Electronic Supplementary Material (ESI) for Dalton Transactions.
This journal is © The Royal Society of Chemistry 2015

Magnetic and magnetocaloric properties of an unusual family of carbonate-panelled $[Ln^{III}_6Zn^{II}_2]$ cages

Waqas Sethi, Sergio Sanz, Kasper S. Pedersen, Mikkel A. Sørensen, Gary S. Nichol, Giulia Lorusso, Marco Evangelisti, Euan K. Brechin and Stergios Piligkos

Table S1. Crystallographic details for complexes **1**-**5**.

	1 (Gd_6Zn_2)	**2** (Dy_6Zn_2)	**3** (Sm_6Zn_2)	**4** (Eu_6Zn_2)	**5** (Tb_6Zn_2)
M, g mol^{-1}	4374.15	4462.38	4549.75	4403.20	4359.87
Crystal system	Triclinic	Triclinic	Triclinic	Triclinic	Triclinic
Space group	P -1	P -1	P -1	P -1	P -1
***a*/ Å**	20.6864(3)	20.6705(3)	20.7294(4)	20.7014(4)	22.1510(3)
***b*/ Å**	22.1669(4)	21.9660(4)	22.2218(4)	22.2355(5)	29.0764(3)
***c*/ Å**	25.2175(4)	25.1531(3)	25.3356(4)	25.2949(5)	32.1304(3)
***α* (°)**	71.9252(14)	71.9837(14)	71.8490(9)	71.8158(18)	75.8497(8)
***β* (°)**	88.2848(12)	88.2024(10)	88.2919(9)	88.3250(15)	88.0840(9)
***γ* (°)**	63.8427(17)	64.4382(15)	63.4640(9)	63.667(2)	79.2672(10)
***V*/ Å^3**	9789.5(3)	9728.1(3)	9839.2(3)	9832.1(4)	19713.8(4)
***T*/ K**	120	120	120	120	120
Z	2	2	2	2	4
***D*$_x$/ Mg m^{-3}**	1.484	1.525	1.536	1.487	1.469
Crystal shape and colour	Pale yellow rods	Colourless rods	Pale yellow blocks	Yellow rods	Pale yellow blocks
Crystal size/ mm	0.578 x 0.3932 x 0.1282	0.4576 x 0.274 x 0.0328	0.335 x 0.219 x 0.144	0.5853 x 0.268 x 0.1082	0.44 x 0.22 x 0.07
***μ*/ mm^{-1}**	2.32	2.61	2.09	2.211	11.33
unique data	57700	44027	45021	57696	81683
unique data, ($I > 2\sigma(I)$)	44403	30393	30965	44399	51679
***R*$_1$,[a] *wR*$_2$[b]**	0.051, 0.124	0.057, 0.145	0.039, 0.103	0.0514, 0.1128	0.057, 0.173
Goodness of fit	1.09	1.05	1.02	1.092	1.03

[a] $R_1 = \sum \left| |F_o| - |F_c| \right| / \sum |F_o|$ for all observations. [b] $wR_2 = \left[\sum w\left(F_o^2 - F_c^2\right)^2 / \sum w\left(F_o^2\right)^2 \right]^{1/2}$ for all data.

