<div align="center">**SUPPORTING INFORMATION**</div>

Increasing the dimensionality of cryogenic molecular coolers: Gd-based polymers and metal-organic frameworks

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Synthesis of compound 2.

Compound **2** was prepared as described in reference 9.

$Gd(NO_3)_3 \cdot 6H_2O$ (300 mg, 0.67 mmol) dissolved in DMF (10 mL) was added to a solution of N-H_2BDC (181 mg, 1.00 mmol) in DMF (10 mL) in a glass tube (diameter 18 mm, height 180 mm). The tube was sealed; the contents were well mixed and then placed in an oven at 120 ºC for 24 h, resulting in the formation of brownish crystals (240 mg, 64%). The crystals were recovered by filtration, washed with a little cold DMF (~5 mL), and then dried in air. Anal. found for **2** $[Gd_2(N\text{-}BDC)_3(dmf)_4]_\infty$: C, 37.64; H, 3.57; N, 8.50%. Calcd: C, 37.79; H, 3.79; N, 8.57%. Selected IR data (Neat, see Fig. S5): 3442 (w) $v(OH)$, 3342 (w) $v(NH)$, 2930 (w) $v(CH)$, 1667 (m) $v(CO)$, 1649 (m) $v_{as}(COO)$, 1540 (m) $v(CdC)$, 1493 (m) $v_s(COO)$, 1417 (m) $v(CO)$, 1373 (s) $v(CN)$, 1252 (m) $v(CO)$, 770 (s) $\delta(OCO)$, 676 (s) $\delta(dCH)$ cm^{-1}.

Physical Measurements.

Magnetic measurements were performed using a Quantum Design MPMS-XL SQUID magnetometer. The measured values were corrected for the experimentally measured contribution of the sample holder, while the derived susceptibilities were corrected for the diamagnetism of the samples, estimated from Pascal's tables.

Heat capacities in the range 0.35-130 K were obtained using the relaxation method and the heat capacity option of a Quantum Design PPMS set-up.

Table S1 Crystal data and structure refinement for compound **1** (eb2081).

Identification code	eb2081
Chemical formula (moiety)	$C_5H_{11}GdO_8$
Chemical formula (total)	$C_5H_{11}GdO_8$
Formula weight	356.39
Temperature	100(2) K
Radiation, wavelength	MoKα, 0.71073 Å
Crystal system, space group	monoclinic, P2$_1$/m
Unit cell parameters	a = 7.9966(4) Å $\alpha = 90°$
	b = 6.5839(2) Å $\beta = 109.425(5)°$
	c = 9.9447(4) Å $\gamma = 90°$
Cell volume	493.77(4) Å^3
Z	2
Calculated density	2.397 g/cm^3
Absorption coefficient μ	6.734 mm^{-1}
F(000)	338
Crystal colour and size	colourless, $0.27 \times 0.18 \times 0.09$ mm^3
Reflections for cell refinement	2173 (θ range 2.8 to 29.1°)
Data collection method	Agilent Technologies XCalibur
	ω scans
θ range for data collection	2.8 to 29.1°
Index ranges	h −10 to 10, k −9 to 8, l −13 to 12
Completeness to $\theta = 25.0°$	99.8 %
Reflections collected	4816
Independent reflections	1283 (R$_{int}$ = 0.0439)
Reflections with F^2>2σ	1095
Absorption correction	analytical
Min. and max. transmission	0.2608 and 0.5825
Structure solution	direct methods
Refinement method	Full-matrix least-squares on F^2
Weighting parameters a, b	0.0444, 0.0602
Data / restraints / parameters	1283 / 16 / 94
Final R indices [F^2>2σ]	R1 = 0.0302, wR2 = 0.0758
R indices (all data)	R1 = 0.0364, wR2 = 0.0819
Goodness-of-fit on F^2	1.079
Largest and mean shift/su	0.000 and 0.000
Largest diff. peak and hole	2.49 and −1.07 e Å^{-3}

Table S2 Bond lengths [Å] and angles [°] for compound **1** (eb2081).

