0282	0.0416	0.0481
R_1[a]	0.0319 (0.0348)[b]	0.0219 (0.0225)[b]	0.0354 (0.0367)[b]	0.0338 (0.0377)[b]
wR_2[c]	0.0651 (0.0669)[b]	0.0523 (0.0527)[b]	0.0846 (0.0854)[b]	0.0707 (0.0731)[b]
Data/restraints/parameters	5966/5/510	5939/4/505	5545/12/504	6161/18/504
GooF on F^2	1.083	1.102	1.089	1.043
Largest diff. peak/hole / e Å^{-3}	0.57/-0.38	0.83/-0.62	1.58/-1.15	0.938/-0.759
Flack parameter	0.059(10)	0.034(7)	0.059(12)	0.081(9)

[a] $R_1 = \Sigma||F_o| - |F_c||/|F_o|$. [b] Values in parentheses for reflections with $I>2\sigma(I)$. [c] $wR_2 = \{\Sigma[w(F^2_o - F^2_c)^2] / \Sigma[w(F^2_o)^2]\}^{½}$ and $w = 1/[\sigma^2(F^2_o) + (aP)^2 + (bP)]$, where $P = (2F^2_c + F^2_o)/3$.

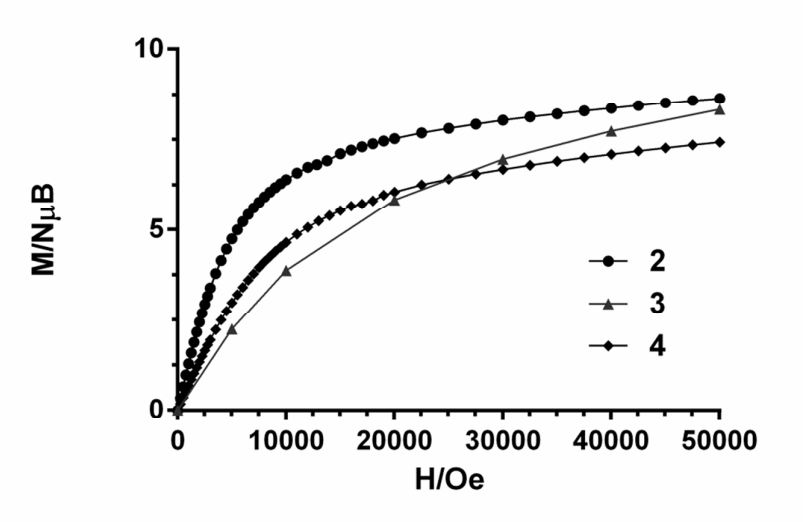

Figure S8. Field dependence of the magnetization at 2K for complexes **2**-**4**.

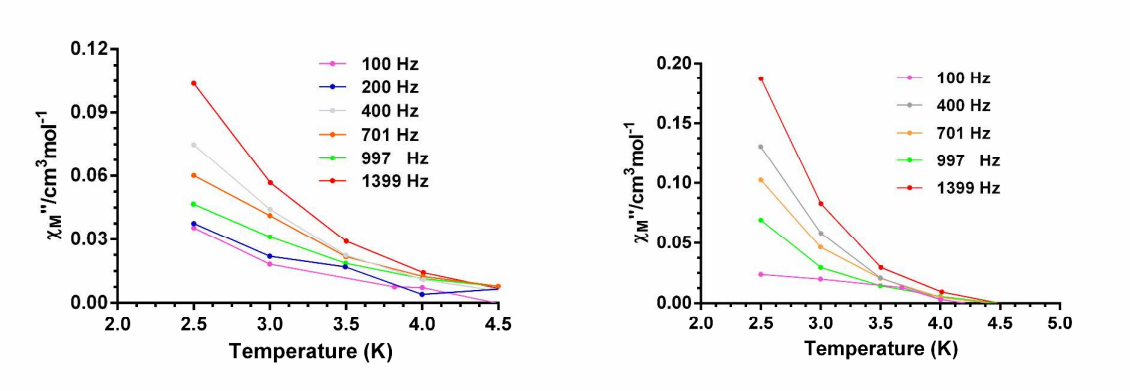

Figure S9. Temperature dependence of the out-of-phase χ''_M component of the ac susceptibility for complex **2**(left) and **4** (right) measured under 1000 Oe applied dc field.

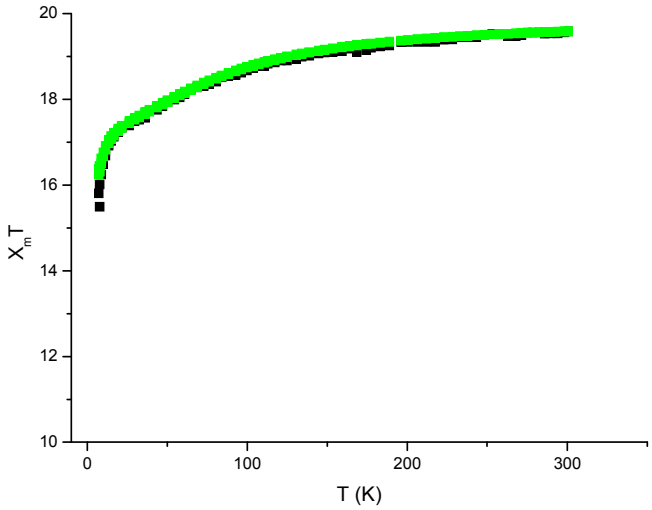

Figure S10. Experimental (black) and *ab initio* calculated (green) temperature dependence of $\chi_M T$ for compound **2**.

