Electronic Supplementary Material (ESI) for Dalton Trans.

Dodecanuclear Mn^{II}–Gd^{III} metallomacrocycles: magnetic and refrigerant response

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1 – Characterization.

2 – Structural aspects.

3 – Magnetic data.

1 – Characterization.

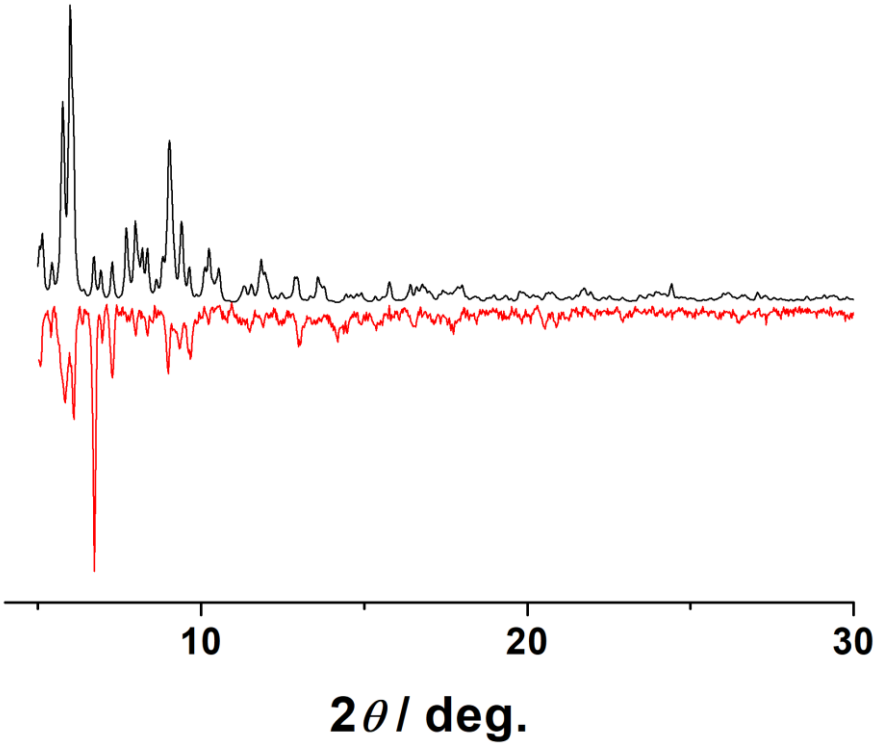

Fig. S1. Calculated (black line) PRXD spectrum and experimental (red line) for complex **1**

