Electronic Supplementary Material (ESI) for Dalton Transactions. This journal is © The Royal Society of Chemistry 2022

SUPPORTING INFORMATION

Magneto-thermal properties and slow magnetic relaxation in Mn(II)Ln(III) complexes: Influence of magnetic coupling on the magneto-caloric effect.

Itziar Oyarzabal, Andoni Zabala-Lekuona, Antonio J. Mota, María A. Palacios, Antonio Rodríguez-Diéguez, Giulia Lorusso, Marco Evangelisti, Corina Rodríguez-Esteban, Euan K. Brechin, José M. Seco and Enrique Colacio



Fig. S1.- For complex **8**, simulated pattern from single-crystal X-ray diffraction (orange line) and experimental PXRD recorded in mother liquor (black line).



Fig. S2.- For complex **8**, experimental PXRD recorded in mother liquor (black line) and at different t values once removed from solution (red, green and blue lines).



Fig. S3.- Experimental PXRD for compounds **8** (blue line) and **9** (purple line) once dried indicating a complete dehydration of the samples followed by a complete phase transformation.



Fig. S4.- Thermogravimetric analysis (TGA) of complex **8** 48 h after filtering the crystals.



Fig. S5.- Perspective view of the molecular structure of complexes **1** and **2**. Hydrogen atoms are omitted for the sake of clarity. Colour code: N = blue, O = red, C = gray, Br = brown, Mn = orange, Ln = pink.



Fig. S6.- A perspective view of the structure of 1 together with intermolecular (blue dotted lines) hydrogen bonds.



Fig. S7.- Perspective view of the molecular structure of complex 3. Hydrogen atoms are omitted for the sake of clarity. Colour code: N = blue, O = red, C = gray, Mn = orange, Dy = pink.



Fig. S8.- A perspective view of the structure of 3 together with intermolecular (blue dotted lines) hydrogen bonds.



Fig. S9.- Perspective view of the molecular structure of complexes 4 and 5. Hydrogen atoms are omitted for the sake of clarity. Colour code: N = blue, O = red, C = gray, Mn = orange, Ln = pink.



Fig. S10.- Perspective view of the molecular structure of complexes 6 and 7. Hydrogen atoms and solvent molecules are omitted for the sake of clarity. Colour code: N = blue, O = red, C = gray, Mn = orange, Ln = pink.



Fig. S11.- Perspective view of the molecular structure of complexes 8 and 9. Hydrogen atoms and solvent molecules are omitted for the sake of clarity. Colour code: N = blue, O = red, C = gray, Mn = orange, Ln = pink.



Fig. S12.- Temperature dependence of the $\chi_M T$ product and field dependence of the magnetization at 2 K (inset) for **2** (top), **3** (middle) and **5** (bottom). Red and blue lines represent the best fits using the Hamiltonians in Equation 4 and 5, respectively.



Fig. S13.- Temperature dependence of the $\chi_M T$ product and field dependence of the magnetization at 2 K (inset) for 7 (top) and 9 (bottom). Red and blue lines represent the best fits using the Hamiltonians in Equation 4 and 5, respectively.



Fig. S14.- Temperature dependence of the $\chi_{\rm M}T$ product and the difference $\Delta \chi_{\rm M}T = \chi_{\rm M}T_{\rm (MnDy)} - \chi_{\rm M}T_{\rm (ZnDy)}$ for complex **2**.



Fig. S15.- Schematic view of the model compound.



Fig. S16.- Scatter plot of experimental J (black circles) vs. the mean Mn-O-Gd angle (θ) for complexes prepared from ligands H₂L¹ and H₂L². The open circles represent the values obtained from DFT calculations. The solid line represents the linear fitting of the experimental values.



Fig. S17.- Isothermal field dependent curves for 1 between 2 and 7 K (top) and magnetic entropy changes (bottom) simulated with J = -0.82 cm⁻¹ and g = 2.00 between 2 and 7 K (solid lines) and extracted from the experimental magnetization data with the Maxwell equation between 1 to 7 T and temperatures from 3 to 6 K (points).