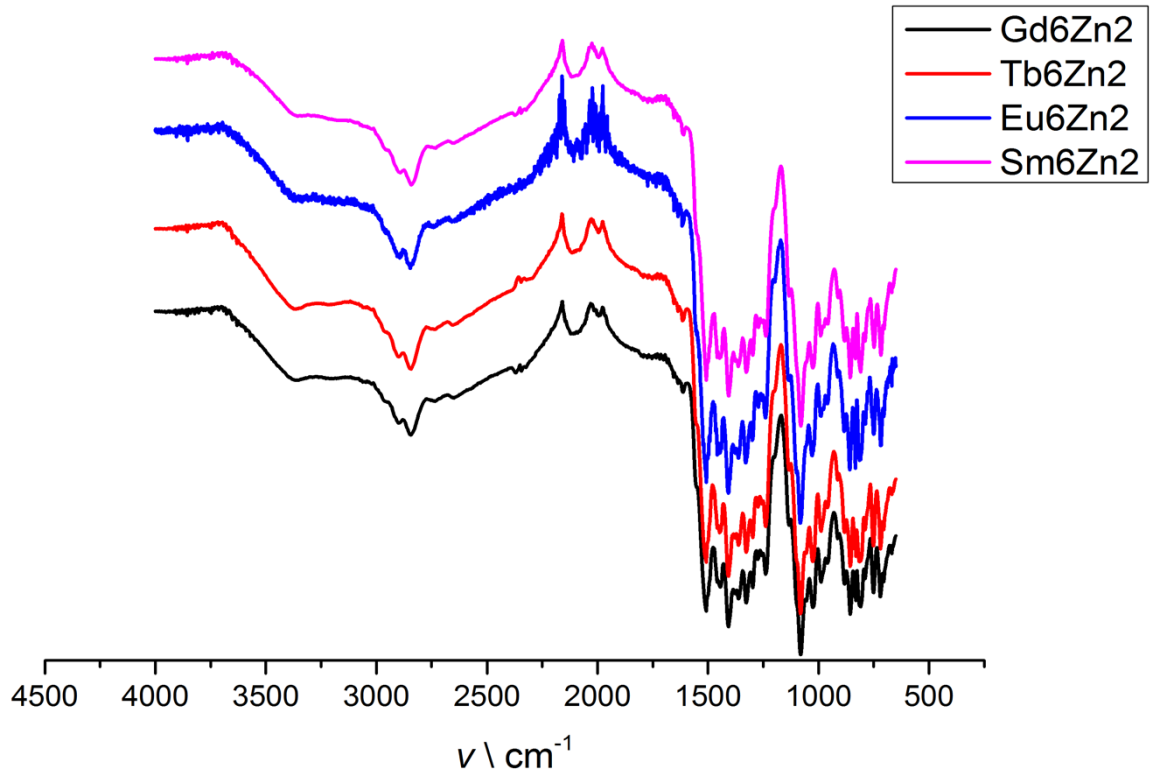

Figure S1. IR data of compounds **1**, **3**, **4** and **5**.