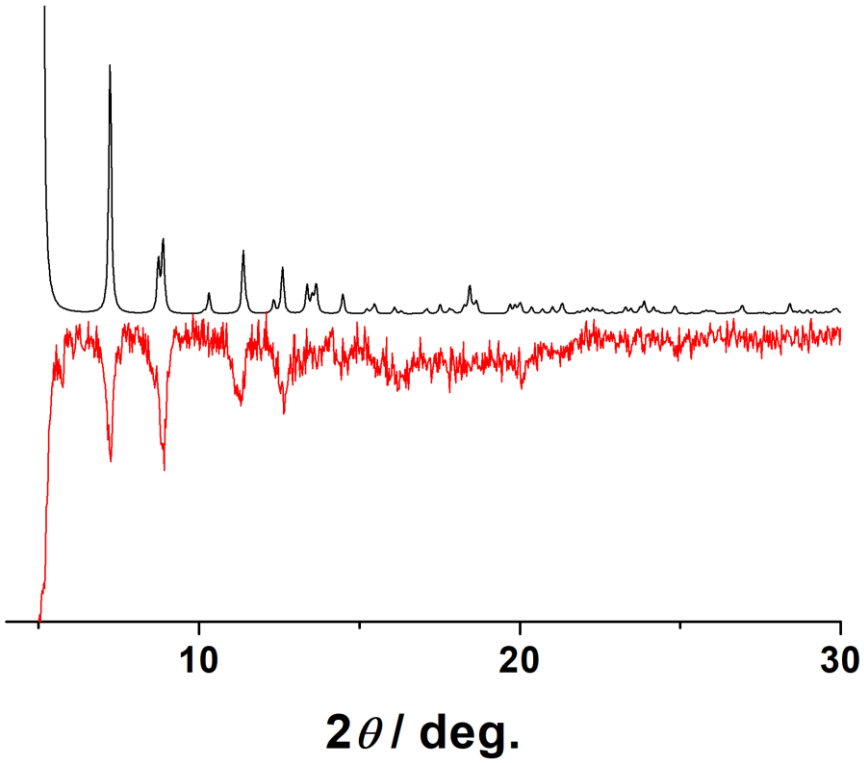

Fig. S2. Calculated (black line) PRXD spectrum and experimental (red line) for complex **2**.

Table S1. PRXD peak position for complexes **1** and **2** in the low 2θ range.

Complex 1			**Complex 2**	
2θ (calculated)	**2θ (experimental)**		**2θ (calculated)**	**2θ (experimental)**
5.14	5.08		5.06	5.02
5.42	5.39		7.22	7.15
5.76	5.84		8.88	8.91
5.98	6.07		10.30	10.30
6.72	6.73		11.38	11.30
6.94	6.97		12.32	12.38
7.28	7.28		12.60	12.64
8.00	7.99			
8.36	8.36			
8.62	8.52			
9.02	8.99			
9.40	9.33			
9.64	9.67			
10.24	10.22			

Table S2. Crystallographic data for compounds **1** and **2**

	1	**2**
Form.	$C_{340}H_{424}Gd_{18}Mn_{18}N_{104}O_{232}$	$C_{144}H_{132}Gd_{6}Mn_{6}N_{36}O_{78}$
Mr	13499.23	4887.99
System	Triclinic	Trigonal
Space group	P -1	R -3
a [Å]	21.8814(10)	34.2922(12)
b [Å]	22.2623(9)	34.2922(12)
c [Å]	35.8239(17)	21.5263(13)
α [°]	97.262(2)	90
β [°]	104.428(2)	90
γ [°]	90.817(2)	120
V [Å^3]	16745.9 (13)	21923(2)
Z	1	3
T [K]	100(2)	293
λ(Mo-Kα) [Å]	0.71073	0.71073
$\rho_{calcd.}$ [gcm^{-3}]	1.339	1.111
μ [mm^{-1}]	2.159	1.654
Θ range [deg.]	1.71-30.67	1.67-26.44
Data / restraints / parameters	103058 / 24 / 3243	10024 / 4 / 372
Reflections I>2σ(I)	78595	6267
R	0.0540	0.0864
wR^2	0.1328	0.2241