Fig. S18.- Isothermal field dependent curves for 4 between 2 and 7 K (top) and magnetic entropy changes (bottom) simulated with J = -0.08 cm⁻¹ and g = 2.00 between 2 and 7 K (solid lines) and extracted from the experimental magnetization data with the Maxwell equation between 1 to 7 T and temperatures from 3 to 6 K (points).



Fig. S19.- Isothermal field dependent curves for 6 between 2 and 7 K (top) and magnetic entropy changes (bottom) simulated with J = -0.16 cm⁻¹ and g = 2.03 between 2 and 7 K (solid lines) and extracted from the experimental magnetization data with the Maxwell equation between 1 to 7 T and temperatures from 3 to 6 K (points).



Fig. S20.- Temperature dependence of in-phase $\chi_{M'}$ (left) and out-of phase $\chi_{M''}$ (right) components of the *alternating current* (*ac*) susceptibility for complex **3** under zero *dc* applied field.



Fig. S21.- Temperature dependence of in-phase χ_M' (inset) and out-of phase χ_M''
components of the *alternating current* (*ac*) susceptibility for complexes 2 (a), 5 (b), 7
(c) and 9 (d) under an applied field of 1000 Oe.

Complex	1	2	3	4
Formula	$C_{24}H_{28}Br_2GdMnN_5O_{13}$	C24H28Br2DyMnN5O13	C26H41DyMnN6O14	C27H40GdMnN5O12
M_r	966.52	971.77	879.09	838.83
Crystal system	Monoclinic	Monoclinic	Monoclinic	Monoclinic
Space group (no.)	$P2_{1}/n$ (14)	$P2_{1}/n$ (14)	$P2_{1}/n$ (14)	$P2_{1}/n$ (14)
<i>a</i> (Å)	13.5996(4)	13.5722(2)	12.7783(8)	11.3864(7)
<i>b</i> (Å)	15.0087(4)	14.9625(2)	16.8706(11)	14.6689(7)
<i>c</i> (Å)	15.7090(5)	15.7042(2)	15.5190(10)	20.13390(10)
<i>a</i> (°)	90	90	90	90
eta (°)	90.7330(10)	90.4760(10)	92.7364(12)	101.147(2)
γ (°)	90	90	90	90
$V(Å^3)$	3206.14(16)	3189.01(8)	3341.7(4)	3299.4(3)
Ζ	4	4	4	4
$D_c (\mathrm{g \ cm^{-3}})$	2.002	2.024	1.747	1.689
μ (MoKa) (mm ⁻¹)	5.007	5.297	2.671	2.442
Т (К)	100(2)	100(2)	100(2)	100(2)
Observed reflections	7727 (6641)	6600 (5979)	5872 (4936)	8425 (6097)
Rint	0.0477	0.0362	0.0414	0.0515
Parameters	422	422	445	421
GOF	1.057	1.059	1.035	1.030
$R_{l}^{a,b}$	0.0328 (0.0246)	0.0287 (0.0244)	0.0443 (0.0343)	0.0859 (0.0531)
wR_2^c	0.0617 (0.0585)	0.0572 (0.0550)	0.0779 (0.0732)	0.1166 (0.1047)
Largest difference in peak and hole (e Å ⁻³)	1.085 and -1.597	0.897 and -0.976	1.262 and -0.627	4.555 and -1.614

 Table S1.- Crystallographic data.