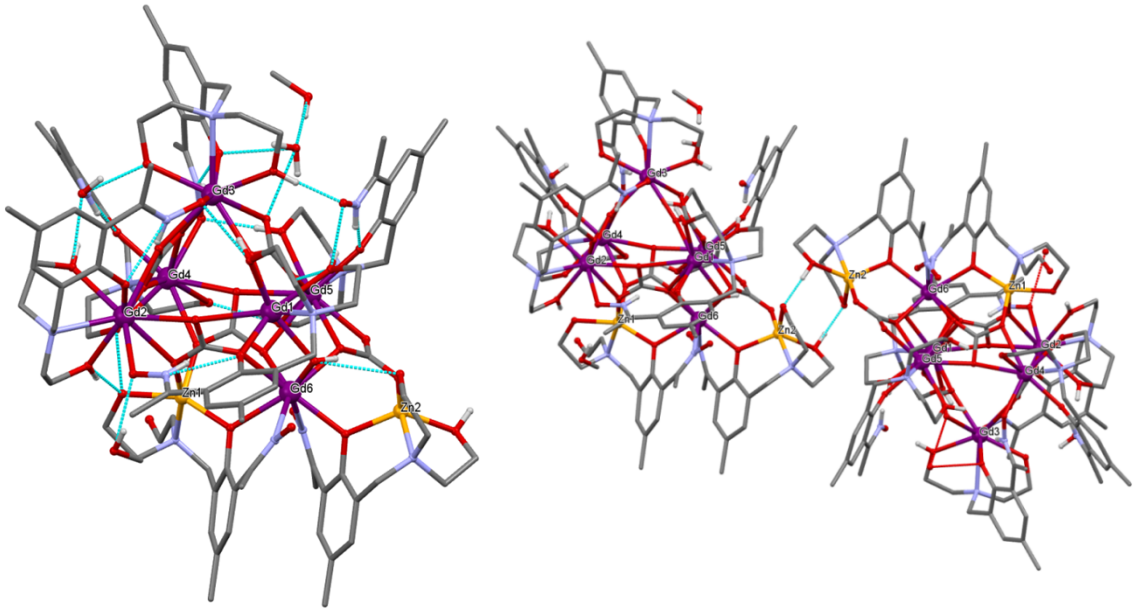

Figure S2. Intramolecular H-bonding in the cation of **1** represented by the dashed light-blue lines (left). H-bonded dimers of the cations of **1** *via* the diethanolamine units bonded to Zn2 (right).