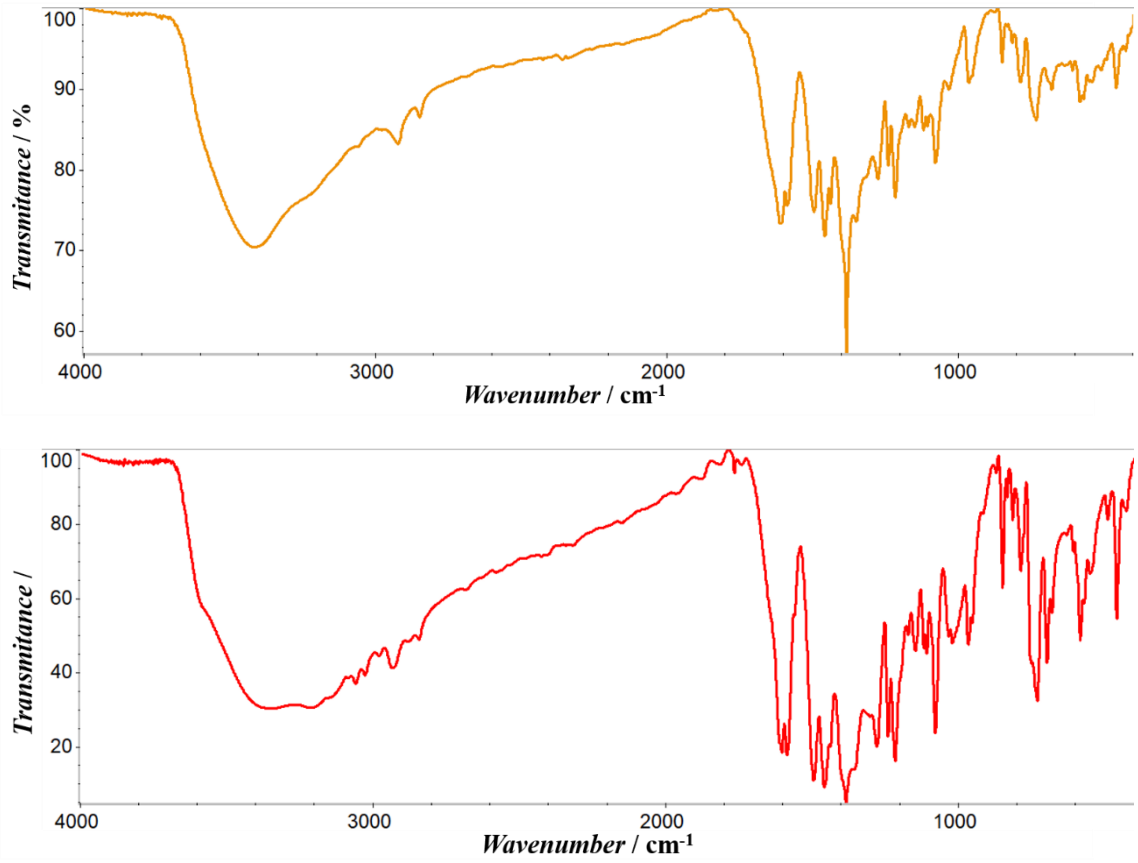

Fig. S3. IR spectra for complexes **1** (top) and **2** (bottom). Characteristic bands: st. O-H benzoyl alcohol (shoulder) 3600 cm^{-1}, st. O-H 3400 cm^{-1}, st. C-H 3000-2800 cm^{-1}; N=C iminic ~1600 cm^{-1}; O=C carbonyl ~1600 cm^{-1}; st. NO_3^- 1390 cm^{-1}. Strong set of H-bonds is reflected in the shape of the spectrum of **2** as broad absorptions between 2800-2000 cm^{-1}.

Table S3. CNH analytical results, calc/found%.

	C	N	H
(1)*	29.39/29.7%	11.02/10.8%	3.13/3.2%
(2)**	35.34/35.6%	10.30/10.0%	2.84/2.97%

*Vacuum dried

** Elemental analysis on powdered samples gave problems due to the very large number of solvent molecules present in **2** (see structural description), lost during the preparation the sample. Measurements on powdered samples, dried in desiccator for 48 h yield a value close to **2**·6BzOH that is clearly low taking into account the available space in the unit cell. The weight loss on crystals, obtained from the thermogravimetric measurement, maintained under benzoyl alcohol atmosphere just to prepare the sample holder yield a ~ **2**·15BzOH which is consistent either with the network available space and the $\chi_M T$ room temperature value assuming a M.W. of 5850 $g \cdot mol^{-1}$.

2 – Structural Aspects.

Table S4. Selected bond lengths (Å) for compound **1** ("A" labelled molecule).

