Supporting Information:

A novel alb metalloring organic framework with a $\{Ni_{12}Gd_{24}\}$ cage exhibiting significant magnetocaloric effect

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1. Experiment Section

1.1 Materials and Physical Measurements.

All the materials were purchased from the commercial sources and used without further purification. Thermogravimetric experiments were performed using a GA/NETZSCH STA449C instrument heated from 40−1000 °C (heating rate of 10 °C min^{-1}, nitrogen stream). Elemental analyses of C, H and N were carried out with a Vario EL III elemental analyzer. High-resolution PXRD patterns were collected using Miniflex II (Cu-$K\alpha$ radiation: λ = 1.54056 Å) in the range of 5° < 2θ < 60°. IR spectra were performed on a Perkin-Elmer Spectrum One using KBr pellets in the range 2300-500 cm^{-1}. Magnetic susceptibilities were measured for **1** with a Quantum Design PPMS-9T system. Diamagnetic corrections were made using Pascal's constants.

1.2 Synthesis of 1.

A mixture of Gd(NO)$_3$·6H$_2$O (0.50 mmol, 0.226 g), 6-mercapto-3-pyridinecarboxylic acid (0.50 mmol, 0.078 g), NiCl$_2$·6H$_2$O (0.25 mmol, 0.059 g) and KOH (1.00 mmol, 0.056 g) was kept in a 20 mL of Teflon-lined stainless steel vessel with 4 ml H$_2$O, and was heated at 210 ºC for one day under autogenous pressure. After cooling to room temperature, green-brown hexagonal crystals of **1** were obtained. Yield: 82 mg (45.38% based on Ni). Anal. calcd. for C$_{72}$H$_{124}$N$_{12}$O$_{74}$S$_{12}$Gd$_8$Ni$_6$ (4336.81): C 19.94, H 2.88, N 3.88; found: C 19.56, H 3.11, N 3.65. IR (KBr, cm^{-1}): 3403 m, 1601 vs, 1541 m, 1410 vs, 1385 vw, 1261 w, 1169 m, 1128 vw, 1103 s, 1032 w, 853 w, 779 m, 729 w, 735 vw, 542 w.

1.3 Crystal Structure Analysis.

A suitable single crystal of the compound was carefully selected and glued to thin glass fibers with epoxy resin. Intensity data were collected at room temperature on a Rigaku 724 CCD area-detector Diffractometer with a graphite monochromator utilizing Mo Kα radiation (λ = 0.71073 Å). *CrystalClear* software was used for data reduction and empirical absorption correction. The structure was solved by direct methods using SHELXL-97[1] and refined by full-matrix least-squares on F^2 using *SHELX-2016* program.[2] All the non-hydrogen atoms were refined anisotropically. C-

bound H atoms were placed geometrically and refined as riding, whereas H atoms of coordinated water molecules were located in difference Fourier maps, assigned isotropic thermal parameters, and allowed to ride on their respective parent atoms before the final cycle of least-squares refinement. Crystallographic data and other pertinent information for compound **1** are summarized in Table S1. In compound **1**, some constraints (FLAT, SADI, SIMU and DFIX) were applied to 6-mnaH$_2$ and coordination water molecules to obtain the chemical-reasonable models and reasonable atomic displacement parameters. Since the position of the disordered guest water molecules and OH$^-$ anions could not be resolved, SQUEEZE/PLATON was used to compensate the data for their contributions to the diffraction patterns.[3] The final chemical formula of **1** was calculated from SQUEEZE results combined with the TGA and elemental analysis data.

2 Results and Discussion.

2.1 Syntheses

In the last few decades, 3d-4f heterometallic frameworks have become one of the most important issues in the field of metal organic frameworks. However, as the inevitable competition between positive transition metal (TM) and lanthanide (Ln) ions toward the same negative supporting ligands usually lead to the formation of homometallic rather than heterometallic complexes, it is a big challenge to syntheses 3d-4f heterometallic compounds. The bifunctional ligands with mixed donors (N/O, S/O, or N/S/O) may be good candidates to fabricate 3d-4f heterometallic compounds, since Ln ions have strong affinity for O atoms whereas TM ions tend to have a higher affinity towards N and S donors. Moreover, the assembly of the TM and Ln with the mixed donor bifunctional ligands can induce the respective aggregations of the TM and Ln ions, which can result in two discrete 3d and 4f nodes. In this contribution, we select the bifunctional 6-mercaptonicotinic acid (6-mnaH$_2$) to assemble with Gd^{III} and Ni^{II} ions which generates a novel cluster-based 3d-4f heterometallic compound.

