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Magnetocaloric Effect and Slow Magnetic Relaxation in Two Dense (3,12)-connected Lanthanide Complexes

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Experimental Section

Materials and methods.

All chemicals were of reagent grade and used as purchased without further purification.

Elemental analyses were performed on a Perkin-Elmer 240C analyzer (Perkin-Elmer, USA). IR spectra were measured on a MAGNA-560 (Nicolet) FT-IR spectrometer with KBr pellets. Powder X-ray diffraction (PXRD) spectra were recorded on a Bruker D8 FOCUS diffractometer with a Cu-target tube and a graphite monochromator. Simulation of the PXRD spectra were carried out by the single-crystal data and diffraction-crystal module of the Mercury (Hg) program available free of charge *via* the Internet at http://www.iucr.org. The magnetic measurements were performed by using an MPMS XL-7 SQUID magnetometer. Diamagnetic corrections were estimated by using Pascal constants and background corrections by experimental measurement on sample holders.

Synthesis of 1 and 2

The ligand Hbms·HCl was prepared according to the method described in the literature.[1] The colorless single crystals of **1** and **2** were solvothermally synthesized under autogenous pressure. A mixture of Hbms·HCl (0.050 g, 0.25 mmol), $Ln(NO_3)_3 \cdot 6H_2O$ (0.175 g for **1**, 0.187 g for **2**), H_2O (7 mL) and CH_3OH (3 mL) was sealed in a Teflon-lined autoclave (20 mL) and heated to 140°C for 48 h then slowly cooled to 30°C in 24 h. Yield: ca. 25% and 15% with respect to Hbms·HCl for **1** and **2**, respectively.

Crystal data for **1**: $Gd_4H_{12}O_{24}S_4$, *M*r = 1153.34; Orthorhombic, $P2_12_12_1$; a = 10.743(2) Å, b = 10.981(2) Å, c = 16.751(3) Å, α = β = γ = 90°; V = 1976.1(7) Å^3; Z = 4; D_{calc} = 3.877 g/cm^3; T = 113(2) K.; Reflections collected/unique = 19551 / 4688, R_{int} = 0.0386; R_1 = 0.0215, wR_2 = 0.0561 (I > 2θ(I)); R_1 = 0.0235, wR_2 = 0.0565 (all data) and *GOF* = 1.112; Elemental analysis (%): Calcd. for $Gd_4H_{12}O_{24}S_4$ (1153.34): H 1.05; Found: H 1.22. IR (KBr pellets, cm^{-1}): 3624(m), 3612(m),

3594(m), 3424(s), 2156(w), 1640(s), 1192(m), 1144(s), 1112(w), 1095(w), 1077(w), 1022(m), 744(w), 707(s), 611(s).

Crystal data for **2**: $Dy_4H_{10}O_{23}S_4$, *M*r = 1156.32; Orthorhombic, $P2_12_12_1$; a = 10.278(2) Å, b = 10.761(2) Å, c = 16.613(3) Å, α = β = γ = 90°; V = 1837.4(6) Å^3; Z = 4; D_{calc} = 4.180 g/cm^3; T = 113(2) K.; Reflections collected/unique = 14990 / 3246, R_{int} = 0.1982; R_1 = 0.0873, wR_2 = 0.2018 (I > 2θ(I)); R_1 = 0.0891, wR_2 = 0.2028 (all data) and *GOF* = 1.060. Elemental analysis (%): Calcd. for $Dy_4H_{10}O_{23}S_4$ (1156.32): H 0.87; Found: H 1.02. IR (KBr pellets, cm^{-1}): 3608(m), 3589(m), 3504(w), 3424(s), 2176(w), 1624(s), 1205(w), 1145(s), 1122(w), 1101(w), 1040(w), 1022(w), 709(s), 633(w), 610(s).

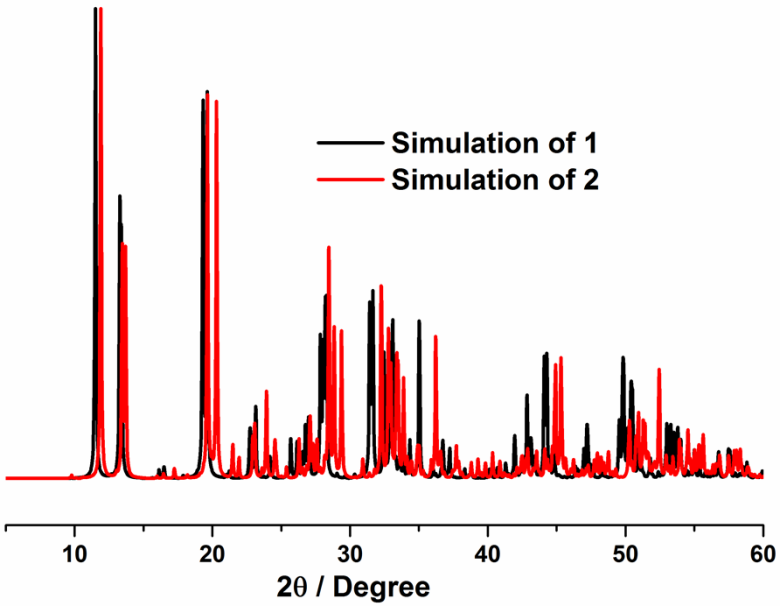
Synthetic Discussion:

The *in situ* generated sulfate may be attributed to the oxidation of thiol under acid conditions in the presence of NO_3^-. The *in situ* transformation of thiol to sulfate have been documented in a recent publication.[2] The SO_4^{2-} in **1** and **2** can also be confirmed by the IR characteristic peaks at about 1100 cm^{-1} (Fig. S9). Similar lanthanide-sulfate frameworks (Ln = Y, Er) with differences only in terminal ligands of Gd^{III} ions for **1** have been reported.[3] These complexes were prepared by the hydrothermal reactions of corresponding Ln_2O_3, H_2SO_4, D-camphoric acid at 170 °C for 6 days. However, attempts to make the targeted lanthanide-sulfate frameworks (Ln = Gd, Dy) with this method were fruitless. We also attempted to introduce the sulfate directly to synthesize **1**, whereas, the product was $[Gd_2(SO_4)_3{\cdot}8H_2O]$. Interestingly, although **1** and **2** are prepared under similar conditions, their structures show small differences in terminal ligands of one lanthanide ion. Due to the poor quality of the crystal of **2** (twinning), there are still some residual Q-peaks even if the framework of **2** was well resolved. We have also tried our best to optimize the quality of the crystal, but twining still exists. The structural difference of **1** and **2** could also be corroborated by the relatively obvious differences in the simulated PXRD plots of **1** and **2**

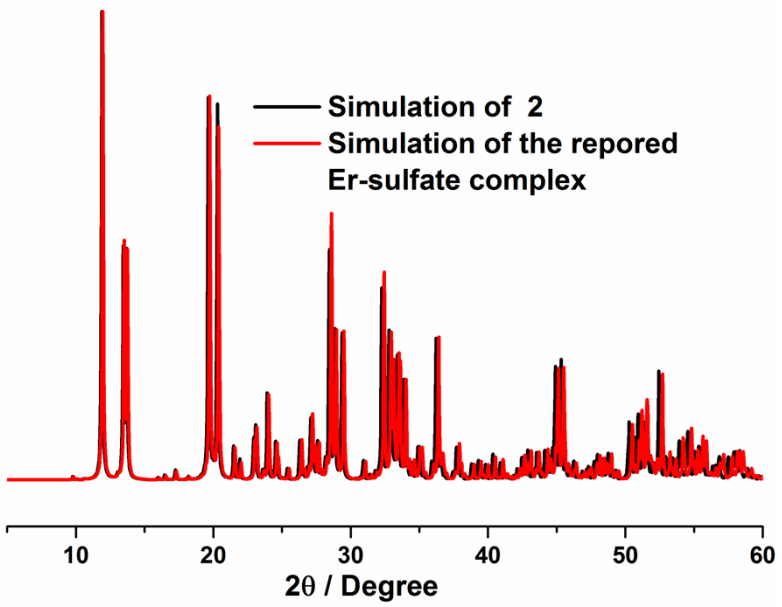
(Scheme S1). The simulated PXRD pattern of **2** shows beautiful agreement with the simulated PXRD pattern of the known lanthanide-sulfate frameworks (Ln = Y, Er), indicating the isomorphism (Scheme S2).

X-ray Crystallography.