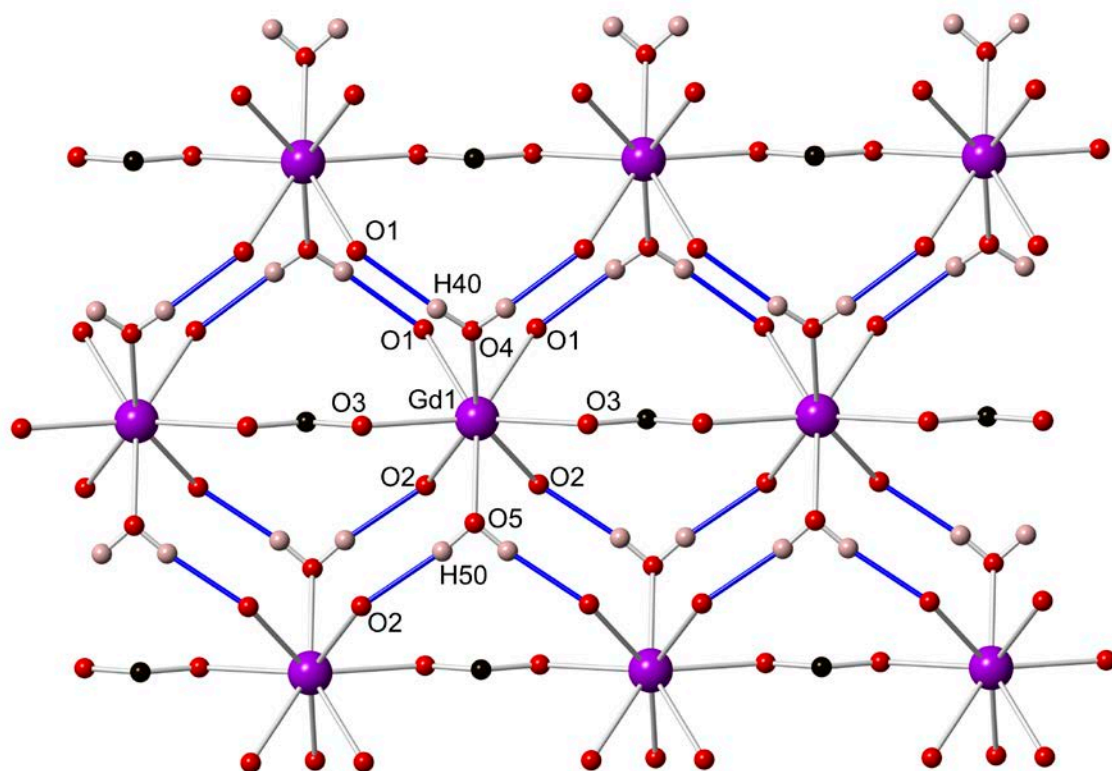| Gd(1)–O(1)	2.450(3)	Gd(1)–O(1A)	2.450(3)
Gd(1)–O(2)	2.455(3)	Gd(1)–O(2A)	2.455(3)
Gd(1)–O(3)	2.347(3)	Gd(1)–O(3A)	2.347(3)
Gd(1)–O(4)	2.368(4)	Gd(1)–O(5)	2.373(5)

Symmetry operations for equivalent atoms

A: x,–y+1/2,z   B: x,–y–1/2,z

Table S3 Hydrogen bonds for eb2081 [Å and °].

| D–H...A	d(D–H)	d(H...A)	d(D...A)	<(DHA)
O(4)–H(4O)...O(1C)	0.84(3)	1.91(4)	2.720(4)	164(4)
O(5)–H(5O)...O(2D)	0.84(3)	1.89(4)	2.715(4)	171(5)