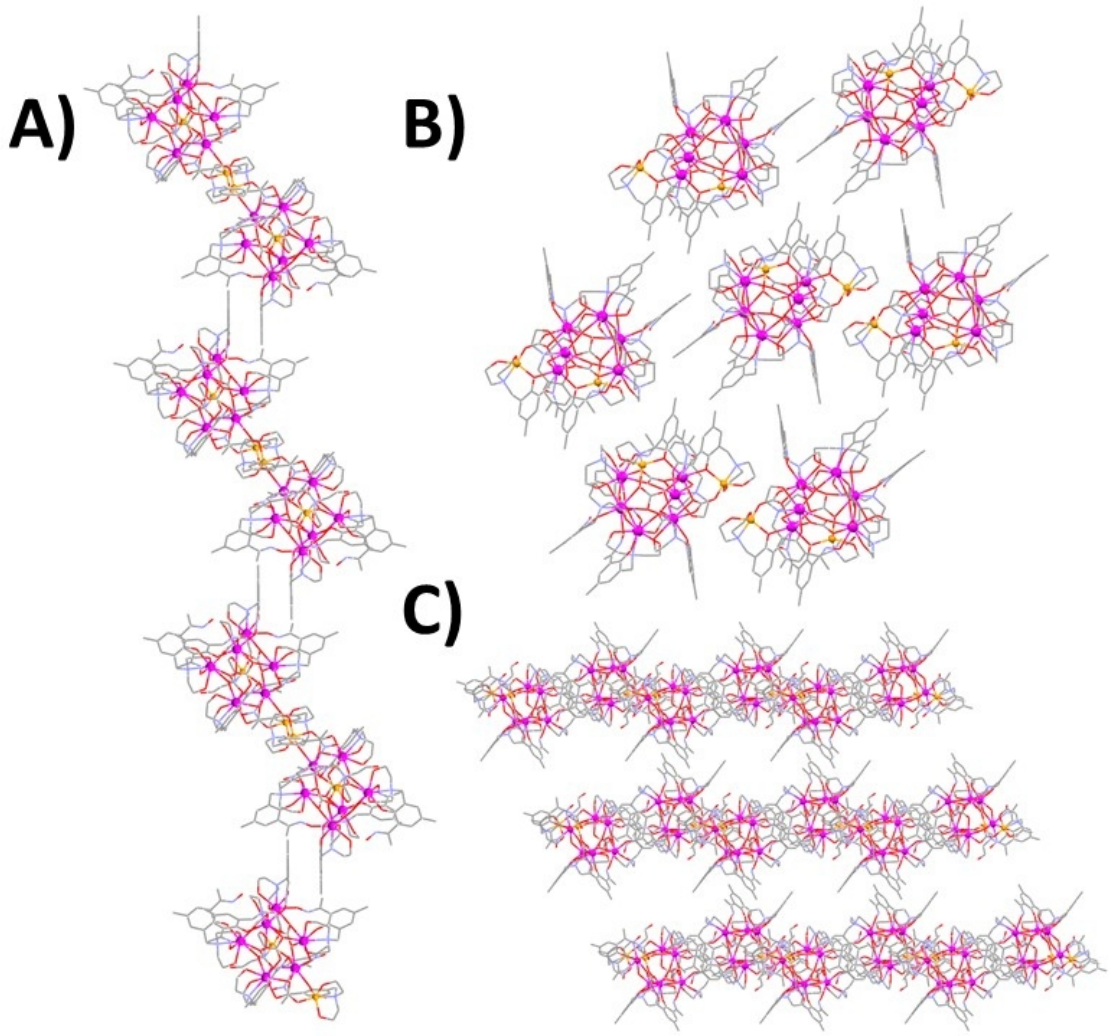

Figure S3. The packing of the cations of **1** in the crystal. A) Serpentine-like H-bonded chain of the cations of **1**. B) 2D sheets of the cations in **1**. C) The layered structure of the cations in **1** in the extended structure.

Bond lengths (consituents of the metal ion core)					
	1	**2**	**3**	**4**	**5**
Ln(1)···Ln(2)	5.0206(7)	5.0206(7)	5.0602(7)	5.0360(7)	4.9932(9)
Ln(1)···Ln(3)	4.6393(6)	4.6393(6)	4.6827(6)	4.6432(6)	4.6236(8)
Ln(1)···Ln(5)	5.2925(5)	5.2925(5)	5.2763(5)	5.2865(5)	5.2817(8)
Ln(1)···Ln(6)	3.8858(7)	3.8858(7)	3.9167(7)	3.8967(7)	3.8728(7)
Ln(2)···Ln(3)	5.0430(7)	5.0430(7)	5.0780(7)	5.0506(7)	5.0492(7)
Ln(2)···Ln(4)	4.9842(5)	4.9842(5)	5.0069(4)	4.9762(5)	4.9569(8)
Ln(2)···Ln(6)	6.3462(6)	6.3462(6)	6.3955(6)	6.3611(6)	6.314(1)
Ln(3)···Ln(4)	5.0327(7)	5.0327(7)	5.0740(7)	5.0486(7)	5.0160(7)
Ln(3)···Ln(5)	5.7941(6)	5.7941(6)	5.8117(6)	5.8070(6)	5.7785(8)
Ln(4)···Ln(5)	4.8057(7)	4.8057(7)	4.8309(7)	4.8195(7)	4.799(1)
Ln(5)···Ln(6)	4.0720(6)	4.0720(6)	4.1061(6)	4.0674(6)	4.0550(7)
Ln(2)···Zn(1)	4.3627(8)	4.345(1)	3.3902(8)	4.3728(8)	4.365(1)
Ln(4)···Zn(1)	4.3143(8)	4.297(1)	4.3351(8)	4.3143(8)	4.3130(9)
Ln(6)···Zn(1)	3.7692(7)	3.7444(9)	3.7930(7)	3.7811(7)	3.758(1)
Ln(6)···Zn(2)	3.7624(7)	3.7519(9)	3.7808(7)	3.7729(7)	3.774(1)
Bond angles (constituents of the metal ion core)					
	1	**2**	**3**	**4**	**5**
Ln(1)-(μ_2-O)-Ln(2)	170.5(2)	153.8(2)	170.0(1)	170.6(2)	170.4(2)
Ln(1)-(μ_2-O)-Ln(3)	152.3(2)	150.1(2)	153.9(2)	152.4(2)	152.1(2)
Ln(1)-(μ_2-O)-Ln(6)	111.6(1)	111.1(2)	111.3(1)	111.6(1)	112.0(2)
Ln(1)-(μ_2-O)-Ln(6)‘	109.3(1)	112.5(2)	108.6(1)	109.3(1)	109.2(2)
Ln(2)-(μ_2-O)-Ln(3)	161.0(2)	163.9(2)	160.8(1)	161.0(2)	160.7(2)
Ln(2)-(μ_2-O)-Ln(4)	164.2(2)	164.3(2)	163.9(1)	164.2(2)	164.9(2)
Ln(2)-(μ_2-O)-Zn(1)	139.9(2)	143.1(2)	139.9(2)	139.9(2)	140.7(2)
Ln(3)-(μ_2-O)-Ln(4)	163.7(2)	160.8(2)	163.1(1)	163.7(2)	163.7(2)
Ln(4)-(μ_2-O)-Ln(5)	153.3(2)	171.4(2)	153.1(1)	153.5(2)	153.9(2)
Ln(4)-(μ_2-O)-Zn(1)	142.6(2)	140.1(3)	142.3(2)	142.6(2)	143.4(2)
Ln(5)-(μ_2-O)-Ln(6)	111.7(1)	112.4(2)	111.4(1)	111.3(1)	111.0(2)
Ln(5)-(μ_2-O)-Ln(6)‘	111.5(1)	109.8(2)	111.1(1)	111.5(1)	111.5(2)
Ln(6)-(μ_2-O)-Zn(1)	118.2(2)	118.2(2)	118.3(2)	118.3(2)	117.8(2)
Ln(6)-(μ_2-O)-Zn(2)	120.5(2)	121.5(2)	120.3(2)	120.5(2)	121.5(2)