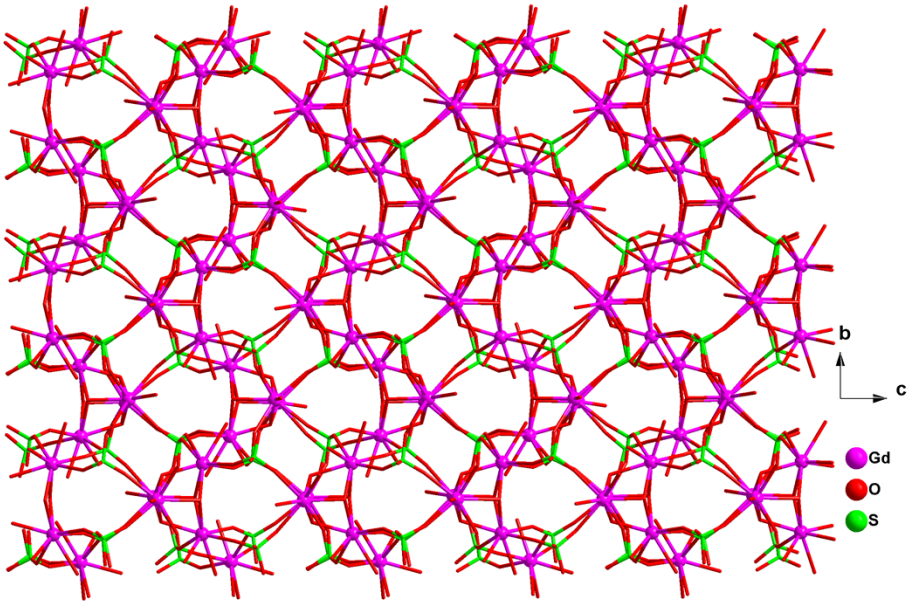
The crystallographic data of **1** and **2** were collected on a Rigaku MSC diffractometer at 113(2) K with Mo-Kα radiation (λ = 0.71073 Å). The program *CrystalClear* was used for integration of the diffraction profiles.[4a] The crystal data were solved by direct methods and refined by a full-matrix least-square method on F^2 using the *SHELXL-97* crystallographic software package.[4b,c] Full crystallographic data for **1** and **2** have been deposited with the CCDC (981569-981570). These data can be obtained free of charge from The Cambridge Crystallographic Data Centre *via* www.ccdc.cam.ac.uk/data_request/cif.



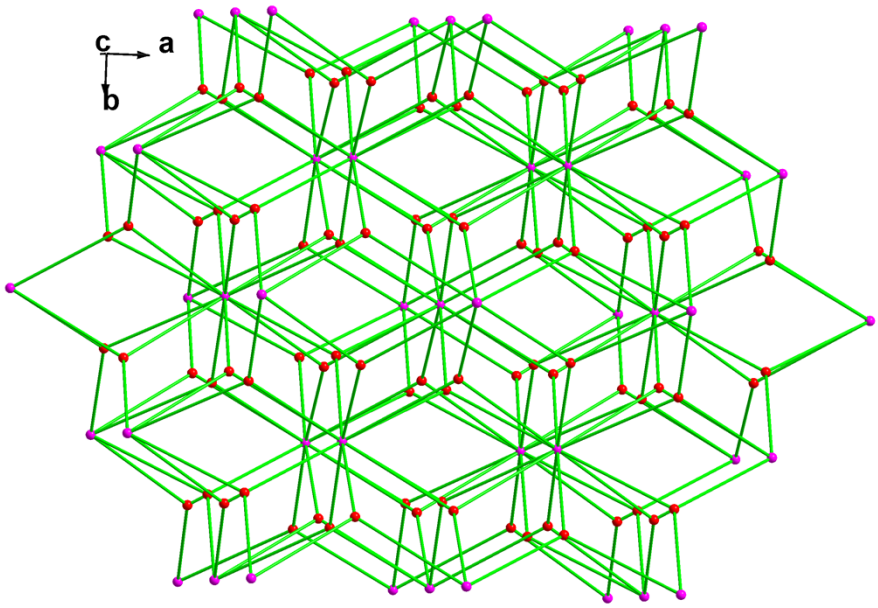
Scheme S1 The simulated PXRD patterns of **1** and **2**.



Scheme S2 The simulated PXRD patterns of **2** and the reported Er-sulfate complex.



Scheme S3 The 3D framework of **1** along the *a* axis.



Scheme S4 The (3,12)-connected topology of **1**.

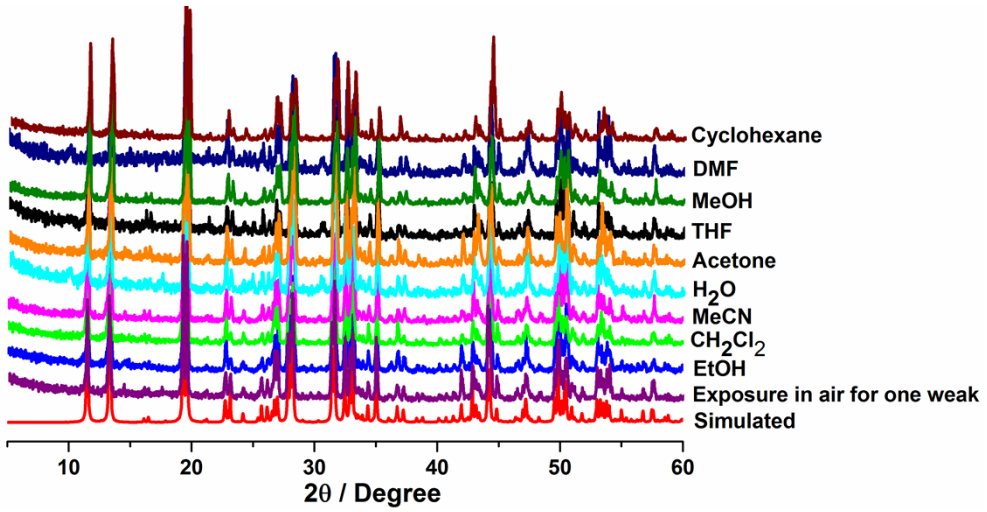


Fig. S1 The simulated and experimental PXRD patterns of **1**, and **1** in different solvents.

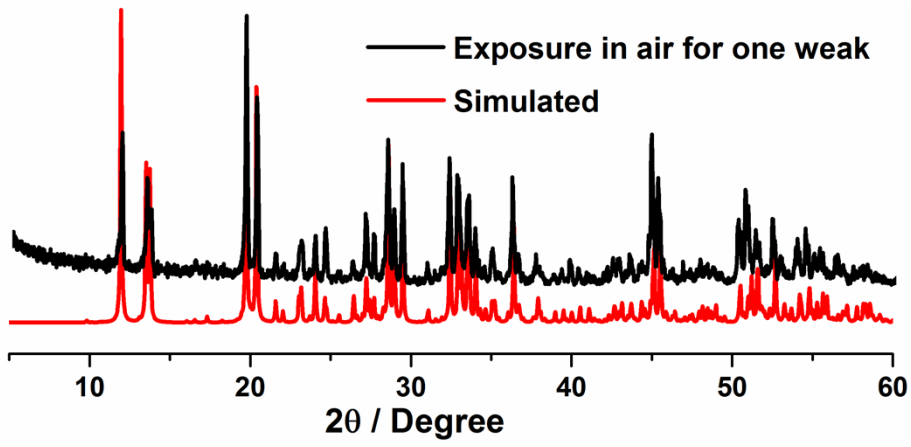


Fig. S2 PXRD patterns of **2**.

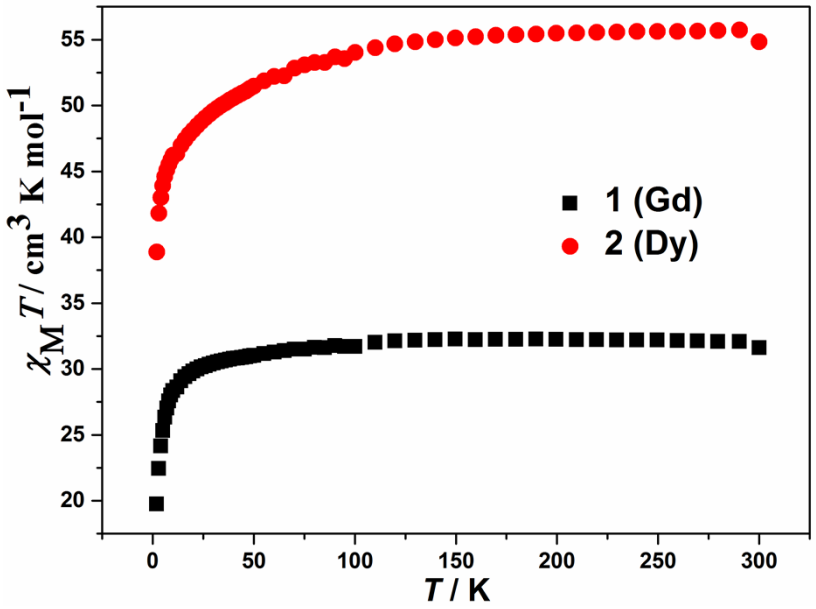


Fig. S3 The plots of $\chi_M T$ *vs* T for **1** and **2**.