^a $R_I = S||F_o| - |F_c||/S|F_o|$. ^b Values in parentheses for reflections with I > 2s(I). ^c $wR_2 = \{S[w(F_o^2 - F_c^2)^2] / S[w(F_o^2)^2]\}^{\frac{1}{2}}$

Complex	5	6	7	8	9
Formula	C ₂₇ H ₄₀ DyMnN ₅ O ₁₂	C44H52GdMnN7O12	C44H52DyMnN7O12	$C_{56}H_{94}Gd_2Mn_2N_8O_{26}$	C56H90Dy2Mn2N8O24
M_r	844.08	1083.11	1088.36	1719.77	1694.23
Crystal system	Monoclinic	Monoclinic	Monoclinic	Triclinic	Triclinic
Space group (no.)	$P2_{1}/n$ (14)	$P2_{1}/n$ (14)	$P2_{1}/n$ (14)	<i>P-1</i> (2)	<i>P-1</i> (2)
<i>a</i> (Å)	11.3886(6)	13.4699(19)	13.4614(16)	11.079(5)	10.702(2)
b (Å)	14.6602(7)	23.620(3)	23.617(3)	12.456(5)	12.462(3)
<i>c</i> (Å)	20.2613(11)	14.908(2)	14.8845(18)	14.319(5)	14.270(3)
<i>a</i> (°)	90	90	90	111.133(5)	111.316(3)
β (°)	101.593(2)	102.7733(16)	102.6754(12)	105.343(5)	104.241(3)
γ (°)	90	90	90	98.898(5)	98.203(3)
$V(Å^3)$	3313.8(3)	4625.7(11)	4616.7(10)	1707.4(12)	1660.6(6)
Ζ	4	4	4	1	1
$D_c (\mathrm{g \ cm^{-3}})$	1.692	1.555	1.566	1.673	1.694
μ (MoKa) (mm ⁻¹) ^d	2.685	1.763	1.948	16.024	2.678
<i>T (</i> K)	100(2)	100(2)	100(2)	150.00(10)	100(2)
Observed reflections	8548 (6793)	8122 (7558)	8111 (7795)	6808 (5774)	5813 (4633)
Rint	0.0863	0.0246	0.0233	0.0634	0.0651
Parameters	421	595	595	433	426
GOF	1.025	1.037	1.051	1.015	0.998
$R_l^{a,b}$	0.0484 (0.0289)	0.0262 (0.0240)	0.0212 (0.0203)	0.0641 (0.0534)	0.0645 (0.0457)
wR_2^c	0.0592 (0.0551)	0.0600 (0.0585)	0.0511 (0.0505)	0.1411 (0.1320)	0.1052 (0.0975)
Largest difference in peak and hole (e Å ⁻³)	1.397 and -0.980	0.940 and -0.474	0.993 and -0.341	1.809 and -1.415	1.873 and -0.884

 Table S1.- Continuation.

^a $R_I = S||F_o| - |F_c||/S|F_o|$. ^b Values in parentheses for reflections with I > 2s(I). ^c $wR_2 = \{S[w(F_o^2 - F_c^2)^2] / S[w(F_o^2)^2]\}^{\frac{1}{2}}$

 $^{d}\mu(CuKa) \text{ (mm}^{-1}) \text{ for } 8.$

Complex	1	2
Ln(1)-Mn(1)	3.414(1)	3.400(1)
Ln(1)-O(1A)	2.384(2)	2.354(2)
Ln(1)-O(2A)	2.394(2)	2.373(2)
Ln(1)-O(3A)	2.389(2)	2.364(2)
Ln(1)-O(4A)	2.392(2)	2.367(2)
Ln(1)-O(2P)bridge	2.329(2)	2.295(2)
Ln(1)-O(1C)nitrate	2.525(2)	2.517(2)
Ln(1)-O(2C)nitrate	2.470(2)	2.442(2)
Ln(1)-O(1D)nitrate	2.505(2)	2.480(2)
Ln(1)-O(2D)nitrate	2.478(2)	2.447(2)
Mn(1)-N(1A)	2.224(2)	2.230(2)
Mn(1)-N(2A)	2.227(2)	2.220(2)
Mn(1)-O(2A)	2.139(2)	2.140(2)
Mn(1)-O(3A)	2.148(2)	2.144(2)
Mn(1)-O(1P)bridge	2.060(2)	2.053(2)
Ln(1)-O(2A)-Mn(1)	97.59(7)	97.64(8)
Ln(1)-O(3A)-Mn(1)	97.48(7)	97.80(8)
	71.00(())	
O(2A)-Ln(1)-O(3A)	71.09(6)	71.30(7)
O(2A)-Ln(1)- $O(2P)$ bridge	78.88(7)	79.58(8)
O(3A)-Ln(1)- $O(2P)$ bridge	79.87(7)	80.54(8)
O(2A)-Mn(1)-O(3A)	80.89(7)	80.25(8)
O(2A)-Mn(1)-O(1P)bridge	104.54(7)	103.85(9)
O(3A)-Mn(1)-O(1P)bridge	101.58(8)	101.13(9)