Table S2 Selected bond lengths (Å) and angles (°) for compounds **1-5**.

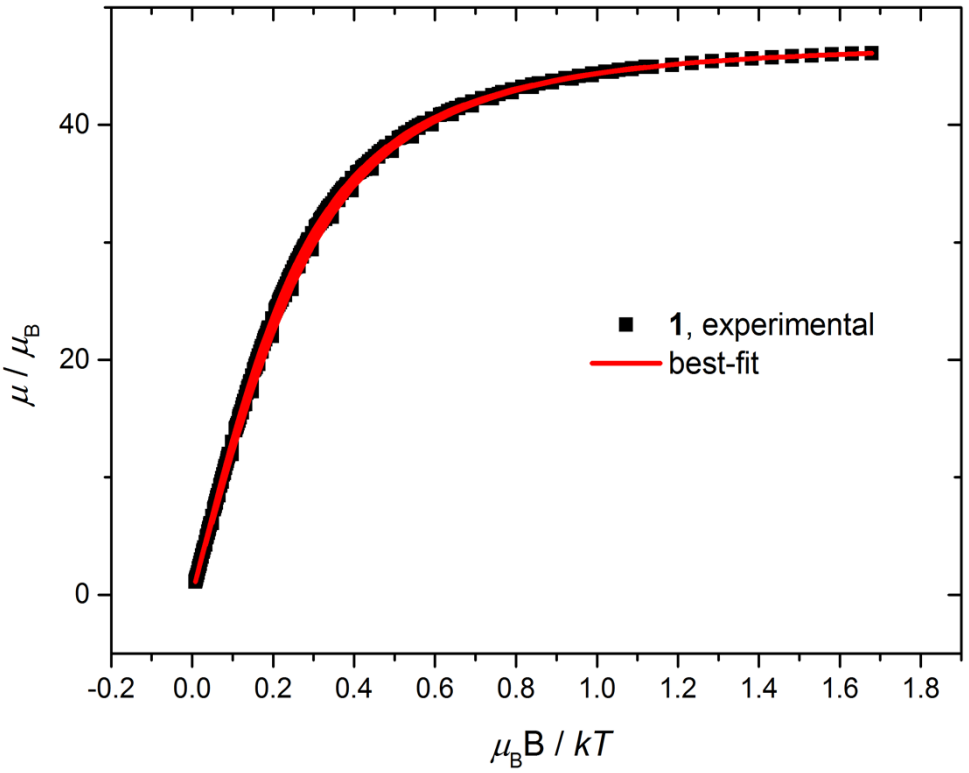

Figure S4. *M* vs. *H*/*T* data and best-fits for **1**. The fitted parameter is $g_{Gd} = 2$.