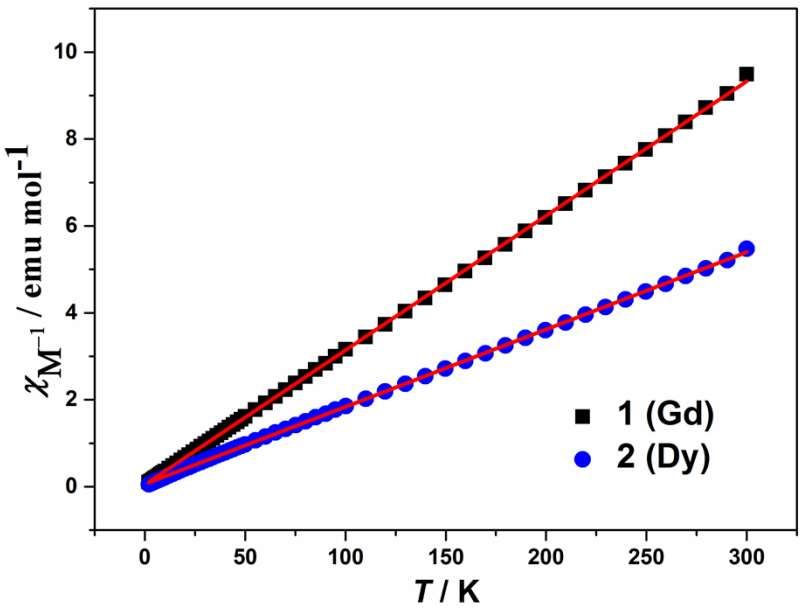


Fig. S4 The χ_M^{-1} *vs T* plots of **1** and **2**. Solid lines represent the Curie-Weiss fitting.

The temperature dependence of molar susceptibility in 2-300 K is well described by Curie-Weiss law, yielding Curie constant C = 32.32 cm^3 mol^{-1} K and Weiss constant θ = -1.57 K for **1** (Gd), C = 56.18 cm^3 mol^{-1} K and θ = -3.31 K for **2** (Dy), respectively (Fig. S4). The negative θ value for **1** supports the presence of antiferromagnetic coupling between Gd^{III}. However, negative θ value of **2** will not indicate the antiferromagnetic coupling between Dy^{III} because of the large orbital angular momentum and strong spin-orbit coupling for Dy^{III}, which is similar with those of the Co^{II}-based complexes. Considering the relatively complicated framework of **2** and strong spin-orbital coupling of Dy^{III} ion, fitting the magnetic susceptibility of **2** goes out of the scope of our abilities. Due to the efficient shielding of the 4*f* orbitals of the Dy^{III} ion, the magnetic interactions of Dy^{III}-Dy^{III} in **2** are anticipated to be weak.

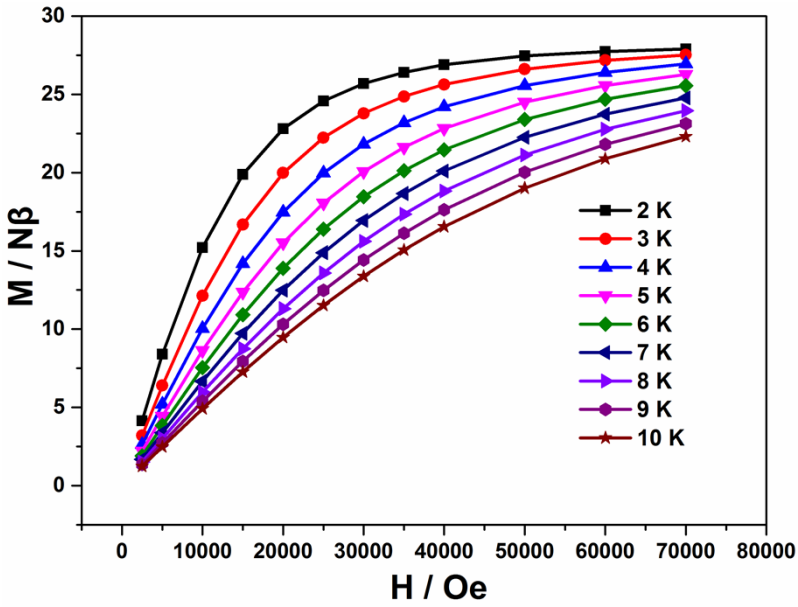


Fig. S5 Field dependence magnetization plots at indicated temperatures for **1**.

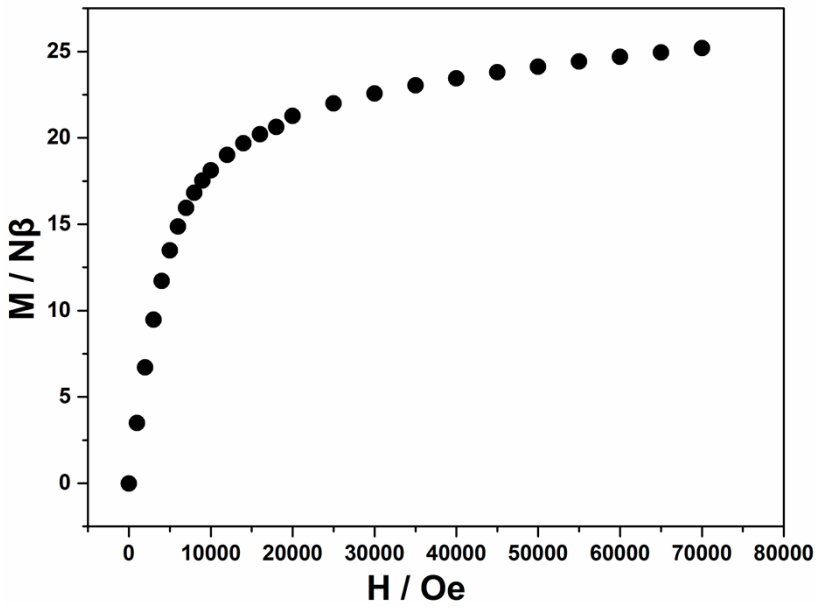


Fig. S6 The *M vs H* plot of **2**.

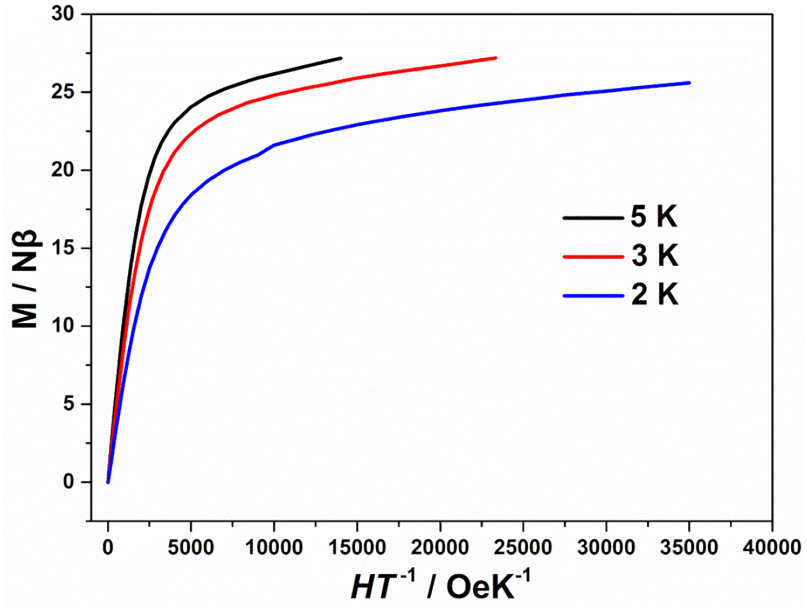


Fig. S7 The curves of *M vs. H*/*T* for **2** in the field range 2.5-70 kOe.

