SUPPORTING INFORMATION

A Ferromagnetically Coupled Diphenoxo-bridged Gd^{3+}-Mn^{2+} Dinuclear Complex with a Large Magneto-Caloric Effect.

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EXPERIMENTAL SECTION

General Procedures: Unless stated otherwise, all reactions were conducted in oven-dried glassware in aerobic conditions, with the reagents purchased commercially and used without further purification. The ligand H_2L was prepared as previously described.[1]

Preparation of 1. To a solution of H_2L (55.7 mg, 0.125 mmol) in 5 mL MeOH were subsequently added with continuous stirring 31.4 mg (0.125 mmol) of $Mn(NO_3)_2{\cdot}4H_2O$ and 56.4 mg (0.125 mmol) of $Gd(NO_3)_3{\cdot}6H_2O$. The resulting colorless solution was filtered and allowed to stand at room temperature. After one day, well-formed prismatic colorless crystals of $[Mn(CH_3OH)(\mu\text{-}L)Gd(NO_3)_3]$ (**1**) were obtained with a yield of 55% based on Mn. IR (KBr, cm^{-1}): 3401 (m), 2972(m), 2919(m) , 2867 (m), 1492 (s), 1384 (vs), 1310 (s) 1249 (s), 1069 (m), 812 (m). Anal. Calcd. for $C_{26}H_{40}N_6O_{14}MnGd$: C, 35.78 ; H, 4.62; N, 9.63. Found: C, 35.41; H, 5.05; N, 9.32.

Physical measurements

Elemental analyses were carried out at the "Centro de Instrumentación Científica" (University of Granada) on a Fisons-Carlo Erba analyser model EA 1108. The IR spectra on powdered samples were recorded with a ThermoNicolet IR200FTIR by using KBr pellets. Magnetisation and variable temperature (2-300 K) magnetic susceptibility measurements on polycrystalline samples were carried out with a Quantum Design SQUID MPMS XL-5 device operating at different magnetic fields. The experimental susceptibilities were corrected for the diamagnetism of the constituent atoms by using Pascal's tables.

Single-Crystal Structure Determination.

A Suitable crystal of **1** was mounted on glass fibre and used for data collection. Data were collected with a dual source Oxford Diffraction SuperNova diffractometer equipped with an Atlas CCD detector and an Oxford Cryosystems low temperature device operating at 100 K and using Mo-K_α. Semi-empirical (multi-scan) absorption corrections were applied using Crysalis

Pro.[2] The structures were solved by direct methods[2] and refined with full-matrix least-squares calculations on F^2.[3] Anisotropic temperature factors were assigned to all atoms except for the hydrogens, which are riding their parent atoms with an isotropic temperature factor arbitrarily chosen as 1.2 times that of the respective parent. Final *R(F)*, $wR(F^2)$ and goodness of fit agreement factors, details on the data collection and analysis can be found in Table S1. Selected bond lengths and angles are given in Table S2.

1. Colacio, E.; Ruiz-Sanchez, J.; White, F. J.; Brechin, E. K., *Inorg. Chem*. **2011**, *50*, 7268.
2. Altomare, A.; Cascarano, G.; Giacovazzo, C.; Guagliardi, A.; Moliterni, A. G. G.; Burla, M. C.; Polidori, G.; Cavalli, M.; Spagna, R. *SIR97: package for structure solution by direct methods*; University of Bari: Bari, Italy, **1997**.
3. Sheldrick, G. M. *SHELX97: program for crystal structure refinement*; University of Göttingen: Göttingen, Germany, **1997**.

Table S1. Crystal data and structure refinement for **1**.

Complex	**1**
Formula	$C_{26}H_{40}N_6O_{14}MnGd$
M_r	872.83
Crystal system	Monoclinic
Space group (no.)	*P21/n* (14)
a (Å)	12.7772(9)
b (Å)	16.9237(11)
c (Å)	15.5766(10)
α (°)	90.00
β (°)	92.700(3)
γ (°)	90.00
V (Å^3)	3364.5(4)
Z	4
D_c (g cm^{-1})	1.723
μ(MoK_α) (mm^{-1})	2.404
T (K)	100(2)
Observed reflections	6907 (5939)
R_{int}	0.0603
Parameters	441
*G*OF	1.047
R_1[a]	0.0349 (0.0267)[b]
wR_2[c]	0.0657 (0.0616)
Largest difference in peak and hole (e Å^{-3})	1.222 and -1.081

[a] $R_1 = \Sigma||F_o| - |F_c||/\Sigma|F_o|$.
[b]Values in parentheses for reflections with $I > 2\sigma(I)$.
[c]$wR_2 = \{\Sigma[w(F_o^2 - F_c^2)^2] / \Sigma[w(F_o^2)^2]\}^{½}$