Symmetry operations for equivalent atoms

C: –x+1,–y,–z   D: –x+1,y+1/2,–z+1

Fig. S1 Packing plot along the *a* axis of the structure of **1**. H-bonds between adjacent chains in the *bc* plane are shown as blue thick lines. The Gd1, its coordination sphere (Table S2) and atoms involved in H-bonds (Table S3) are labelled. The acetate methyl groups and the formate hydrogens are omitted for clarity.
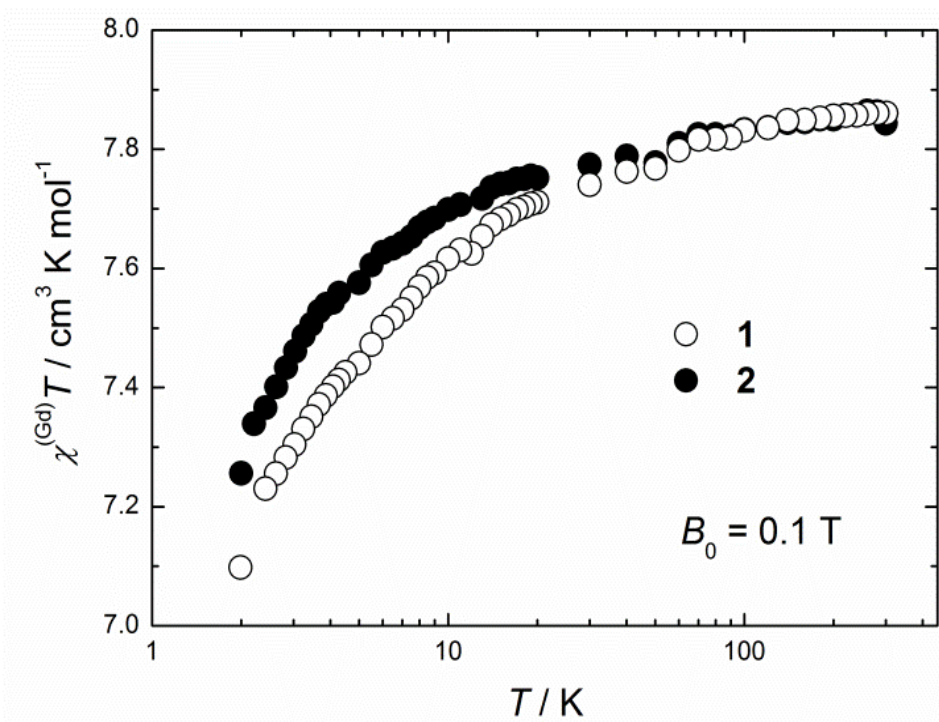
Fig. S2 Temperature-dependencies (2–300 K) of the dc molar susceptibility per Gd^{3+} ion for **1** (empty markers) and **2** (filled markers) collected in an applied field of 0.1 T.