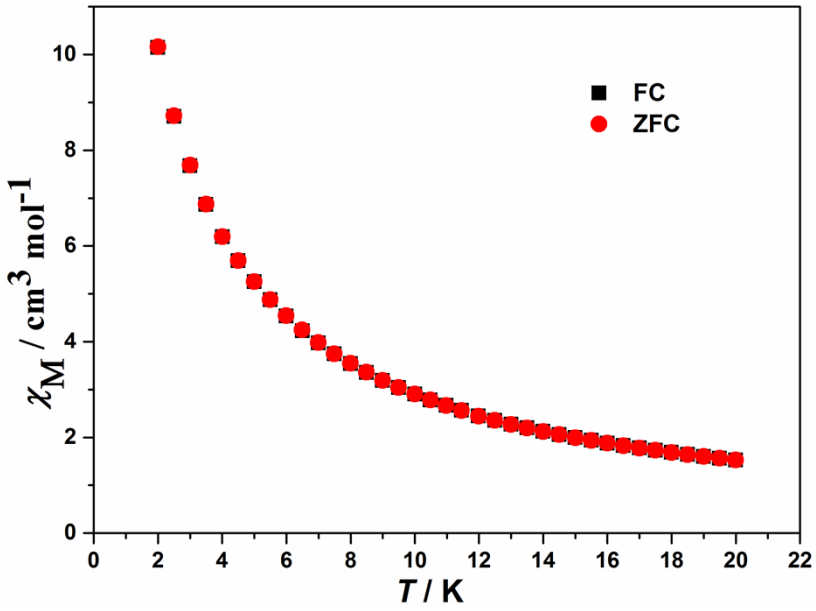


Fig. S8 FC and ZFC magnetization of **1** in the dc field of 50 Oe.

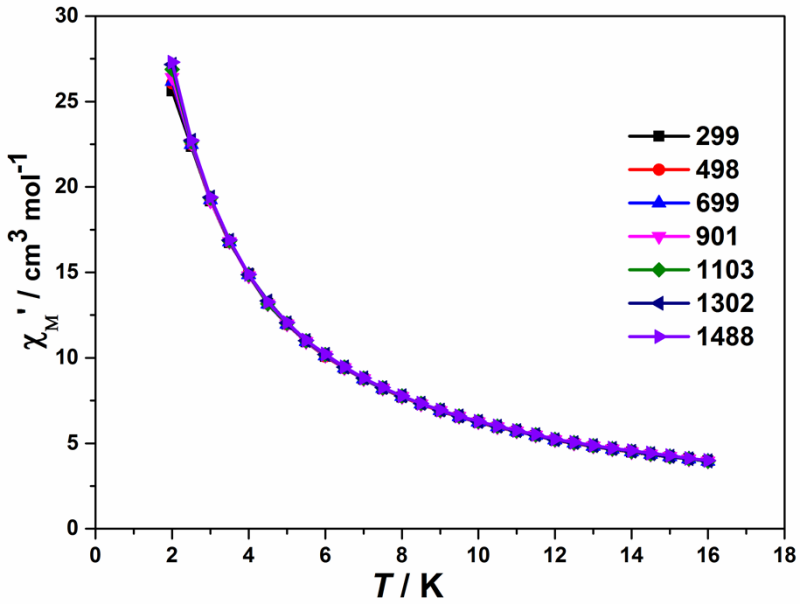
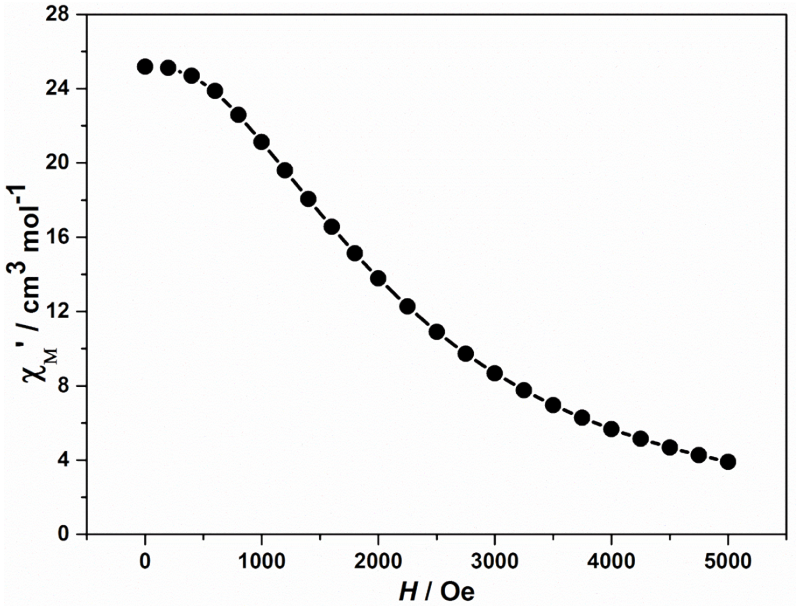


Fig. S9 Temperature dependence of the in-phase (χ') ac susceptibility components for **2** at the indicated frequencies and in zero dc field.



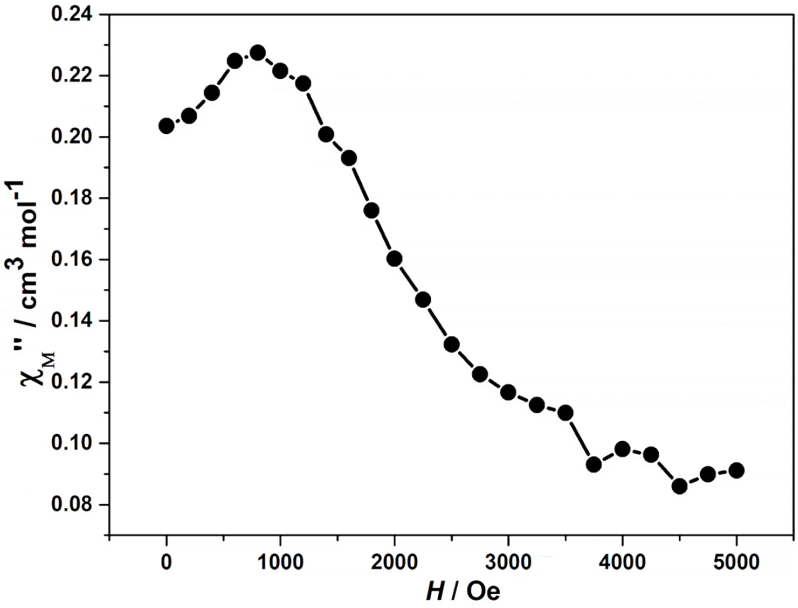
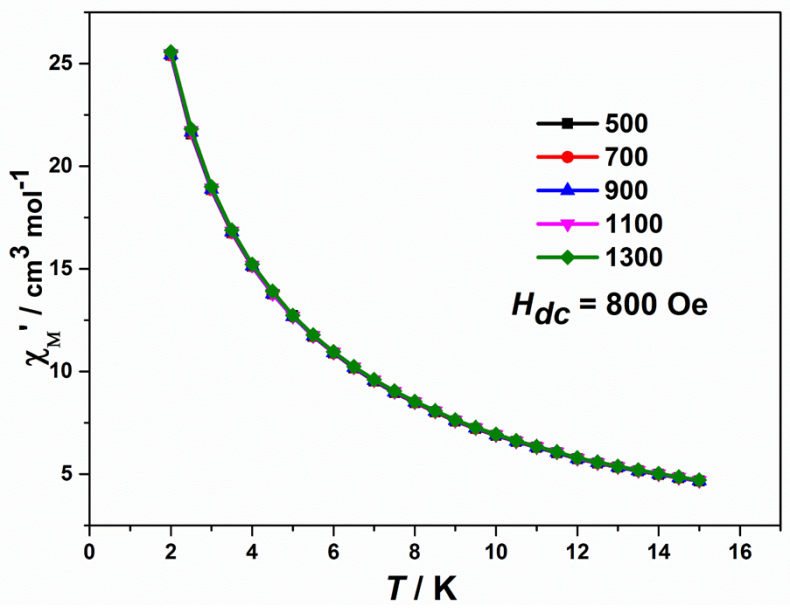


Fig. S10 Field dependence of the χ' (top) and χ'' (bottom) ac susceptibility components for **2** with f = 700 Hz.