Mn(1)A-N(10)A	2.184(4)	Mn(2)A-N(2)A	2.196(4)
Mn(1)A-N(12)A	2.266(4)	Mn(2)A-N(4)A	2.294(5)
Mn(1')A-O(1)A	2.339(4)	Mn(2)A-O(4)A	2.156(3)
Mn(1)A-O(2)A	2.199(3)	Mn(2)A-O(6)A	2.379(3)
Mn(1)A-O(14)A	2.133(4)	Mn(2)A-O(7)A	2.204(3)
Mn(1)A-O(18)	2.182(12)	Mn(2)A-O(21)A	2.109(5)
Mn(1)A-O(19)	2.245(11)		
		Gd(2)A-N(5)A	2.524(4)
Mn(3)A-N(6)A	2.196(4)	Gd(2)A-O(4)A	2.311(3)
Mn(3)A-N(8)A	2.270(4)	Gd(2)A-O(5)A	2.561(3)
Mn(3)A-O(9)A	2.142(3)	Gd(2)A-O(7)A	2.313(3)
Mn(3)A-O(11)A	2.356(3)	Gd(2)A-O(8)A	2.286(3)
Mn(3)A-O(12)A	2.202(3)	Gd(2)A-O(22)A	2.597(3)
Mn(3)A-O(26)A	2.147(6)	Gd(2)A-O(23)A	2.499(4)
		Gd(2)A-O(25)A	2.431(3)
Gd(1)A-N(1)A	2.536(4)	Gd(2)A-O(35)A	2.451(4)
Gd(1)A-O(2)A	2.318(3)		
Gd(1)A-O(3)A	2.294(4)	Gd(3)A-N(9)A	2.528(4)
Gd(1)A-O(14')A	2.300(4)	Gd(3)A-O(9)A	2.313(3)
Gd(1)A-O(15')A	2.575(5)	Gd(3)A-O(10)A	2.581(4)
Gd(1)A-O(16)A	2.476(5)	Gd(3)A-O(12)A	2.316(3)
Gd(1)A-O(17)A	2.583(4)	Gd(3)A-O(13)A	2.280(3)
Gd(1)A-O(19)A	2.427(4)	Gd(3)A-O(27)A	2.571(3)
Gd(1)A-O(20)A	2.431(5)	Gd(3)A-O(28)A	2.504(4)
		Gd(3)A-O(30)A	2.456(3)
		Gd(3)A-O(31)A	2.408(5)

Table S5. Selected bond and torsion angles (º) for compound **1** ("A" labelled molecule).

Mn(1)A-O(2)A-Gd(1)A	100.31(12)	N(1)A-Gd(1)A-O(3)A	64.73(13)
Mn(1)A-O(14)A-Gd(1)A	102.89(14)	O(2)A-Gd(1)A-O(14)A	73.12(12)
Mn(2)A-O(4)A-Gd(2)A	101.66(12)	N(5)A-Gd(2)'A-O(8)A	65.11(11)
Mn(2)A-O(7)A-Gd(2)A	100.16(12)	O(4)A-Gd(2)A-O(7)A	73.94(11)
Mn(3)A-O(9)A-Gd(3)A	102.76(13)	N(9)A-Gd(3)A-O(13)A	65.41(11)
Mn(3)A-O(12)A-Gd(3)A	100.82(12)	O(9)A-Gd(3)A-O(12)A	72.60(11)
O(2)A-Mn(1)A-O(14)A	78.82(13)	Gd(1)A-O(2)A-O(14)A-Mn(1)A	159.0(2)
O(4)A-Mn(2)A-O(7)A	79.23(12)	Gd(2)A-O(4)A-O(7)A-Mn(2)A	158.5(2)
O(9)A-Mn(3)A-O(12)A	78.21(12)	Gd(3)A-O(9)A-O(12)A-Mn(3)A	157.5(1)
Mn(1)A-N(12)A-N(11)A	111.5(3)	Gd(1)A-N(1)A-N(2)A-Mn(2)A	163.7(3)
Mn(2)A-N(2)A-N(1)A	132.2(3)	Gd(2)A-N(5)A-N(6)A-Mn(3)A	164.4(2)
Mn(3)A-N(8)A-N(7)A	112.8(3)	Gd(3)A-N(9)A-N(10)A-Mn(1)A	168.0(2)
Gd(1)A-N(1)A-N(2)A	115.8(3)	Mn(1)A-N(10)A-N(9)A	132.4(3)
Gd(2)A-N(5)A-N(6)A	115.6(2)	Mn(2)A-N(4)A-N(3)A	110.0(3)
Gd(3)A-N(9)A-N(10)A	115.8(2)	Mn(3)A-N(6)A-N(5)A	131.9(3)

Table S6. BVS calculations for complexes **1** and **2** (manganese cations).