2.2 Thermogravimetric analysis and elemental analysis.

To investigate the thermal stability of compound **1**, thermal analysis has been carried out on crystalline sample in a nitrogen atmosphere at a heating rate of 10°C min^{-1}

(Figure S5). The TGA curve of **1** indicates that there is a weight loss of 15.17% from 40 to 453°C, which can be attributed to the loss of eighteen lattice H_2O molecules and twenty coordinated H_2O molecules (calcd = 15.78%). This result is in accordance with the result of elemental analysis.

3 Tables and Figures.

Table S1. Crystallographic data for **1**.

	1
formula	$C_{72}H_{124}N_{12}O_{74}S_{12}Gd_8Ni_6$
formula mass	4336.81
crystal system	trigonal
space group	P-3
a/Å	17.551(4)
b/Å	17.551(4)
c/Å	12.722(4)
α/°	90.00
β/°	90.00
γ/°	120.00
V/Å^3	3394.0(14)
Z	1
D_{calc}/g cm^{-3}	2.122
μ/mm^{-1}	4.943
F(000)	2104
Parameters	277
R_1^a,wR_2^b [I>2σ(I)]	0.0671/0.1928
R_1^a,wR_2^b [all data]	0.0864/0.2068
GOF on F^2	1.111

[a] $R_1 = \sum \left| \left| F_o \right| - \left| F_c \right| \right| / \sum \left| F_o \right|$, [b] $wR_2 = [\sum w(F_o^2 - F_c^2)^2 / \sum w(F_o^2)^2]^{0.5}$.

Table S2. Selected Bond Lengths (Å) and Angles (º) for **1**.

Ni1—N1	2.029 (8)	Ni1—N2	2.054 (9)
Ni1—S1	2.614 (3)	Ni1—S2	2.477 (3)
Ni1—S1G	2.451 (3)	Ni1—S2F	2.433 (3)
Gd1—O2A	2.356 (10)	Gd1—O5	2.416 (7)
Gd1—O3B	2.370 (14)	Gd1—O8	2.475 (11)
Gd1—O5C	2.392 (7)	Gd1—O7	2.434 (12)
Gd1—O6	2.368 (5)	Gd1—O9	2.590 (15)
Gd1—O1	2.392 (10)	Gd2—O4D	2.340 (11)
Gd2—O4B	2.340 (11)	Gd2—O5A	2.392 (7)
Gd2—O4E	2.340 (11)	Gd2—O5	2.392 (7)
Gd2—O5C	2.393 (7)	Gd2—O10	2.57 (2)
Ni1—S1—Ni1F	88.03 (10)	Ni1—S1—Ni1G	91.65 (9)
Gd1—O5—Gd1A	106.1 (3)	Gd1—O5—Gd2	105.5 (3)
Gd2—O5—Gd1A	106.3 (3)	Gd1—O6—Gd1C	108.4 (3)

Symmetry codes: (A) − y + 1, x − y + 1, z; (B) − y + 1, x − y + 1, z − 1; (C) − x + y, − x + 1, z; (D) x, y, z − 1; (E) − x + y, − x + 1, z − 1; (F) y − 1, − x + y, − z + 1; (G) x − y + 1, x + 1, − z + 1;

Table S3. The $-\Delta S_M$ of **1** and related Ni^{II}-Gd^{III} compounds.