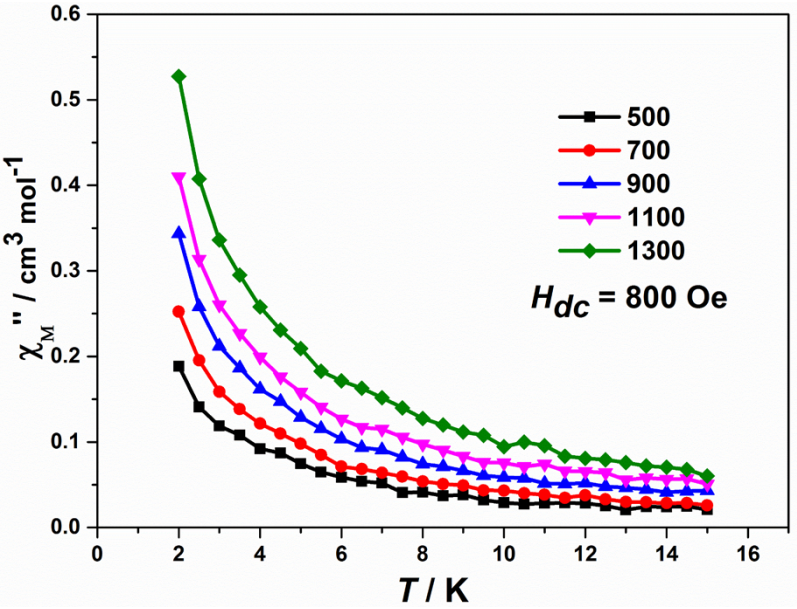


Fig. S11 Temperature dependence of the χ' (top) and χ'' (bottom) ac susceptibility components for **2** at the indicated frequencies and in 800 Oe dc field.

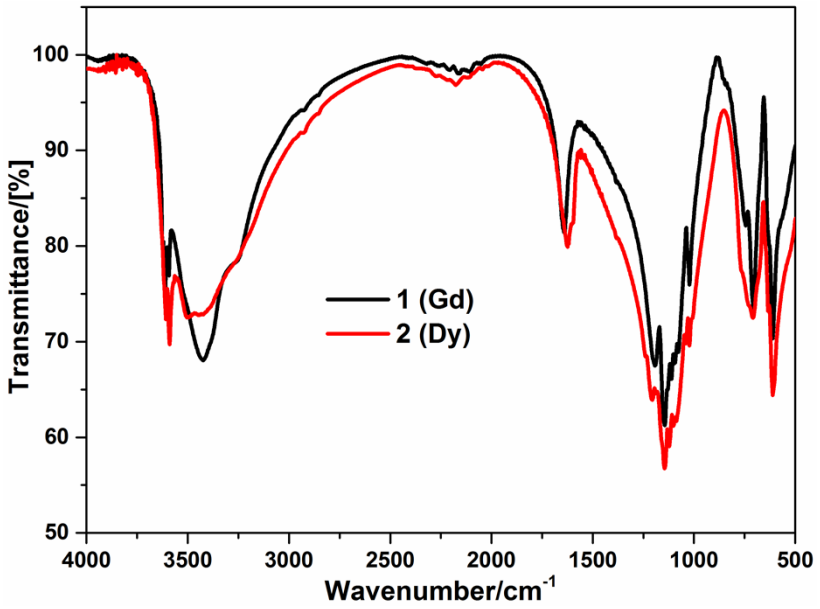


Fig. S12 IR spectra of **1** and **2**.

Table S1 Comparison of $-\Delta S_m^{max}$ (larger than 30.0 J kg^{-1} K^{-1} with $\Delta H \leq 9$ T) among Gd^{III}-containing complexes associated with potential magnetic refrigeration.

Complex	Dimen-sionality	$-\Delta S_m^{max}$ [J kg^{-1} K^{-1}] (ΔH)	$-\Delta S_m^{max}$ [mJ cm^{-3} K^{-1}]	Ref.
$[Gd(OH)CO_3]_n$	3D	66.4 (7 T)	355	5
$[Gd(O_2CH)_3]_n$	3D	55.9 (7 T)	215.7	6
$[Gd_4(SO_4)_4(\mu_3\text{-}OH)_4(H_2O)_4]_n$	3D	51.29 (7 T)	198.85	this work
$\{[Mn(H_2O)_6][MnGd(oda)_3]_2\cdot 6H_2O\}_n$	3D	50.1 (7 T)	114.28	7
$[Gd_6(OH)_8(suc)_5(H_2O)_2]_n\cdot 4nH_2O$	3D	48.0 (7T)	144	8
$[Gd(OAc)_3(H_2O)_{0.5}]_n$	1D	47.7 (7 T)	106.28	9
$[Gd(HCOO)(C_8H_4O_4)]_n$	3D	47.0 (9 T)	125.11	10
$\{[Ln_6(\mu_6\text{-}O)(\mu_3\text{-}OH)_8(\mu_4\text{-}ClO_4)_4\text{-}(H_2O)_6](OH)_4\}_n$	3D	46.6 (7 T)	206.81	11
$[Gd_{24}]$	0D	46.12 (7 T)	90.03	12
$[Gd(HCOO)(OAc)_2(H_2O)_2]_n$	2D	45.9 (7 T)	110.02	13
$[Gd(OAc)_3(MeOH)]_n$	1D	45.0 (7 T)	96.71	9
$[Gd(C_4O_4)(OH)(H_2O)_4]_n$	2D	43.8 (7 T)	104.38	14
$[Gd_{48}]$	0D	43.6 (7 T)	120.7	15
$[Gd(cit)(H_2O)]_n$	2D	43.6 (7 T)	115.23	16
$[Gd_2(OH)_2(suc)_2(H_2O)]_n\cdot 2nH_2O$	3D	42.8 (7 T)	120	8
$\{[Gd(OAc)_3(H_2O)_2]\}_2\cdot 4H_2O$	0D	41.6 (7 T)	82.78	17
$[Co_{10}Gd_{42}]$	0D	41.26 (7 T)	112.64	18
$\{[Gd_2(IDA)_3]\cdot 2H_2O\}_n$	3D	40.6 (7 T)	100.69	19
$[Gd_{36}]_n$	2D	39.66 (7 T)	91.34	20
$[Ni_{10}Gd_{42}]$	0D	38.2 (7 T)	105.47	18
$[Gd_{38}]$	0D	37.9 (7 T)	102.0	15
$[Gd_4(OAc)_4(acac)_8(H_2O)_4]$	0D	37.7 (7 T)	70.24	9
$[Gd_2(piv)_5(\mu_3\text{-}OH)(H_2O)]_n$	1D	37.5 (7 T)	61.13	16
$[Ni_{12}Gd_{36}]$	0D	36.3 (7 T)	83.49	21

$[Cu_3Gd_6]_n$	3D	35.76 (7 T)	90.36	22
$[Mo_4Gd_{12}]$	0D	35.3 (7 T)	76.99	23
$[Mn_4Gd_6P_6]$	0D	33.7 (7 T)	54.12	24
$[Co_4Gd_{10}]$	0D	32.6 (7 T)	54.31	25
$[Gd_{10}]$	0D	31.22 (7 T)	68.84	26
$[Cu_5Gd_4]$	0D	31 (9 T)	61.66	27
$[Gd_5Zn]_n$	3D	30.7 (7 T)	57.96	28

$-\Delta S_m^{max}$ [mJ cm^{-3} K^{-1}] = $-\Delta S_m^{max}$ [J kg^{-1} K^{-1}]*ρ_{cald} [g cm^{-3}]

Table S2 The summary of the (3,12)-connected complexes and corresponding Schläfli symbols.

Complex	Schläfli symbol	Ref.
$\{[Ln_6(\mu_6\text{-}O)(\mu_3\text{-}OH)_8(\mu_4\text{-}ClO_4)_4(H_2O)_6](OH)_4\}_n$	$(4^{20}\cdot6^{26}\cdot8^{20})(4^3)_4$	11
$[Zn_8(\mu_3\text{-}OH)_4(oba)_6(bbi)(H_2O)_2]$	$(3^2\cdot4)_2(3^8\cdot4^{22}\cdot5^{16}\cdot6^{18}\cdot7^2)$	29
$[Na_{0.5}Zn_{4.75}(\mu_3\text{-}OH)_2(BTB)_2(HBTB)(H_2O)_{0.5}]$ $\cdot5DMF\cdot1.5EtOH\cdot10H_2O$	$(4^3)_{12}(4^{12}\cdot6^{36}\cdot8^{18})_2(4^{12}\cdot6^{24}\cdot8^{30})$	30
$[Co_5(\mu_3\text{-}OH)_2(5\text{-}NH_2\text{-}bdc)_4(H_2O)_2]\cdot7.5H_2O$	$(4^{19}\cdot6^{27}\cdot8^{20})(4^3)_4$	31
$[Co_8(\mu_3\text{-}OH)_4(SO_4)_2(dcpbpy)_4(H_2O)_4]$ $\cdot12DMF\cdot4EtOH\cdot24H_2O$	$(4^{12}\cdot6^{34}\cdot8^{20})(4^3)_4$	32
Complex **1** in this work	$(4^{20}\cdot6^{28}\cdot8^{18})(4^3)_4$	
$[Ln_4(OH)_4(3\text{-}SBA)_4(H_2O)_4]\cdot nH_2O$ (Ln = Eu, Gd, Tb)	$(4^{20}\cdot6^{28}\cdot8^{18})(4^3)_4$	33
$[Ln(TTP)_2]\cdot(CF_3SO_3)_3\cdot C_3H_6O\cdot5H_2O$ (Ln = Eu, Gd)	$(4^{20}\cdot6^{28}\cdot8^{18})(4^3)_4$	34
$[Eu_6(\mu_6\text{-}O)(\mu_3\text{-}OH)_8(H_2O)_6(SO_4)_4]_n$	$(4^{20}\cdot6^{28}\cdot8^{18})(4^3)_4$	35

Table S3 The selected bond lengths [Å] and angles [°] of **1**.