Table S2.- Selected bond lengths (Å) and angles (°).

	2		_	6		0	
Complex	3	4	5	6	7	8	9
Ln(1)- $Mn(1)$	3.661(1)	3.474(2)	3.462(1)	3.485(1)	3.466(1)	3.522(2)	3.498(1)
Ln(1)-Ln(1)						4.081(1)	4.063(1)
Ln(1)-O(1A)	2.556(3)	2.434(4)	2.421(2)	2.481(2)	2.461(2)	2.458(4)	2.437(4)
Ln(1)-O(2A)	2.312(3)	2.341(4)	2.329(2)	2.320(2)	2.290(2)	2.364(4)	2.331(4)
Ln(1)-O(3A)	2.291(3)	2.263(4)	2.236(2)	2.258(2)	2.231(2)	2.300(4)	2.266(4)
Ln(1)-O(4A)	2.611(3)	2.691(4)	2.723(2)	2.606(2)	2.601(2)	2.569(4)	2.567(4)
Ln(1)-O(1C)nitrate	2.464(3)	2.474(4)	2.445(2)	2.465(2)	2.433(2)	2.505(6)	2.485(5)
Ln(1)-O(2C)nitrate	2.468(3)	2.485(4)	2.460(2)	2.519(2)	2.497(2)	2.571(5)	2.528(4)
$I_{n}(1) O(1D)$ nitrate	2 187(3)	2 470(4)	2 156(2)	2,475(2)	2.440(2)		
Ln(1) - O(1D)intrate	2.467(3)	2.479(4)	2.430(2)	2.473(2)	2.440(2)		
Ln(1) - O(2D)intrate	2.472(3) 2.517(3)	2.497(4)	2.463(2)	2.307(2)	2.463(2)		
Ln(1) - O(1E) intrate	2.517(3) 2.517(3)						
Ln(1) O(2P)bridge	2.317(3)	2342(4)	2317(2)	2 366(2)	2344(2)	2 402(4)	2382(4)
Ln(1)-O(2P)bridge		2.342(4)	2.317(2)	2.300(2)	2.344(2)	2.402(4) 2.423(4)	2.382(4) 2.420(4)
Ln(1)-O(3P)bridge						2.412(4)	2.375(4)
Mn(1)-N(1A)	2.377(3)	2.317(4)	2.323(2)	2.273(2)	2.271(2)	2.340(5)	2.333(5)
Mn(1)-N(2A)	2.295(4)	2.305(5)	2.307(2)	2.333(2)	2.332(2)	2.354(5)	2.341(5)
Mn(1)-N(3A)	2.365(3)	2.334(4)	2.332(2)	2.353(2)	2.348(2)	2.365(5)	2.362(5)
Mn(1)-O(2A)	2.146(3)	2.213(3)	2.205(2)	2.206(2)	2.205(2)	2.215(4)	2.199(4)
Mn(1)-O(3A)	2.152(3)	2.128(3)	2.139(2)	2.110(2)	2.115(2)	2.175(4)	2.184(4)
Mn(1)-O(1M)	2.217(3)	. /		. /			~ ~
Mn(1)-O(1P)bridge		2.108(4)	2.112(2)	2.156(2)	2.156(2)	2.126(4)	2.117(4)

Table S2.- Continuation.