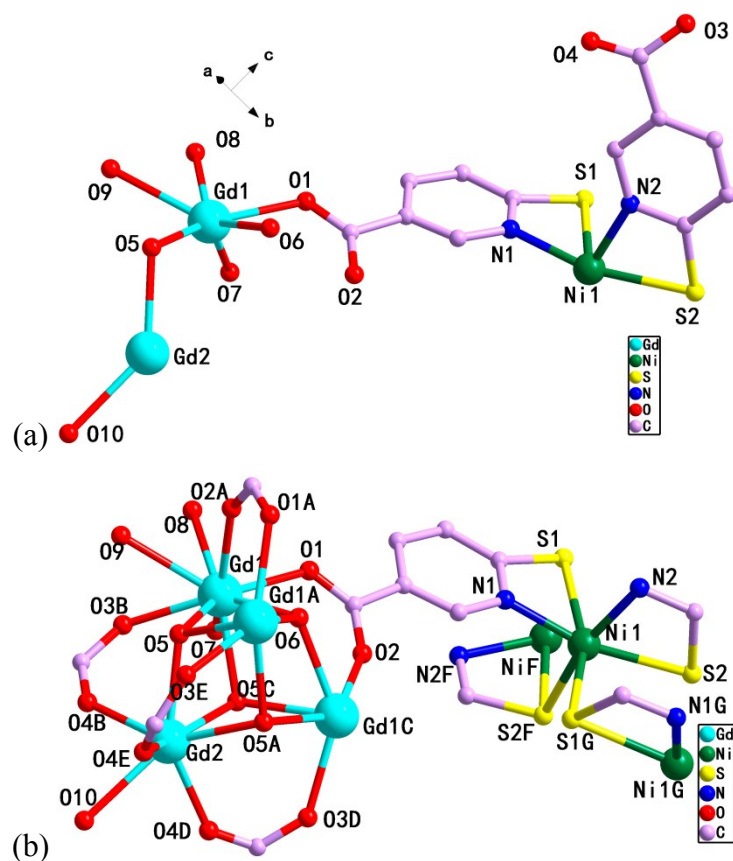| Compounds	Dimensionality	ΔH/ T	$-\Delta S_M$/J kg^{-1} K^{-1}	Ref
$Ni_{64}Gd_{96}$	0 D	7 T	42.8	4
$Ni_{10}Gd_{42}$	0 D	7 T	38.2	5
$Ni_{12}Gd_{36}$	0 D	7 T	36.3	6
Ni_6Gd_6	0 D	7 T	32	7
Ni_3Gd_2	3 D	7 T	31.6	8
1	3 D	8 T	29.85	This work
Ni_6Gd_6	0 D	7 T	26.5	9
Ni6Gd8	0 D	7 T	25.8	10
Ni_8Gd_4	0 D	7 T	22	11
$Ni_{12}Gd_5$	0 D	7 T	21.8	12
Ni_4Gd_4	0 D	7 T	19	13
Ni_2Gd_2	0 D	5 T	18.5	14
Ni_6Gd_3	0 D	5 T	17.6	15
Ni_2Gd	0 D	7 T	13.74	16
Ni_8Gd_6	0 D	7 T	12.6	17
Ni_2Gd_4	0 D	5 T	10.2	18
NiGd	0 D	7 T	5.65	19

Figure S1. (a) View of the asymmetric unit of **1**. (b) View of the coordination environment of Gd^{III} and Ni^{II} ions in **1**.
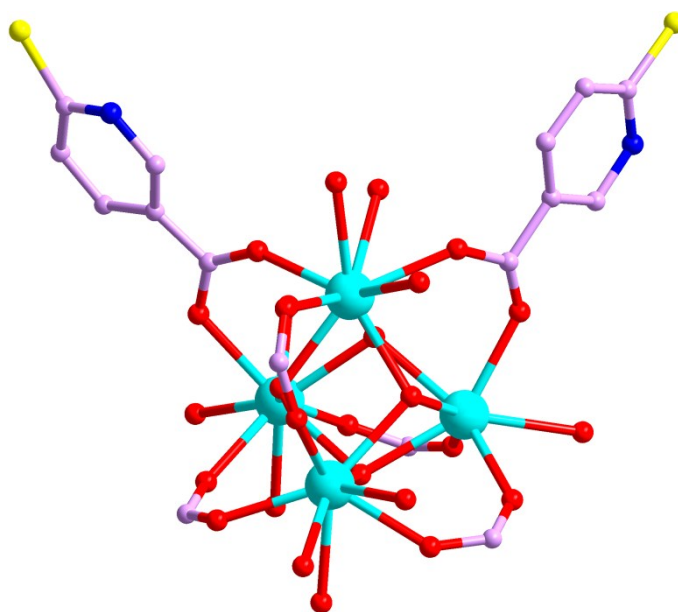