Gd(1)-O(10)	2.334(5)	Gd(1)-O(14)#1	2.347(4)
Gd(1)-O(20)	2.355(3)	Gd(1)-O(19)	2.371(4)
Gd(1)-O(11)	2.395(4)	Gd(1)-O(16)	2.420(4)
Gd(1)-O(1W)	2.433(4)	Gd(1)-O(17)	2.479(3)

Gd(2)-O(3)	2.305(4)	Gd(2)-O(18)	2.333(3)
Gd(2)-O(7)	2.376(4)	Gd(2)-O(4)	2.423(4)
Gd(2)-O(20)	2.413(4)	Gd(2)-O(6)#2	2.515(4)
Gd(2)-O(19)	2.430(4)	Gd(2)-O(2W)	2.576(4)
Gd(3)-O(5)#3	2.352(5)	Gd(3)-O(17)	2.381(4)
Gd(3)-O(9)#3	2.375(4)	Gd(3)-O(12)	2.390(4)
Gd(3)-O(8)	2.384(4)	Gd(3)-O(20)	2.421(4)
Gd(3)-O(18)	2.404(4)	Gd(3)-O(3W)	2.467(4)
Gd(4)-O(1)#3	2.322(4)	Gd(4)-O(19)	2.352(4)
Gd(4)-O(13)	2.353(4)	Gd(4)-O(15)#4	2.395(4)
Gd(4)-O(17)	2.417(4)	Gd(4)-O(18)	2.422(4)
Gd(4)-O(2)#5	2.436(4)	Gd(4)-O(4W)	2.583(5)
O(10)-Gd(1)-O(14)#1	79.01(13)	O(10)-Gd(1)-O(20)	116.35(14)
O(14)#1-Gd(1)-O(20)	74.62(14)	O(10)-Gd(1)-O(19)	77.27(14)
O(14)#1-Gd(1)-O(19)	118.86(14)	O(20)-Gd(1)-O(19)	67.52(12)
O(10)-Gd(1)-O(11)	144.01(15)	O(14)#1-Gd(1)-O(11)	79.82(15)
O(20)-Gd(1)-O(11)	85.20(13)	O(19)-Gd(1)-O(11)	138.70(14)
O(10)-Gd(1)-O(16)	82.25(15)	O(14)#1-Gd(1)-O(16)	148.73(15)
O(20)-Gd(1)-O(16)	136.53(14)	O(19)-Gd(1)-O(16)	80.46(13)
O(11)-Gd(1)-O(16)	102.06(12)	O(10)-Gd(1)-O(1W)	81.37(16)
O(14)#1-Gd(1)-O(1W)	81.72(16)	O(20)-Gd(1)-O(1W)	146.28(15)
O(19)-Gd(1)-O(1W)	146.17(14)	O(11)-Gd(1)-O(1W)	67.00(16)
O(16)-Gd(1)-O(1W)	70.85(15)	O(10)-Gd(1)-O(17)	140.51(13)
O(14)#1-Gd(1)-O(17)	135.72(13)	O(20)-Gd(1)-O(17)	69.41(13)
O(19)-Gd(1)-O(17)	69.30(13)	O(11)-Gd(1)-O(17)	72.37(13)
O(16)-Gd(1)-O(17)	72.23(13)	O(1W)-Gd(1)-O(17)	116.19(15)
O(3)-Gd(2)-O(18)	132.25(14)	O(3)-Gd(2)-O(7)	93.51(14)
O(18)-Gd(2)-O(7)	128.24(14)	O(3)-Gd(2)-O(20)	72.12(14)
O(18)-Gd(2)-O(20)	70.45(13)	O(7)-Gd(2)-O(20)	113.41(13)
O(3)-Gd(2)-O(4)	143.09(15)	O(18)-Gd(2)-O(4)	72.77(13)
O(7)-Gd(2)-O(4)	83.48(14)	O(20)-Gd(2)-O(4)	142.30(14)
O(3)-Gd(2)-O(19)	118.92(14)	O(18)-Gd(2)-O(19)	69.32(13)
O(7)-Gd(2)-O(19)	67.17(14)	O(20)-Gd(2)-O(19)	65.66(12)

O(4)-Gd(2)-O(19)	93.83(13)	O(3)-Gd(2)-O(6)#2	81.98(15)
O(18)-Gd(2)-O(6)#2	78.93(13)	O(7)-Gd(2)-O(6)#2	139.63(14)
O(20)-Gd(2)-O(6)#2	103.33(13)	O(4)-Gd(2)-O(6)#2	77.15(14)
O(19)-Gd(2)-O(6)#2	148.24(14)	O(3)-Gd(2)-O(2W)	70.26(14)
O(18)-Gd(2)-O(2W)	138.34(13)	O(7)-Gd(2)-O(2W)	71.04(14)
O(20)-Gd(2)-O(2W)	142.33(13)	O(4)-Gd(2)-O(2W)	74.04(14)
O(19)-Gd(2)-O(2W)	137.53(13)	O(6)#2-Gd(2)-O(2W)	69.70(14)
O(5)#3-Gd(3)-O(9)#3	82.19(15)	O(5)#3-Gd(3)-O(17)	79.56(13)
O(9)#3-Gd(3)-O(17)	109.25(12)	O(5)#3-Gd(3)-O(8)	145.47(15)
O(9)#3-Gd(3)-O(8)	86.27(15)	O(17)-Gd(3)-O(8)	134.91(13)
O(5)#3-Gd(3)-O(12)	79.89(16)	O(9)#3-Gd(3)-O(12)	145.49(14)
O(17)-Gd(3)-O(12)	96.18(13)	O(8)-Gd(3)-O(12)	92.05(15)
O(5)#3-Gd(3)-O(18)	125.67(13)	O(9)#3-Gd(3)-O(18)	69.77(12)
O(17)-Gd(3)-O(18)	68.11(13)	O(8)-Gd(3)-O(18)	79.29(13)
O(12)-Gd(3)-O(18)	143.63(13)	O(5)#3-Gd(3)-O(20)	137.36(13)
O(9)#3-Gd(3)-O(20)	135.38(13)	O(17)-Gd(3)-O(20)	69.96(11)
O(8)-Gd(3)-O(20)	69.76(13)	O(12)-Gd(3)-O(20)	74.70(14)
O(18)-Gd(3)-O(20)	69.14(12)	O(5)#3-Gd(3)-O(3W)	76.81(15)
O(9)#3-Gd(3)-O(3W)	74.84(13)	O(17)-Gd(3)-O(3W)	155.22(14)
O(8)-Gd(3)-O(3W)	68.77(15)	O(12)-Gd(3)-O(3W)	72.49(14)
O(18)-Gd(3)-O(3W)	133.28(14)	O(20)-Gd(3)-O(3W)	125.08(14)
O(1)#3-Gd(4)-O(19)	131.03(14)	O(1)#3-Gd(4)-O(13)	85.37(17)
O(19)-Gd(4)-O(13)	135.64(14)	O(1)#3-Gd(4)-O(15)#4	83.16(16)
O(19)-Gd(4)-O(15)#4	76.68(14)	O(13)-Gd(4)-O(15)#4	140.98(15)
O(1)#3-Gd(4)-O(17)	71.32(13)	O(19)-Gd(4)-O(17)	70.65(12)
O(13)-Gd(4)-O(17)	108.19(12)	O(15)#4-Gd(4)-O(17)	103.13(13)
O(1)#3-Gd(4)-O(18)	120.75(13)	O(19)-Gd(4)-O(18)	69.14(12)
O(13)-Gd(4)-O(18)	70.06(13)	O(15)#4-Gd(4)-O(18)	145.79(13)
O(17)-Gd(4)-O(18)	67.26(12)	O(1)#3-Gd(4)-O(2)#5	145.18(14)
O(19)-Gd(4)-O(2)#5	74.24(13)	O(13)-Gd(4)-O(2)#5	88.09(15)
O(15)#4-Gd(4)-O(2)#5	80.67(15)	O(17)-Gd(4)-O(2)#5	142.57(13)
O(18)-Gd(4)-O(2)#5	88.53(12)	O(1)#3-Gd(4)-O(4W)	71.40(14)
O(19)-Gd(4)-O(4W)	136.52(14)	O(13)-Gd(4)-O(4W)	71.55(13)
O(15)#4-Gd(4)-O(4W)	69.44(14)	O(17)-Gd(4)-O(4W)	142.60(13)