 Table S2.- Continuation.

Complex	3	4	5	6	7	8	9
Ln(1)-O(2A)-Mn(1)	110.36(11)	99.37(13)	99.53(7)	100.70(6)	100.89(5)	100.54(15)	101.06(15)
Ln(1)-O(3A)-Mn(1)	110.93(11)	104.51(15)	104.62(8)	105.80(6)	105.77(6)	103.80(17)	103.60(16)
Ln(1)-O(2P)-Ln(1)						115.52(15)	115.59(17)
O(2A)-Ln(1)-O(3A)	66.51(9)	72.45(12)	72.60(6)	71.77(5)	72.27(5)	73.95(14)	74.52(14)
O(2A)-Ln(1)-O(2P)bridge		78.91(13)	79.41(7)	77.99(5)	78.58(5)	75.18(14)	74.92(14)
O(2A)-Ln(1)-O(2P)bridge						137.32(14)	137.70(15)
O(3A)-Ln(1)-O(2P)bridge		80.14(13)	81.00(7)	79.45(6)	79.70(5)	74.41(15)	74.31(14)
O(3A)-Ln(1)-O(2P)bridge						106.34(14)	103.79(14)
O(2A)-Mn(1)-O(3A)	71.95(10)	77.62(13)	76.96(7)	76.86(6)	76.20(5)	79.43(15)	78.87(15)
O(2A)-Mn(1)-O(1P)bridge		91.68(14)	91.46(7)	91.84(6)	91.70(5)	93.71(16)	93.82(16)
O(3A)-Mn(1)-O(1P)bridge		95.61(15)	95.30(8)	93.42(6)	93.13(5)	89.36(16)	89.31(16)

Complex	PP-5	vOC-5	TBPY-5	SPY-5	JTBPY-5
1	31.455	3.183	3.590	0.731	6.531
2	31.297	3.272	3.616	0.806	6.521

Table S3.- Shape measures for MnN_2O_3 coordination environments in complexes 1 and

2.

*PP-5: pentagon (D_{5h}); vOC-5: vacant octahedron (C_{4v}); TBPY-5: trigonal bipyramid (D_{3h}); SPY-5: square pyramid (C_{4v}); JTBPY-5: Johnson trigonal bipyramid (D_{3h}).

Table S4.- Shape measures for MnN₃O₃ coordination environments in complexes 3-9.

Complex	HP-6	PPY-6	OC-6	TPR-6	JPPY-6
3	30.083	13.279	6.579	5.541	16.838
4	28.818	17.502	3.335	8.020	20.779
5	28.793	17.450	3.372	8.072	20.731
6	28.978	19.112	2.591	9.692	22.616
7	29.043	19.078	2.631	9.697	22.577
8	26.973	16.604	3.405	9.844	19.654
9	27.374	16.487	3.458	9.475	19.472

*HP-6: hexagon (D_{6h}); PPY-6: pentagonal pyramid (C_{5v}); OC-6: octahedron (O_h); TPR-6: trigonal prism (D_{3h}); JPPY-6: Johnson pentagonal pyramid J2 (C_{5v}).

Complex	JCSAPR-9	CSAPR-9	JTCTPR-9	TCTPR-9	MFF-9
1	2.088	1.324	3.058	1.750	1.550
2	1.942	1.243	2.980	1.740	1.501
4	3.904	2.682	4.225	3.014	2.527
5	3.776	2.561	3.974	2.909	2.405
6	3.062	2.107	4.949	2.987	1.773
7	2.882	1.954	4.755	2.866	1.670
8	3.921	3.255	5.047	3.914	2.499
9	3.928	3.062	4.792	3.689	2.231

 Table S5.- Shape measures for LnO9 coordination environments in complexes 1, 2 and

4-9.