Figure S2. The {6-mna−Gd$_4$(OH)$_4$(COO)$_6$−6-mna} moiety in **1**.
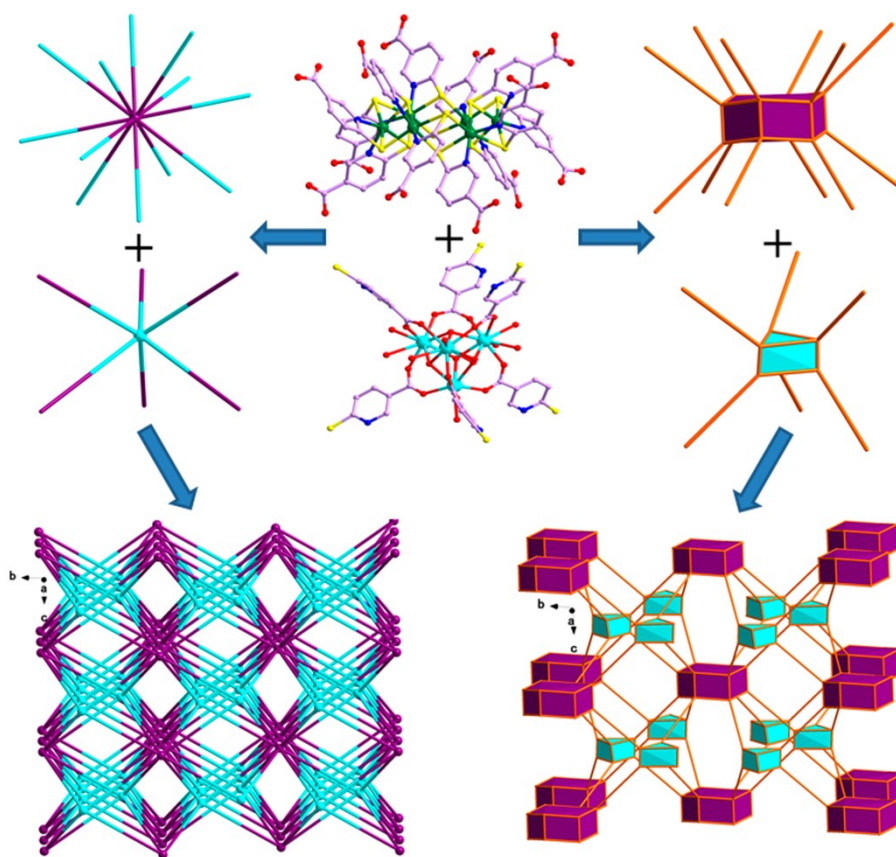
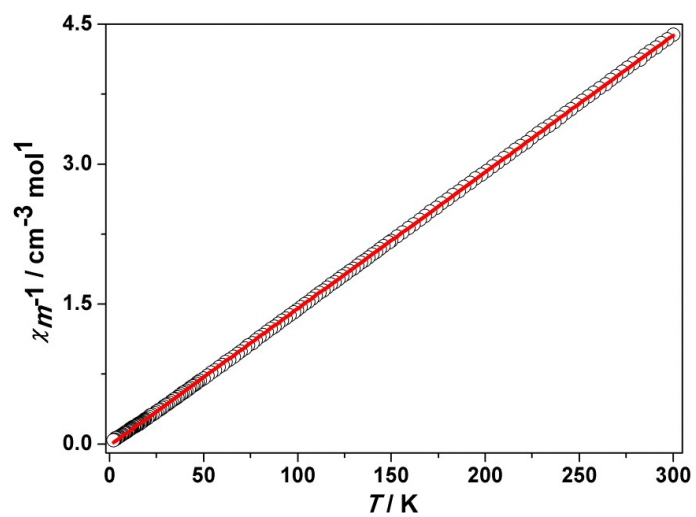**Figure S3.** View of the (6, 12)-connected topological network of **1**.
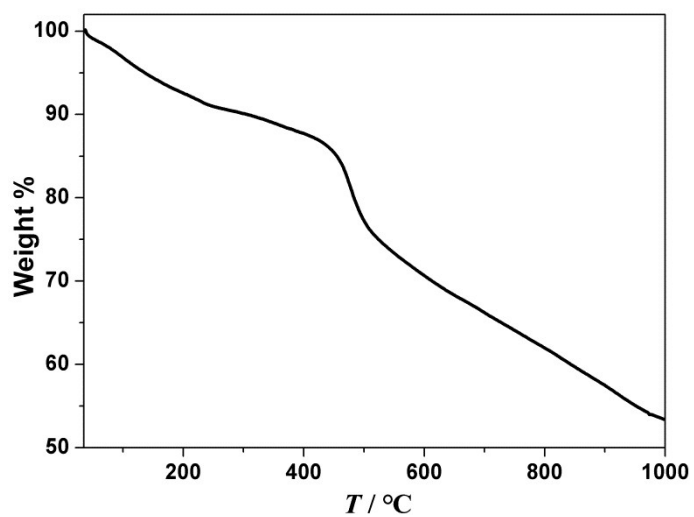