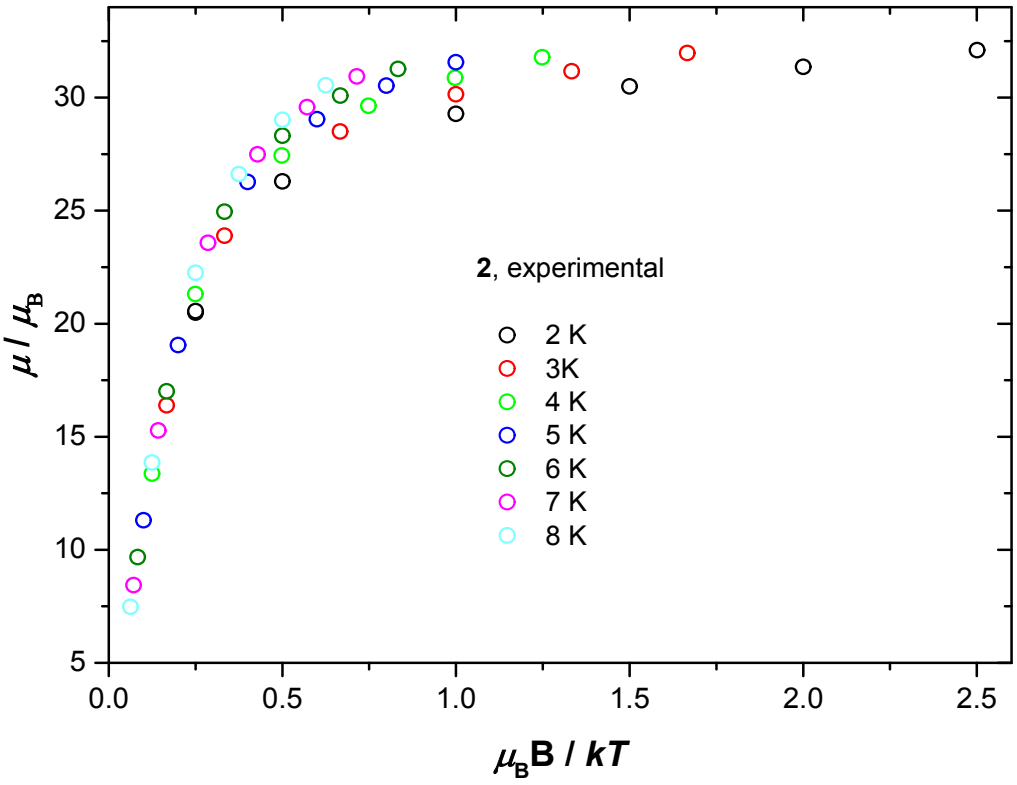

Figure S5. *M* vs. *H*/*T* data for **2**.

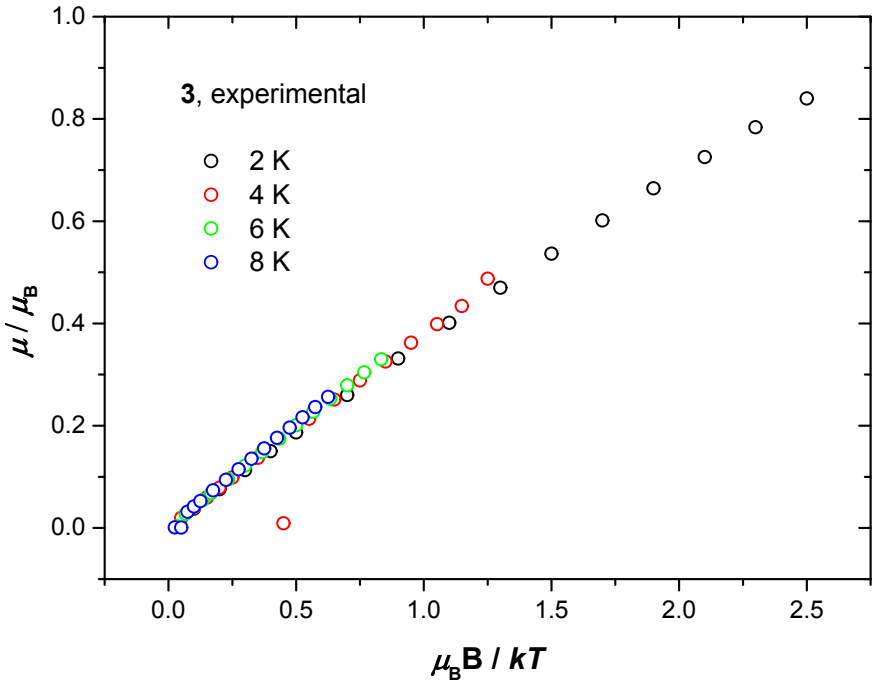

Figure S6. *M* vs. *H*/*T* data for **3**.