	Mn^{2+}	Mn^{3+}
	Complex 1	
Mn(1)	**1.889**	1.767
Mn(2)	**1.974**	1.845
Mn(3)	**1.970**	1.841
	Complex 2	
Mn(1)	**1.746**	1.634

Table S7. SHAPE measures for the Mn^{II} cations of complex **1**. *S*(*P*) = 0 corresponds to a structure fully coincident in shape with the reference polyhedron P, regardless of size and orientation. The closest polyhedron is highlighted in red.

Mn^{II}1		**Mn^{II}2**		**Mn^{II}3**	
S(HP-6)	23.52	*S*(HP-6)	31.40	*S*(HP-6)	31.38
S(PPY-6)	9.05	*S*(PPY-6)	6.37	*S*(PPY-6)	6.85
S(OC-6)	12.23	*S*(OC-6)	16.66	*S*(OC-6)	16.63
***S*(TPR-6)**	**5.30**	***S*(TPR-6)**	**4.26**	***S*(TPR-6)**	**4.23**
S(JPPY-6)	11.85	*S*(JPPY-6)	9.20	*S*(JPPY-6)	9.50

Ideal ML_6 polyhedra**:** HP-6 (D6h) Hexagon; PPY-6 (C5v) Pentagonal pyramid; OC-6 (Oh) Octahedron; **TPR-6 (D3h) Trigonal prism**; JPPY-6 (C5v) Johnson pentagonal pyramid J2

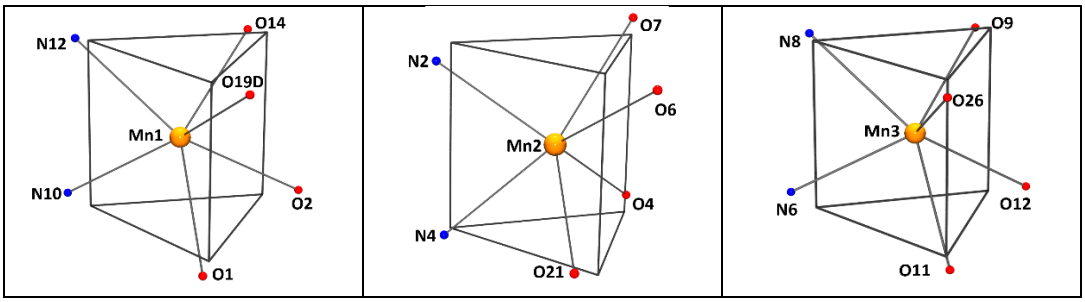

Fig. S4. Plot of the coordination sphere of the non-equivalent Mn^{II} cations and the closest polyhedra for complex **1**.

Table S8. SHAPE measures for the Gd^{III} cations of complex **1**. *S*(*P*) = 0 corresponds to a structure fully coincident in shape with the reference polyhedron P, regardless of size and orientation. The closest polyhedron is highlighted in red.

Gd^{II}1		**Gd^{II}2**		**Gd^{II}3**	
S(EP-9)	32.98	*S*(EP-9)	33.11	*S*(EP-9)	33.49
S(OPY-9)	22.49	*S*(OPY-9)	23.06	*S*(OPY-9)	22.97
S(HBPY-9)	15.80	*S*(HBPY-9)	16.02	*S*(HBPY-9)	15.81
S(JTC-9)	14.07	*S*(JTC-9)	14.86	*S*(JTC-9)	14.89
S(JCCU-9)	7.58	*S*(JCCU-9)	8.44	*S*(JCCU-9)	7.80
S(CCU-9)	6.44	*S*(CCU-9)	7.22	*S*(CCU-9)	3.01
S(JCSAPR-9)	3.01	*S*(JCSAPR-9)	3.00	*S*(JCSAPR-9)	6.62
S(CSAPR-9)	2.26	*S*(CSAPR-9)	2.15	*S*(CSAPR-9)	2.22
S(JTCTPR-9)	2.38	*S*(JTCTPR-9)	2.33	*S*(JTCTPR-9)	2.41
S(TCTPR-9)	2.36	*S*(TCTPR-9)	2.16	*S*(TCTPR-9)	2.20
S(JTDIC-9)	12.82	*S*(JTDIC-9)	13.04	*S*(JTDIC-9)	12.96
S(HH-9)	8.16	*S*(HH-9)	8.86	*S*(HH-9)	8.61
***S*(MFF-9)**	**1.67**	***S*(MFF-9)**	**1.97**	***S*(MFF-9)**	**1.74**