Table S9. Topological parameters at BCPs in the Mn^{III}-Gd^{III} complexes with different Mn-O-Gd-O and Md-O-Gd angles. All parameters are in a.u. ρ(r) in units of $eÅ^{-3}$, G(r), V(r), H(r) in units of a.u.

		Gd–OPh bonds							**Gd–OMe bonds**						
		ρ(r)	∇^2_ρ	H(r)	G(r)	ε	V(r)	|V(r)|/G(r)	ρ(r)	∇^2_ρ	H(r)	G(r)	ε	V(r)	|V(r)|/G(r)
Mn-O-Gd-O dihedral	0	0.0274	0.0198	-0.0111	0.0309	0.0893	0.0420	1.3592	0.0321	0.0272	-0.0153	0.0425	0.3922	0.0578	1.3600
	4.7	0.0274	0.0198	-0.0111	0.0308	0.0957	0.0419	1.3604	0.0318	0.0293	-0.0157	0.0450	0.4319	0.0606	1.3467
	8.4	0.0274	0.0198	-0.0110	0.0308	0.0997	0.0419	1.3604	0.0317	0.0308	-0.0162	0.0470	0.4860	0.0633	1.3468
	11.2	0.0274	0.0198	-0.0110	0.0308	0.1004	0.0419	1.3604	0.0319	0.0315	-0.0169	0.0483	0.5411	0.0652	1.3499
	15.7	0.0273	0.0199	-0.0110	0.0309	0.0966	0.0419	1.3560	0.0324	0.0317	-0.0183	0.0500	0.6498	0.0683	1.3660
	19.7	0.0272	0.0200	-0.0110	0.0310	0.0887	0.0420	1.3548	0.0330	0.0312	-0.0199	0.0512	0.7480	0.0711	1.3887
	23.7	0.0273	0.0201	-0.0110	0.0311	0.0780	0.0420	1.3505	0.0337	0.0303	-0.0217	0.0520	0.8281	0.0737	1.4173
Mn-O-Gd angle	104.1	0.0249	0.0174	-0.0094	0.0267	0.0928	0.0363	1.3596	0.0287	0.0295	-0.0144	0.0440	0.7001	0.0584	1.3273
	107.2	0.0274	0.0198	-0.0110	0.0308	0.1004	0.0419	1.3604	0.0319	0.0315	-0.0169	0.0483	0.5411	0.0652	1.3499
	110.7	0.0306	0.0231	-0.0134	0.0364	0.1077	0.0498	1.3681	0.0346	0.0530	-0.0200	0.0553	0.5698	0.0753	1.3617
	114.6	0.0337	0.0266	-0.0159	0.0424	0.1081	0..0583	1.375	0.0385	0.0394	-0.0250	0.0644	0.5952	0.0894	1.3882
	119.0	0.0373	0.0313	-0.0190	0.0503	0.1245	0.0694	1.3797	0.0432	0.0426	-0.0309	0.0736	0.5784	0.1045	1.4198
		Mn–OPh bonds							**Mn–OMe bonds**						
		ρ(r)	∇^2_ρ	H(r)	G(r)	ε	V(r)	|V(r)|/G(r)	ρ(r)	∇^2_ρ	H(r)	G(r)	ε	V(r)	|V(r)|/G(r)
Mn-O-Gd-O dihedral	0	0.0934	0.1264	-0.0133	0.1397	0.0233	0.1530	1.0952	0.1093	0.1301	-0.0218	0.1519	0.0714	0.1737	1.1435
	4.7	0.0934	0.1262	-0.0133	0.1395	0.0264	0.1529	1.0961	0.1069	0.1283	-0.0207	0.1490	0.0603	0.1698	1.1396
	8.4	0.0935	0.1260	-0.0134	0.1394	0.0295	0.1527	1.0954	0.1033	0.1220	-0.0198	0.1418	0.0544	0.1617	1.1403
	11.2	0.0935	0.1258	-0.0134	0.1392	0.0319	0.1526	1.0963	0.0997	0.1147	-0.0192	0.1339	0.0563	0.1531	1.1434
	15.7	0.0936	0.1254	-0.0135	0.1389	0.0358	0.1523	1.0965	0.0927	0.0998	-0.0184	0.1182	0.0669	0.1365	1.1548
	19.7	0.0937	0.1250	-0.0135	0.1385	0.0392	0.1520	1.0975	0.0855	0.0852	-0.0175	0.1027	0.0757	0.1202	1.1704
	23.7	0.0938	0.1245	-0.0135	0.1380	0.0424	0.1515	1.0978	0.0776	0.0711	-0.0162	0.0874	0.0793	0.1036	1.1854
Mn-O-Gd angle	104.1	0.0834	0.1084	-0.0112	0.1197	0.0273	0.1309	1.0936	0.0891	0.0969	-0.0168	0.1137	0.0616	0.1305	1.1478
	107.2	0.0935	0.1258	-0.0134	0.1392	0.0319	0.1526	1.0963	0.0997	0.1147	-0.0192	0.1339	0.0563	0.1531	1.1434
	110.7	0.1075	0.1502	-0.0169	0.1671	0.0427	0.1840	1.1011	0.1089	0.1320	-0.0214	0.1534	0.0589	0.1749	1.1402
	114.6	0.1218	0.1749	-0.0216	0.1965	0.0556	0.2180	1.1094	0.1222	0.1558	-0.0256	0.1814	0.0688	0.2069	1.1406
	119.0	0.1395	0.2054	-0.0290	0.2344	0.0710	0.2634	1.1237	0.1368	0.1821	-0.0312	0.2133	0.0777	0.2445	1.1463