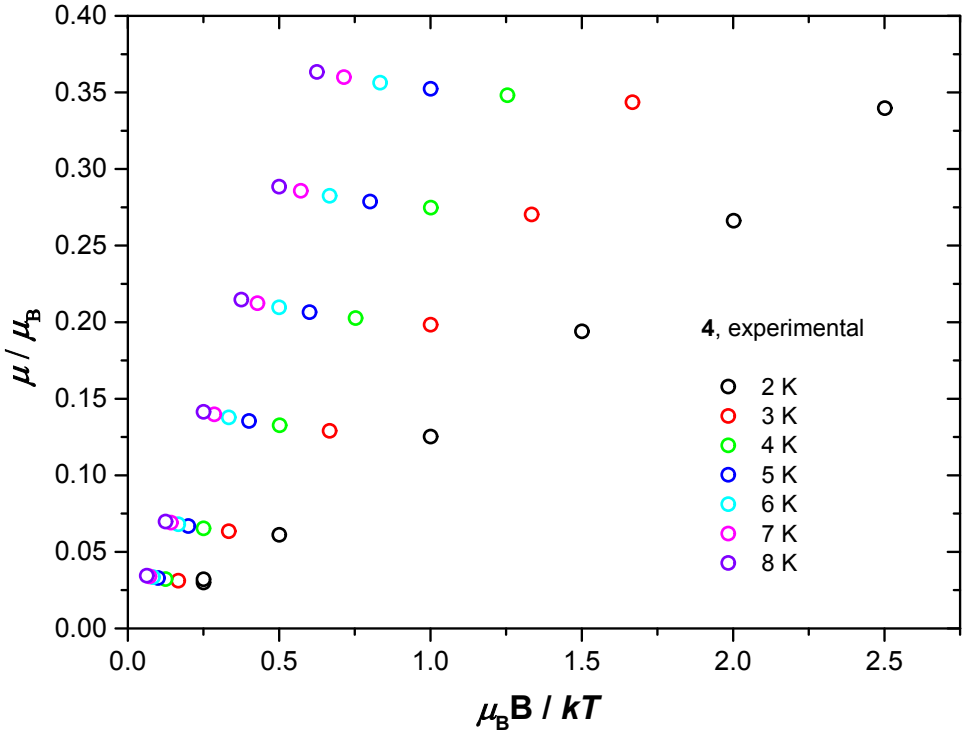

Figure S7. *M* vs. *H*/*T* data for **4**.