Ideal ML_9 polyhedra: EP-9 (D9h) Enneagon; OPY-9 (C8v) Octagonal pyramid; HBPY-9 (D7h) Heptagonal bipyramid; JTC-9 (C3v) Johnson triangular cupola J3; JCCU-9 (C4v) Capped cube J8; CCU-9 (C4v) Spherical-relaxed capped cube; JCSAPR-9 (C4v) Capped square antiprism J10; CSAPR-9 (C4v) Spherical capped square antiprism; JTCTPR-9 (D3h) Tricapped trigonal prism J51; TCTPR-9 (D3h) Spherical tricapped trigonal prism; JTDIC-9 (C3v) Tridiminished icosahedron J63; HH-9 (C2v) Hula-hoop; **MFF-9 (Cs) Muffin**

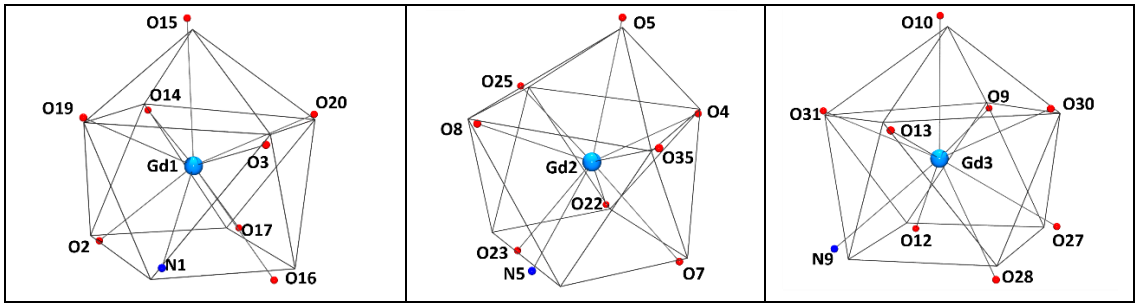

Fig. S5. Plot of the coordination sphere of the non-equivalent Gd^{III} cations and the closest polyhedra for complex **1**.

Table S9. Selected bond lengths (Å) for compound **2**.

Atom	**Distance [Å]**		
Mn(1)-N(1)	2.296(8)	Gd(1)-N(4')	2.512(7)
Mn(1)-N(3)	2.201(9)	Gd(1)-O(1)	2.589(7)
Mn(1)-O(2)	2.156(6)	Gd(1)-O(2)	2.298(8)
Mn(1)-O(4')	2.205(6)	Gd(1)-O(3')	2.279(8)
Mn(1)-O(5')	2.331(6)	Gd(1)-O(4')	2.312(6)
Mn(1)-O(11)	2.368(13)	Gd(1)-O(6)	2.439(10)
Mn(1)-O(13)	2.518(11)	Gd(1)-O(7)	2.482(8)
		Gd(1)-O(8)	2.579(8)
		Gd(1)-O(9)	2.500(9)

Table S10. Selected bond and torsion angles angles (º) for compound **2**.