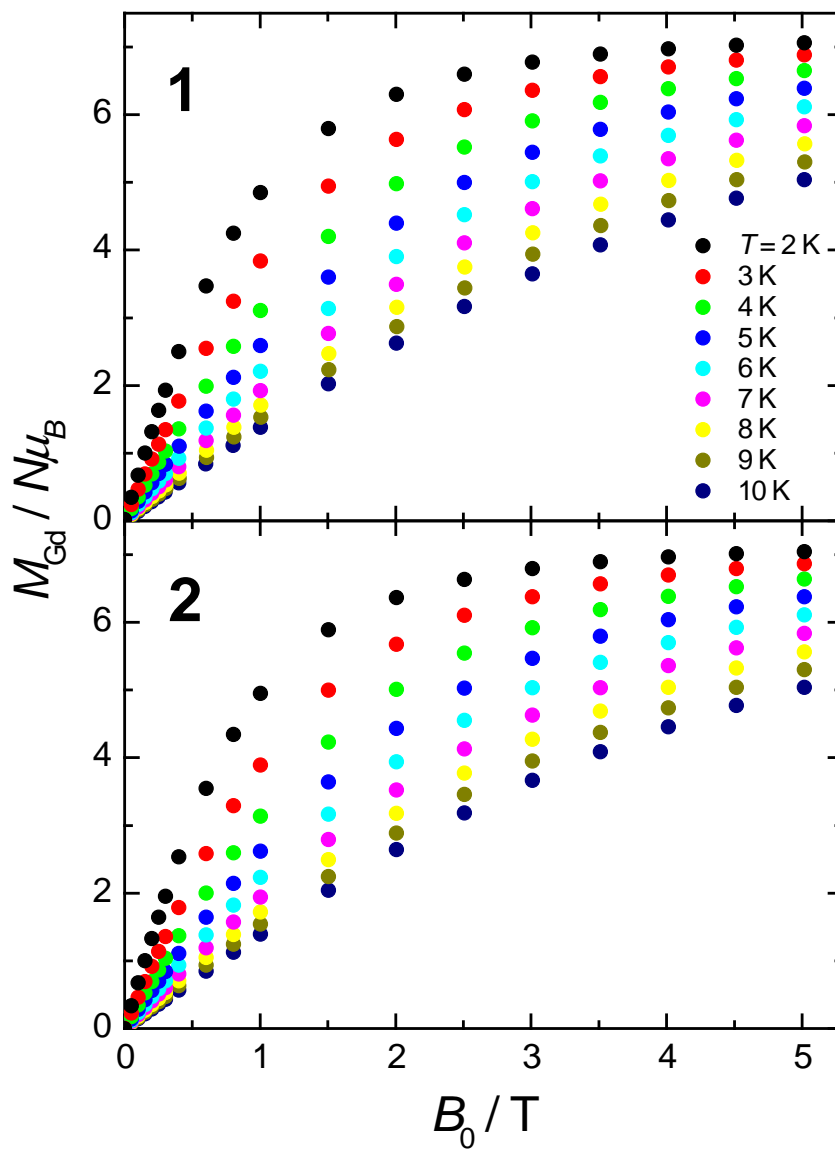
Fig. S3 Field-dependencies of isothermal normalized magnetizations per Gd^{3+} ion, collected for temperatures ranging from 2 to 10 K, for **1** (top panel) and **2** (bottom panel).
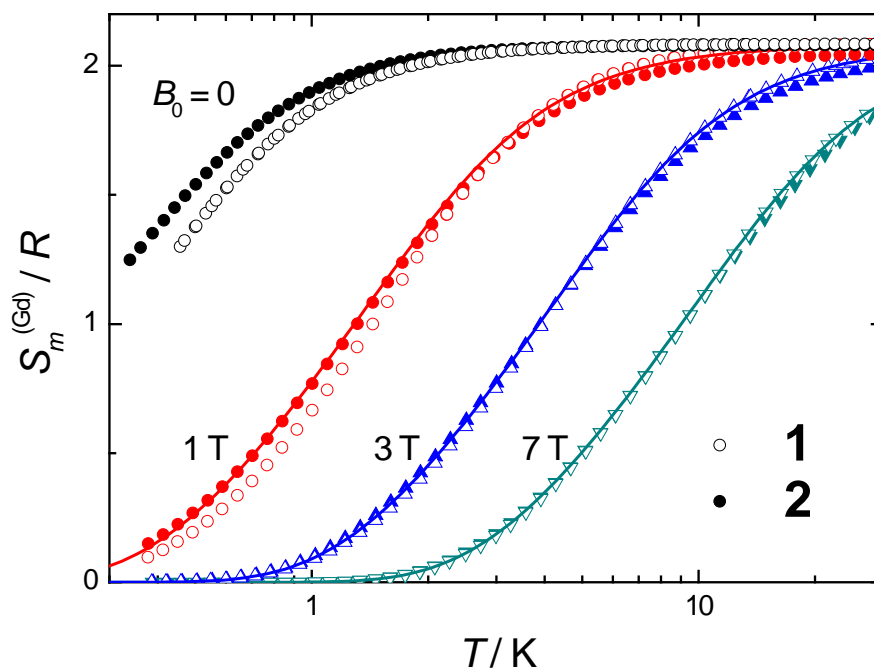
**Fig. S4** Temperature-dependencies of the magnetic entropies per Gd^{3+} ion $S_m^{(Gd)}$, normalized to the gas constant R, for **1** (empty markers) and **2** (filled markers), as obtained from the respective $C_m^{(Gd)}$ (see Fig. 3). In the case of $B_0 = 0$, our experimental blindness for temperatures lower than approximately 0.35 K forced us to add a constant