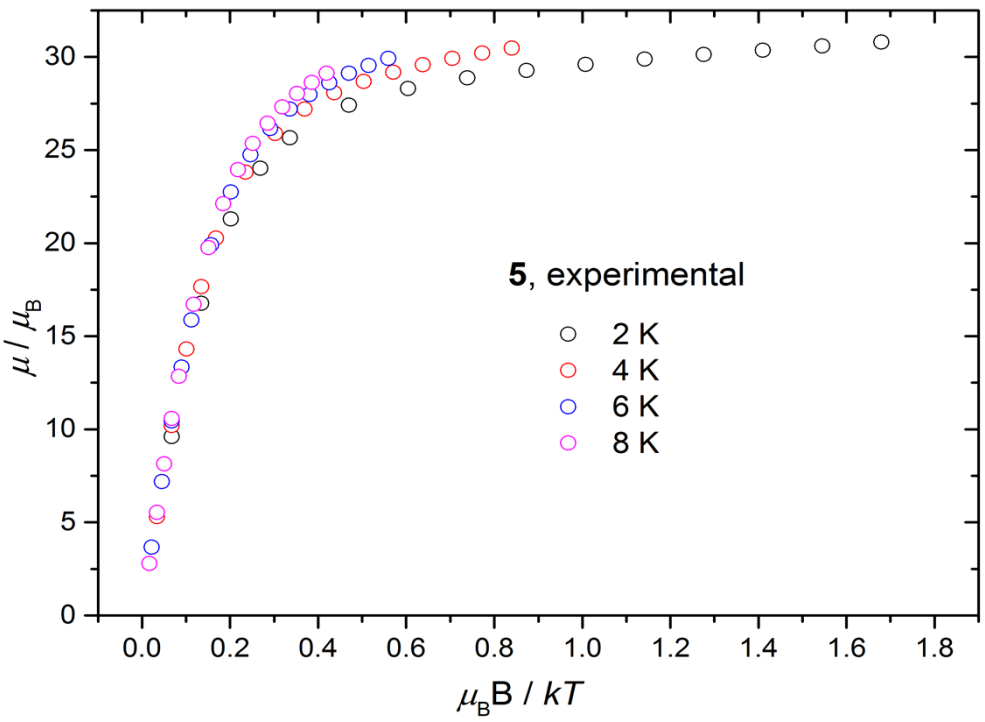

Figure S8. *M* vs. *H*/*T* data for **5**.

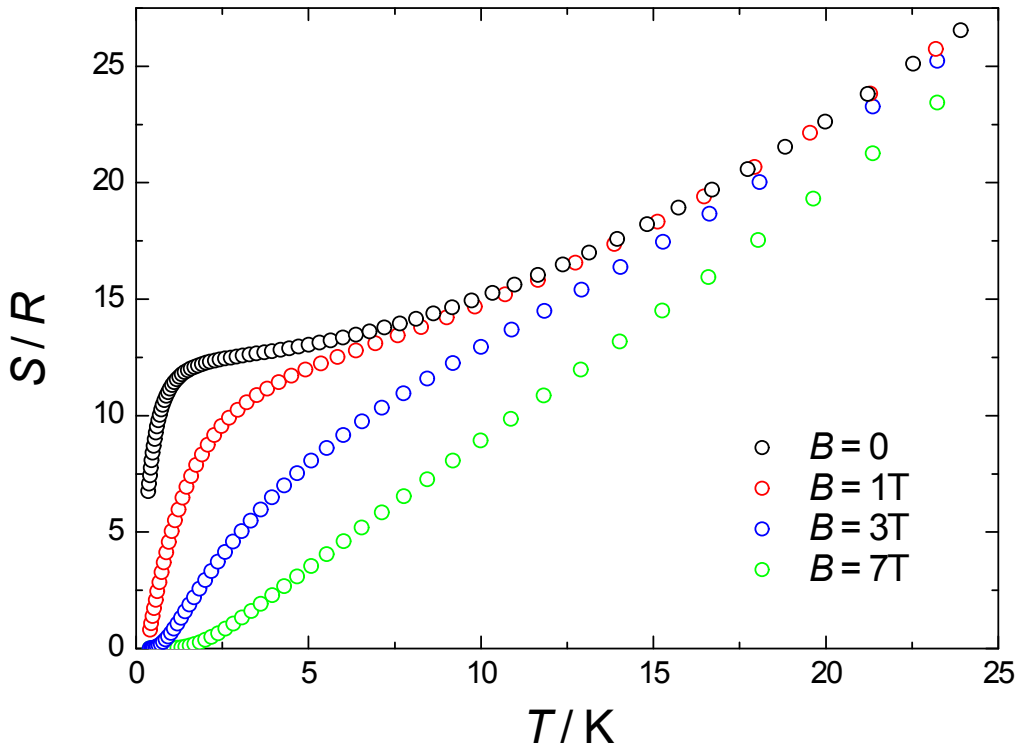

Figure S9. Entropy of **1** vs. *T* for the labelled applied magnetic fields, as obtained from the heat capacity data in Fig. 4.