Atom	Angle [º]		
Mn(1)-O(2)-Gd(1)	102.8(6)	N(4')-Gd(1)-O(3')	65.7(2)
Mn(1')-O(4)-Gd(1')	100.9(2)	N(4')-Gd(1)-O(4')	74.7(2)
N(1)-Mn(1)-N(3)	70.1(3)	O(1)-Gd(1)-O(2)	63.3(3)
N(1)-Mn(1)-O(2)	76.9(3)	O(2)-Gd(1)-O(4')	74.2(2)
O(2)-Mn(1)-O(4')	79.3(2)	Mn(1)-N(1)-N(2)	110.4(5)
O(4')-Mn(1)-O(5')	70.1(2)	Gd(1')-N(4)-N(3)	116.2(5)
Mn(1)-O(2)-O(4)-Gd(1)	164.1(4)	Mn(1)-N(3)-N(4)-Gd(1')	166.8(5)

Table S11. SHAPE measures for the Mn^{II} cation of complex **2**. *S*(*P*) = 0 corresponds to a structure fully coincident in shape with the reference polyhedron P, regardless of size and orientation. The closest polyhedron is highlighted in red.

Mn^{II}1	
S(HP-7)	34.77
S(HPY-7)	18.77
S(PBPY-7)	8.01
***S*(COC-7)**	**3.55**
S(CTPR-6)	3.80
S(JPBPY-6)	12.21
S(JETPY-6)	14.61

Ideal ML_7 polyhedra**:** HP-7 (D7h) Heptagon; HPY-7 (C6v) Hexagonal pyramid; PBPY-7 (D5h) Pentagonal bipyramid; **COC-7 (C3v) Capped octahedron**; CTPR-7 (C2v) Capped trigonal prism; JPBPY-7 (D5h) Johnson pentagonal bipyramid J13; JETPY-7 (C3v) Johnson elongated triangular pyramid J7.

Table S12. SHAPE measures for the Gd^{III} cation of complex **2**. *S*(*P*) = 0 corresponds to a structure fully coincident in shape with the reference polyhedron P, regardless of size and orientation. The closest polyhedron is highlighted in red.

Gd^{III}1	
S(EP-9)	33.80
S(OPY-9)	22.53
S(HBPY-9)	16.99
S(JTC-9)	14.81
S(JCCU-9)	8.40
S(CCU-9)	7.18
S(JCSAPR-9)	2.72
S(CSAPR-9)	1.94
S(JTCTPR-9)	2.22
S(TCTPR-9)	1.93
S(JTDIC-9)	12.87
S(HH-9)	8.97
***S*(MFF-9)**	**1.58**

Ideal ML_9 polyhedra**:** EP-9 (D9h) Enneagon; OPY-9 (C8v) Octagonal pyramid; HBPY-9 (D7h) Heptagonal bipyramid; JTC-9 (C3v) Johnson triangular cupola J3; JCCU-9 (C4v) Capped cube J8; CCU-9 (C4v) Spherical-relaxed capped cube; JCSAPR-9 (C4v) Capped square antiprism J10; CSAPR-9 (C4v) Spherical capped square antiprism; JTCTPR-9 (D3h) Tricapped trigonal prism J51; TCTPR-9 (D3h) Spherical tricapped trigonal prism; JTDIC-9 (C3v) Tridiminished icosahedron J63; HH-9 (C2v) Hula-hoop; **MFF-9 (Cs) Muffin**

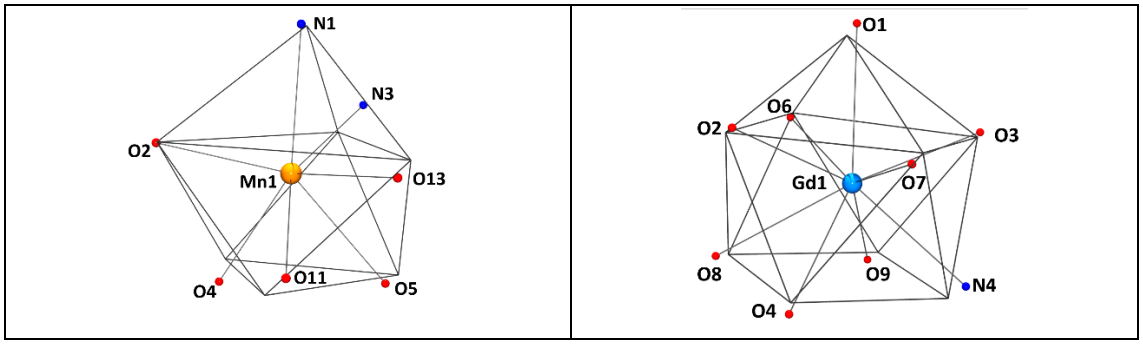

Fig. S6. Plot of the coordination sphere of the Mn^{II} and Gd^{III} cations in the asymmetric unit and the closest polyhedron for complex **2.**

3 – Magnetic Data.