O(18)-Gd(4)-O(4W)	138.14(12)	O(2)#5-Gd(4)-O(4W)	74.08(14)
Symmetry transformations used to generate equivalent atoms: #1: -x+1/2,-y+1,z-1/2; #2: -x+1,y-1/2,-z+3/2; #3: -x+1/2,-y+1,z+1/2; #4: x-1/2,-y+3/2,-z+2; #5: -x+1,y+1/2,-z+3/2.			

Table S3 The selected bond lengths [Å] and angles [º] of **2**.

Dy(1)-O(16)#1	2.27(2)	Dy(1)-O(15)#2	2.289(18)
Dy(1)-O(11)#2	2.298(17)	Dy(1)-O(18)	2.339(19)
Dy(1)-O(19)	2.35(2)	Dy(1)-O(10)#3	2.37(2)
Dy(1)-O(17)	2.40(2)	Dy(1)-O(1W)	2.49(2)
Dy(2)-O(17)	2.31(2)	Dy(2)-O(13)	2.313(19)
Dy(2)-O(1)#4	2.318(19)	Dy(2)-O(14)#1	2.33(2)
Dy(2)-O(2W)	2.35(3)	Dy(2)-O(2)#5	2.36(3)
Dy(2)-O(20)	2.43(2)	Dy(2)-O(18)	2.476(19)
Dy(3)-O(7)#3	2.26(3)	Dy(3)-O(19)	2.33(2)
Dy(3)-O(12)	2.330(19)	Dy(3)-O(8)	2.34(2)
Dy(3)-O(20)	2.35(2)	Dy(3)-O(9)#3	2.36(3)
Dy(3)-O(17)	2.37(2)	Dy(3)-O(3W)	2.52(2)
Dy(4)-O(5)#5	2.27(2)	Dy(4)-O(20)	2.28(2)
Dy(4)-O(18)	2.309(17)	Dy(4)-O(19)	2.32(2)
Dy(4)-O(4)	2.35(2)	Dy(4)-O(6)	2.35(3)
Dy(4)-O(3)#5	2.45(2)		
O(16)#1-Dy(1)-O(15)#2	141.4(9)	O(16)#1-Dy(1)-O(11)#2	80.4(9)
O(15)#2-Dy(1)-O(11)#2	76.6(8)	O(16)#1-Dy(1)-O(18)	101.5(8)
O(15)#2-Dy(1)-O(18)	101.8(8)	O(11)#2-Dy(1)-O(18)	74.7(8)
O(16)#1-Dy(1)-O(19)	143.7(8)	O(15)#2-Dy(1)-O(19)	74.4(8)
O(11)#2-Dy(1)-O(19)	124.3(9)	O(18)-Dy(1)-O(19)	66.2(7)
O(16)#1-Dy(1)-O(10)#3	86.9(8)	O(15)#2-Dy(1)-O(10)#3	97.2(8)
O(11)#2-Dy(1)-O(10)#3	149.0(9)	O(18)-Dy(1)-O(10)#3	135.9(8)
O(19)-Dy(1)-O(10)#3	81.5(9)	O(16)#1-Dy(1)-O(17)	75.5(8)
O(15)#2-Dy(1)-O(17)	141.9(8)	O(11)#2-Dy(1)-O(17)	131.7(8)
O(18)-Dy(1)-O(17)	70.1(7)	O(19)-Dy(1)-O(17)	68.3(7)

O(10)#3-Dy(1)-O(17)	70.4(8)	O(16)#1-Dy(1)-O(1W)	69.8(9)
O(15)#2-Dy(1)-O(1W)	75.0(9)	O(11)#2-Dy(1)-O(1W)	76.8(9)
O(18)-Dy(1)-O(1W)	151.2(7)	O(19)-Dy(1)-O(1W)	136.3(8)
O(10)#3-Dy(1)-O(1W)	72.3(9)	O(17)-Dy(1)-O(1W)	129.7(7)
O(17)-Dy(2)-O(13)	109.3(7)	O(17)-Dy(2)-O(1)#4	84.5(9)
O(13)-Dy(2)-O(1)#4	78.2(9)	O(17)-Dy(2)-O(14)#1	81.3(8)
O(13)-Dy(2)-O(14)#1	151.6(8)	O(1)#4-Dy(2)-O(14)#1	76.6(10)
O(17)-Dy(2)-O(2W)	151.7(11)	O(13)-Dy(2)-O(2W)	89.6(10)
O(1)#4-Dy(2)-O(2W)	78.9(10)	O(14)#1-Dy(2)-O(2W)	72.8(11)
O(17)-Dy(2)-O(2)#5	134.1(9)	O(13)-Dy(2)-O(2)#5	83.1(9)
O(1)#4-Dy(2)-O(2)#5	141.1(10)	O(14)#1-Dy(2)-O(2)#5	109.0(9)
O(2W)-Dy(2)-O(2)#5	67.2(11)	O(17)-Dy(2)-O(20)	67.7(8)
O(13)-Dy(2)-O(20)	69.7(7)	O(1)#4-Dy(2)-O(20)	126.0(8)
O(14)#1-Dy(2)-O(20)	137.2(9)	O(2W)-Dy(2)-O(20)	140.3(11)
O(2)#5-Dy(2)-O(20)	76.7(9)	O(17)-Dy(2)-O(18)	69.2(7)
O(13)-Dy(2)-O(18)	135.0(7)	O(1)#4-Dy(2)-O(18)	142.3(8)
O(14)#1-Dy(2)-O(18)	73.2(8)	O(2W)-Dy(2)-O(18)	112.3(9)
O(2)#5-Dy(2)-O(18)	71.5(9)	O(20)-Dy(2)-O(18)	68.8(7)
O(7)#3-Dy(3)-O(19)	131.4(9)	O(7)#3-Dy(3)-O(12)	80.1(10)
O(19)-Dy(3)-O(12)	138.3(8)	O(7)#3-Dy(3)-O(8)	148.8(10)
O(19)-Dy(3)-O(8)	75.2(8)	O(12)-Dy(3)-O(8)	87.6(10)
O(7)#3-Dy(3)-O(20)	119.6(11)	O(19)-Dy(3)-O(20)	68.1(8)
O(12)-Dy(3)-O(20)	72.4(8)	O(8)-Dy(3)-O(20)	82.9(9)
O(7)#3-Dy(3)-O(9)#3	84.9(11)	O(19)-Dy(3)-O(9)#3	78.1(8)
O(12)-Dy(3)-O(9)#3	139.0(8)	O(8)-Dy(3)-O(9)#3	85.8(9)
O(20)-Dy(3)-O(9)#3	146.1(8)	O(7)#3-Dy(3)-O(17)	71.0(9)
O(19)-Dy(3)-O(17)	69.1(7)	O(12)-Dy(3)-O(17)	107.8(8)
O(8)-Dy(3)-O(17)	140.2(9)	O(20)-Dy(3)-O(17)	68.2(8)
O(9)#3-Dy(3)-O(17)	102.9(9)	O(7)#3-Dy(3)-O(3W)	76.4(9)
O(19)-Dy(3)-O(3W)	134.0(8)	O(12)-Dy(3)-O(3W)	71.6(8)
O(8)-Dy(3)-O(3W)	72.5(8)	O(20)-Dy(3)-O(3W)	136.8(8)
O(9)#3-Dy(3)-O(3W)	67.8(8)	O(17)-Dy(3)-O(3W)	146.9(7)
O(5)#5-Dy(4)-O(20)	146.1(10)	O(5)#5-Dy(4)-O(18)	93.8(9)
O(20)-Dy(4)-O(18)	74.3(7)	O(5)#5-Dy(4)-O(19)	135.7(10)

O(20)-Dy(4)-O(19)	69.3(8)	O(18)-Dy(4)-O(19)	67.3(7)
O(5)#5-Dy(4)-O(4)	80.4(9)	O(20)-Dy(4)-O(4)	133.5(8)
O(18)-Dy(4)-O(4)	111.1(7)	O(19)-Dy(4)-O(4)	71.0(7)
O(5)#5-Dy(4)-O(6)	110.3(11)	O(20)-Dy(4)-O(6)	82.7(10)
O(18)-Dy(4)-O(6)	155.4(8)	O(19)-Dy(4)-O(6)	96.7(7)
O(4)-Dy(4)-O(6)	78.7(9)	O(5)#5-Dy(4)-O(3)#5	75.3(10)
O(20)-Dy(4)-O(3)#5	77.9(8)	O(18)-Dy(4)-O(3)#5	106.6(7)
O(19)-Dy(4)-O(3)#5	147.1(7)	O(4)-Dy(4)-O(3)#5	136.1(7)
O(6)-Dy(4)-O(3)#5	76.2(8)		
Symmetry transformations used to generate equivalent atoms: #1: -x+1, y-1/2, -z+3/2; #2: -x+3/2, -y, z-1/2; #3: -x+2,y-1/2,-z+3/2; #4: -x+3/2, -y, z+1/2; #5: x-1/2, -y+1/2, -z+1.			