Table S2.- Selected bond lengths and angles

Complex	**1**
Gd(1)-Mn(1)	3.6859(5)
Gd(1)-O(2A)	2.564(2)
Gd(1)-O(5A)	2.342(2)
Gd(1)-O(25A)	2.322(2)
Gd(1)-O(27A)	2.608(2)
Gd(1)-O(2B)nitrate	2.543(2)
Gd(1)-O(3B)nitrate	2.551(2)
Gd(1)-O(2C)nitrate	2.499(2)
Gd(1)-O(3C)nitrate	2.522(2)
Gd(1)-O(2D)nitrate	2.492(2)
Gd(1)-O(3D)nitrate	2.492(2)
Mn(1)-N(12A)	2.376(3)
Mn(1)-N16A)	2.298(3)
Mn(1)-N(20A)	2.373(3)
Mn(1)-O(5A)	2.148(2)
Mn(1)-O(25A)	2.158(2)
Mn(1)-O(1E)	2.216(2)
Gd(1)-O(5A)-Mn(1)	110.27(9)
Gd(1)-O(25A)-Mn(1)	110.68(9)
O(5A)-Gd(1)-O(25A)	66.25(7)
O(5A)-Mn(1)-O(25A)	72.59(8)
O(5A)-Mn(1)-O(1E)	100.12(8)
O(25A)-Mn(1)-O(1E)	92.68(8)

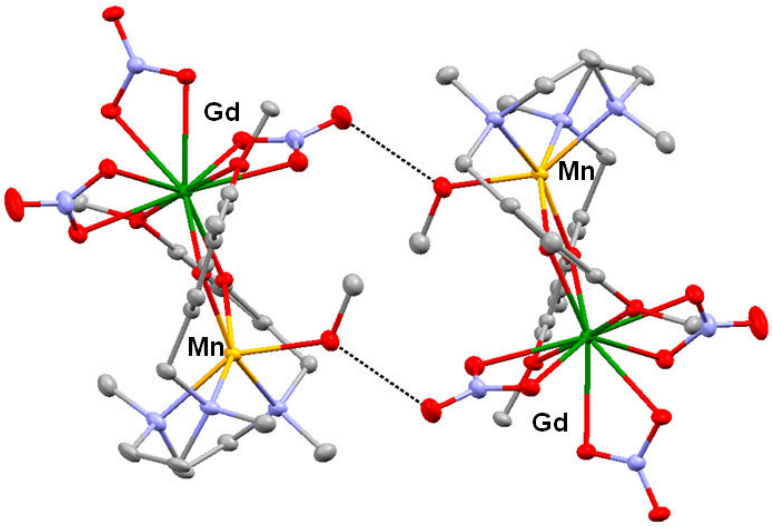

Figure S1.- Hydrogen bonding interactions between the molecules in **1**.

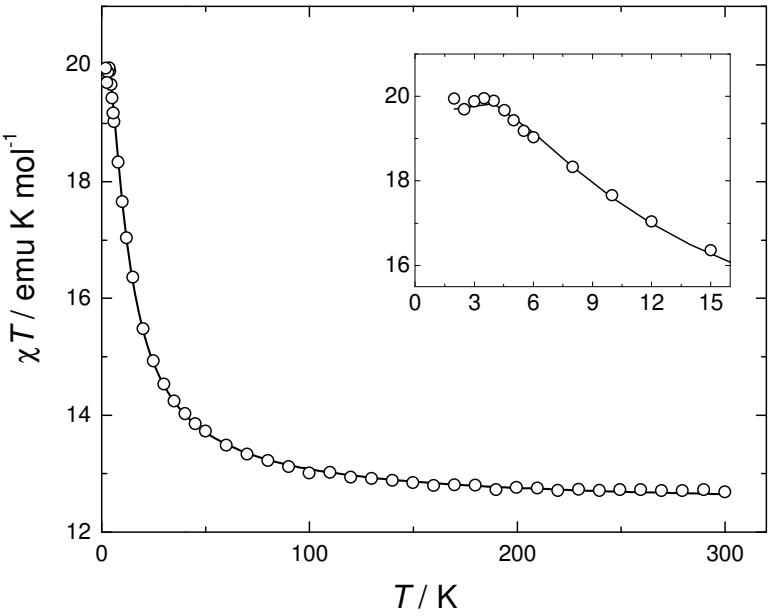

Fig. S2 Temperature dependence of the $\chi_M T$ product for **1**. The low temperature region is highlighted in the inset. The black solid line shows the best fit to the theoretical equation.

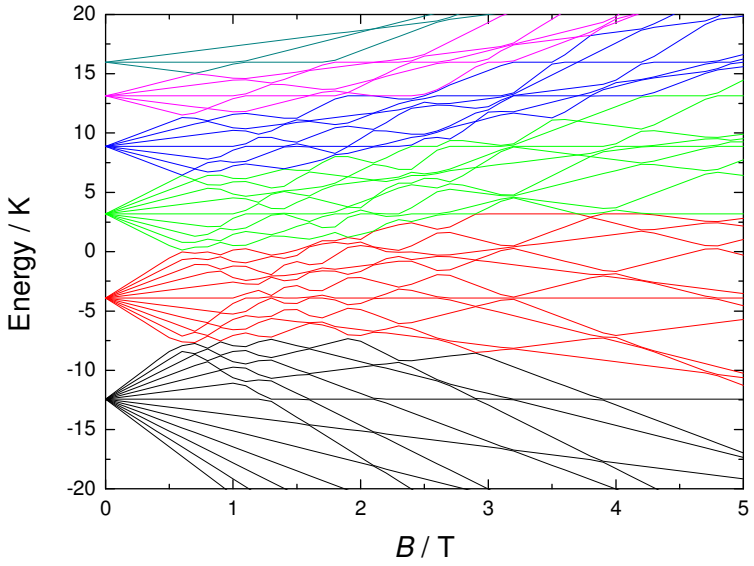

Figure S3. Energy levels patterns for GdMn obtained by diagonalization of the Heisenberg Hamiltonian.