Figure S4. Plots of χ_m^{-1} vs T for compound **1**.
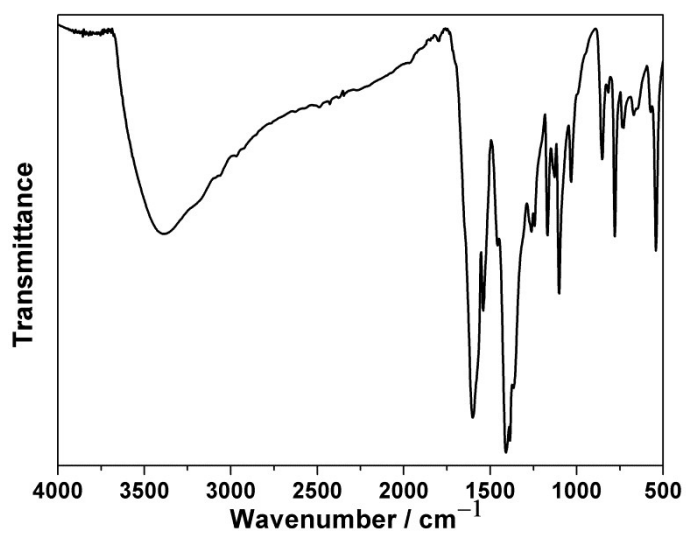
Figure S5. TG curve of compound **1**.

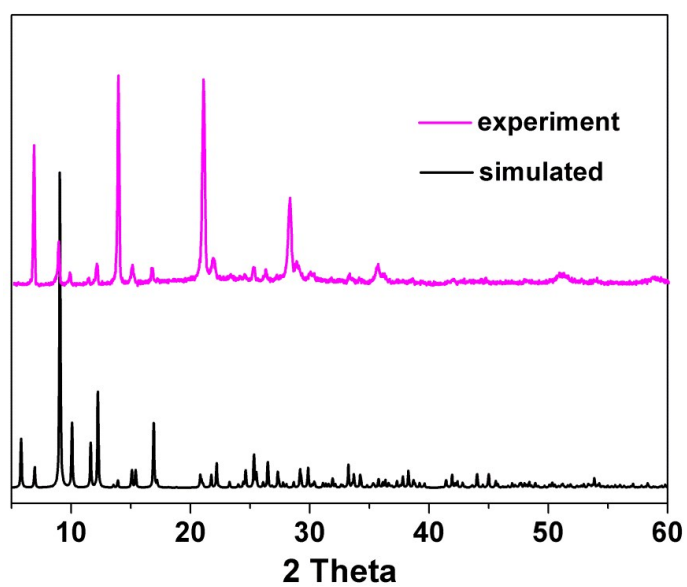**Figure S6**. The IR spectrum of compound **1**.

Figure S7. The PXRD of compound **1**.

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