Reference

1 M. R. Maurya, A. K. Chandrakar, and S. Chand, *J. Mol. Catal. A: Chem.*, 2007, **278**, 12.

2 J. J. Guo, W. Wang, Y.-D. Zhang, L. Yang, S.-H. Zhang and X.-Q. Zhang, *J. Coord. Chem.*, 2013, **66**, 1467.

3 W. H. Wang, H. R. Tian, Z. C. Zhou, Y. L. Feng and J. W. Cheng, *Cryst. Growth Des.*, 2012, **12**, 2567.

4 (a) Rigaku, Process-Auto; Rigaku Americas Corporation: The Woodlands, Texas, 1998; (*b*) G. M. Sheldrick, *SHELXL97, Program for Crystal Structure Refinement*; University of Göttingen: Göttingen, Germany, 1997; (*c*) G. M. Sheldrick, *SHELXS97, Program for Crystal Structure Solution*; University of Göttingen: Göttingen, Germany, 1997.

5 Y.-C. Chen, L. Qin, Z.-S. Meng, D. Yang, C. Wu, Z. Fu, Y.-Z. Zheng, J.-L. Liu, R. Tarasenko, M. Orendáč, J. Prokleska, V. Sechovský and M.-L. Tong, *J. Mater. Chem. A*, 2014, DOI: 10.1039/C4TA01646G

6 G. Lorusso, J. W. Sharples, E. Palacios, O. Roubeau, E. K. Brechin, R. Sessoli, A. Rossin, F. Tuna, E. J. L. McInnes, D. Collison and M. Evangelisti, *Adv. Mater.*, 2013, **25**, 4653.

7 F. S. Guo, Y. C. Chen, J. L. Liu, J. D. Leng, Z. S. Meng, P. Vrábel, M. Orendáč and M. L.Tong, *Chem. Commun*., 2012, **48**, 12219.

8 Y. C. Chen, F. S. Guo, Y. Z. Zheng, J. L. Liu, J. D. Leng, R. Tarasenko, M. Orendáč, J. Prokleška, V. Sechovský and M. L. Tong, *Chem.–Eur. J.*, 2013, **19**, 13504.

9 F. S. Guo, J. D. Leng, J. L. Liu, Z. S. Meng and M. L. Tong, *Inorg. Chem.*, 2012, **51**, 405.

10 R. Sibille, T. Mazet, B. Malaman and M. François, *Chem.–Eur. J.*, 2012, **18**, 12970.

11 Y. L. Hou, G. Xiong, P. F. Shi, R. R. Cheng, J. Z. Cui and B. Zhao, *Chem. Commun.*, 2013, **49**, 6066.

12 L. X. Chang, G. Xiong, L. Wang, P. Cheng and B. Zhao, *Chem.Commun.*, 2013, **49**, 1055.

13 G. Lorusso, M. A. Palacios, G. S. Nichol, E. K. Brechin, O. Roubeau and M. Evangelisti, *Chem. Commun*. 2012, **48**, 7592.

14 S. Biswas, A. Adhikary, S. Goswami and S. Konar, *Dalton Trans.*, 2013, **42**, 13331.

15 F. S. Guo, Y. C. Chen, L. L. Mao, W. Q. Lin, J. D. Leng, R. Tarasenko, M. Orendáč, J. Prokleška, V. Sechovský and M. L. Tong, *Chem.-Eur. J.,* 2013, **19**, 14876.

16 S. J. Liu, C. C. Xie, J. M. Jia, J. P. Zhao, S. D. Han, Y. Cui, Y. Li, and X. H. Bu, *Chem. Asian J.*, 2014, DOI: 10.1002/asia.201301586.

17 M. Evangelisti, O. Roubeau, E. Palacios, A. Camon, T. N. Hooper, E. K. Brechin and J. J. Alonso, *Angew. Chem., Int. Ed.*, 2011, **50**, 6606.

18 J. B. Peng, Q. C. Zhang, Y. Z. Zheng, X. J. Kong, Y. P. Ren, L. S. Long, R. B. Huang, L. S. Zheng and Z. P. Zheng, *J. Am. Chem. Soc.*, 2012, **134**, 3314.

19 J. M. Jia, S. J. Liu, Y. Cui, S. D. Han, T. L. Hu, and X. H. Bu, *Cryst. Growth Des.*, 2013, **13**, 4631.

20 M. Wu, F. Jiang, X. Kong, D. Yuan, L. Long, S. A. Al-Thabaiti and M. Hong, *Chem. Sci.* 2013, **4**, 3104.

21 J. B. Peng, Q. C. Zhang, X. J. Kong, Y. P. Ren, L. S. Long, R. B. Huang, L. S. Zheng and Z. P. Zheng, *Angew. Chem., Int. Ed*., 2011, **50**, 10649.

22 Y. Bing, N. Xu, W. Shi, K. Liu, and P. Cheng, *Chem. Asian J.*, 2013, **8**, 1412.

23 Y. Zheng, Q. C. Zhang, L. S. Long, R. B. Huang, A. Müller, J. Schnack, L. S. Zheng and Z. Zheng, *Chem. Commun*., 2013, **49**, 36.

24 Y. Z. Zheng, E. M. Pineda, M. Helliwell and R. E. P. Winpenny, *Chem.-Eur. J.,* 2012, **18**, 4161;

25 E. M. Pineda, F. Tuna, R. G. Pritchard, A. C. Regan, R. E. P. Winpenny and E. J. L. McInnes, *Chem. Commun*., 2013, **49**, 3522.

26 S. J. Liu, J. P. Zhao, J. Tao, J. M. Jia, S. D. Han, Y. Li, Y. C. Chen and X. H. Bu, *Inorg. Chem.*, 2013, **52**, 9163.

27 S. K. Langley, N. F. Chilton, B. Moubaraki, T. Hooper, E. K. Brechin, M. Evangelisti and K. S. Murray, *Chem. Sci*., 2011, **2**, 1166.

28 P. F. Shi, Y. Z. Zheng, X. Q. Zhao, G. Xiong, B. Zhao, F. F. Wan and P. Cheng, *Chem.-Eur. J.*, 2012, **18**, 15086.

29 Y. Q. Lan, S. L. Li, K. Z. Shao, X. L. Wang, D. Y. Du, Z. M. Su and D. J. Wang, *Cryst. Growth & Des.*, 2008, **8**, 3490.

30 L. Hou, J. P. Zhang, X. M. Chen and S. W. Ng, *Chem. Commun.*, 2008, 4019.

31 M. H. Zeng, H. H. Zou, S. Hu, Y. L. Zhou, M. Du and H. L. Sun, *Cryst. Growth & Des.*, 2009, **9**, 4239.

32 L. Hou, W. X. Zhang, J. P. Zhang, W. Xue, Y. B. Zhang and X. M. Chen, *Chem. Commun.*, 2010, **46**, 6311.

33 X. Li, H. L. Sun, X. S. Wu, X. Qiu and M. Du, *Inorg. Chem.*, 2010, **49**, 1865.

34 Q. Y. Yang, K. Li, J. Luo, M. Pan and C. Y. Su, *Chem. Commun.*, 2011, **47**, 4234.

35 Y, Q. Sun, H. X. Mei, h. H. Zhang, Y. P. Chen and R. Q. Sun, *J. Clust. Sci.*, 2011, **22**, 279.