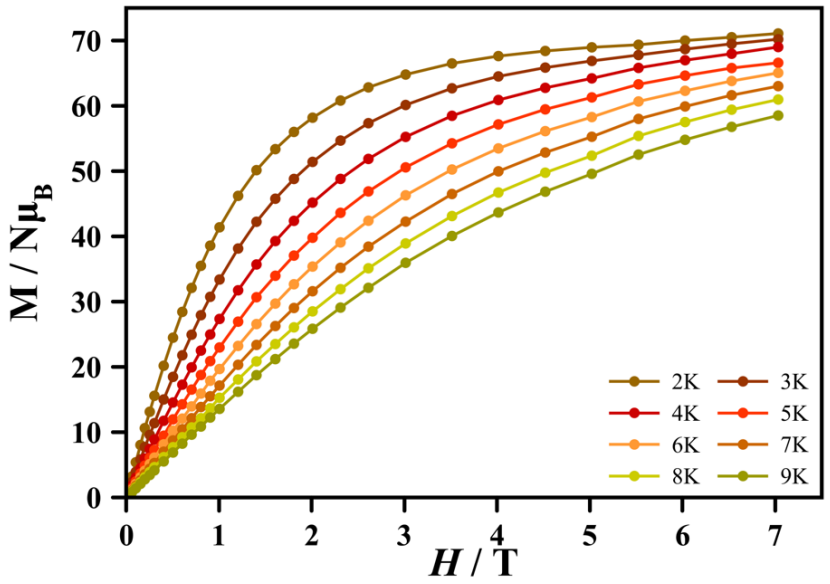

Fig. S7. Magnetization measurements from 0 to 7 T in the 2-9 K interval for complex **1**.

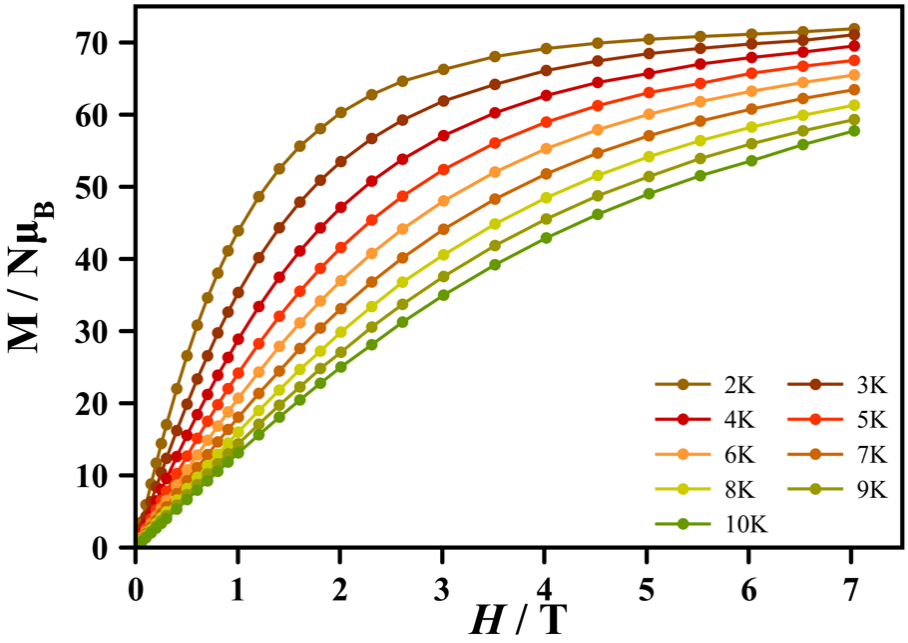

Fig. S8. Magnetization measurements from 0 to 7 T in the 2-10 K interval for complex **2**