value to the zero-field $S_m^{(Gd)}(T)$ to match the limiting value at high temperature. This procedure does not jeopardize our evaluation of the MCE. Solid lines are calculations for non-interacting $S = 7/2$ spin centers for the corresponding applied fields, as labelled.
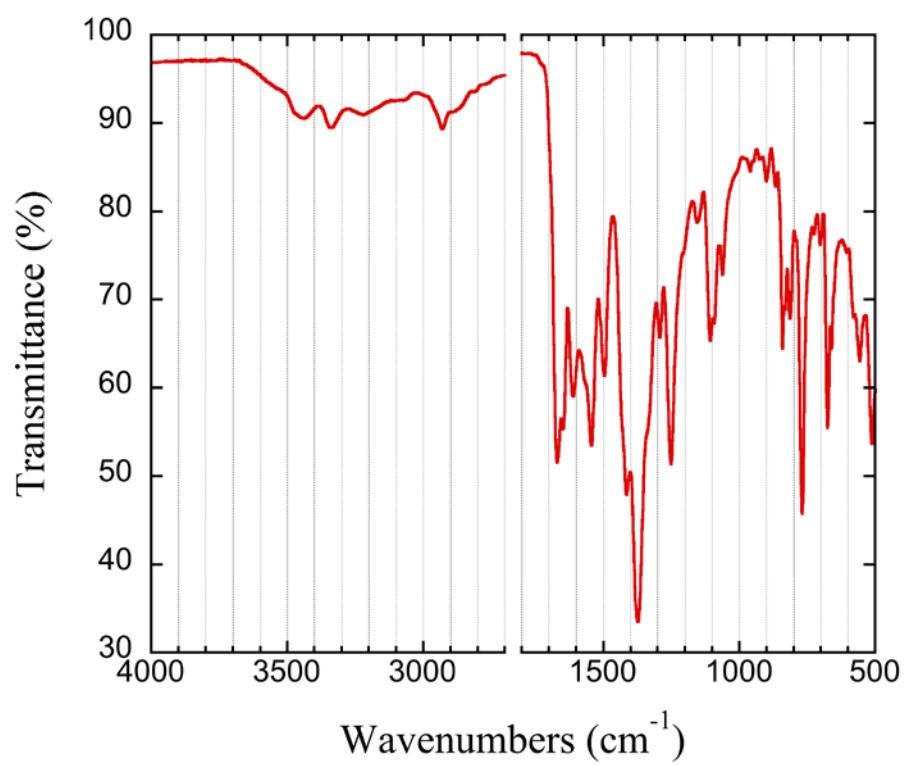
Fig. S5 IR spectrum (neat) of crystals compound **2** (see synthesis section for peak assignements).
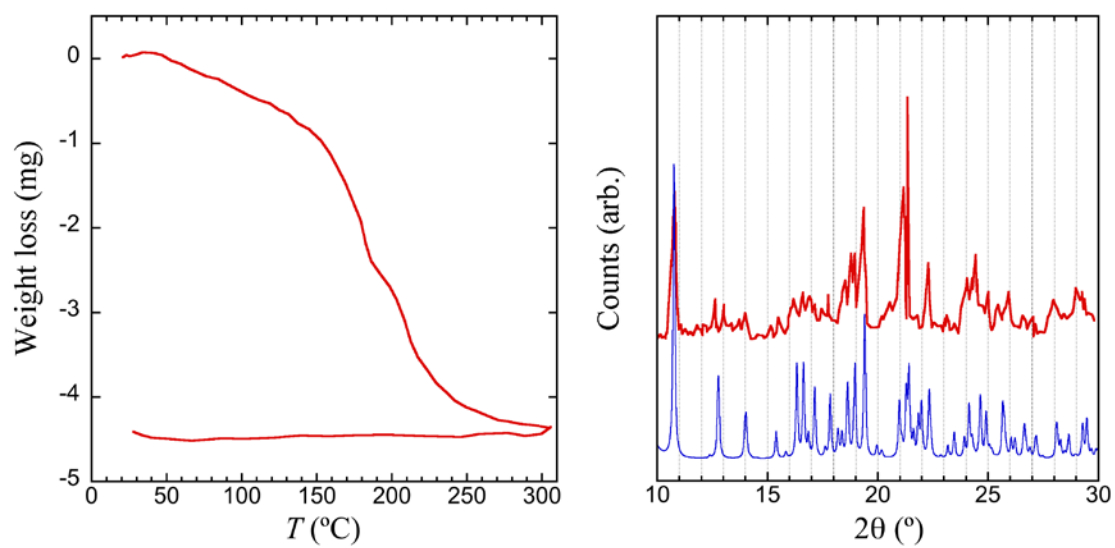
Fig. S6 Left: Thermogravimetric data for compound **2** showing loss of dmf above 150 ºC. Right: Experimental (red) and simulated (blue) powder XRD data for compound **2**.