*JCSAPR-9: capped square antiprism (C_{4v}); CSAPR-9: spherical capped square antiprism (C_{4v}); JTCTPR-9: tricapped trigonal prism (D_{3h}); TCTPR-9: (D_{3h}); spherical tricapped trigonal prism: MFF-9: muffin (C_s).

*Shape measures relative to other reference polyhedron are significantly larger.

Table S6.- Shape measures for LnO₁₀ coordination environments in complex 3.

Complex	JBCSAPR-10	JSPC-10	SDD-10	TD-10	HD-10
3	4.106	2.692	4.181	3.439	5.773

*JBCSAPR-10: bicapped square antiprism J17 (D_{4d}); JSPC-10: sphenocorona J87 (C_{2v}); SDD-10: staggered dodecahedron (D_2); TD-10: (C_{2v}); tetradecahedron: HD-10: hexadecahedron (D_{4h}).

*Shape measures relative to other reference polyhedron are significantly larger.

Table S7.- Best fitting parameters of the magnetic data of complexes 2, 3, 5 and 7.

	J>			$ LS\rangle$				
Compounds	2	3 ^b	5	7	2	3 ^b	5	7
$J_{\rm Mn(II)Dy(III)}(\rm cm^{-1})$	-0.84 (2)	1.46(3)	0.048(5)	0.16(1)	-0.90(1)	1.52(5)	0.046(3)	0.18(1)
$D_{\mathrm{Ln}} (\mathrm{cm}^{-1})$	5.25(3)	7.1(4)	14.1(3)	15.8(2)	39.0(9)	63(1)	120(1)	94(2)
$E_{\mathrm{Ln}}(\mathrm{cm}^{-1})$	0.4(1)	1.43(9)	1.32(7)	1.96(8)	1.45(1)	3.57(6)	3.4(1)	3.69(3)
g_{Ln}^{a}	1.33	1.33	1.33	1.35				
$g_{\mathrm{Mn}}{}^{\mathrm{a}}$	2.0	2.05	2.0	2.05	2.0	2.05	2.0	2.05
σ_{Ln}					0.999(1)	0.999(1)	0.998(1)	1.000(1)

^aThese values were fixed to the indicated values. ^b A mean field intermolecular interaction of zJ = -0.002 cm⁻¹ was considered.

Table S8.- Maximum magnetic entropy change for Mn and Gd-based complexes found in the literature.

Complex	$-\Delta S_{\rm m} ({\rm JKg^{-1}K^{-1}}) (7 {\rm T})$	Dimensionality	<i>T</i> (K)	Ref.
Complex 8	36.4	0D	2.2	T.w.
$Gd_2Mn_2(\mu_3-OH)_2L^6(NO_3)_4]\cdot CH_3CN$	40.59	0D	2	31
$[GdMn_{0.5}(OAc)_4(H_2O)_2] \cdot 3H_2O$	38.7	1D	2.5	31
${[Gd_5Mn(L^7)_3(H_2O)_{10}(\mu_3-OH)_6](NO_3)_5 \cdot 13H_2O}_n$	38.3	3D	2	31
$[Mn(H_2O)_6][MnGd(oda)_3]_2 \cdot 6H_2O$	50.1	3D	1.8	31
$\{(H_3O)_3[Gd_3Mn_2(Trz)_4] \cdot 12H_2O\}_n$	40.3	3D	2	31
$\{[Gd_4Mn(L^7)_3(H_2O)_3(\mu_3\text{-}OH)_4(HCOO)_{1.5}]\cdot (NO_3)_{2.5}\cdot 6H_2O\}_n$	46.0	3D	2	31

T.w. = this work.

HL⁶ = methyl 3-methoxysalicylate

OAc = acetate

 $H_2L^7 = 2,2'$ -dipyridine-4,4'-dicarboxylic acid

Oda = oxydiacetate

 $Trz = H_4Trz = tri(1H-tetrazole-5-yl)methanol$