Electronic Supplementary Material (ESI) for Dalton Transactions.

Supporting Information

$Gd_2Cu(SO_4)_2(OH)_4$: A 3d-4f Hydroxysulfate with Enhanced Cryogenic Magnetocaloric Effect

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Experimental Section

Single crystals of **1** were synthesized by a conventional hydrothermal method. A mixture of 1.5 mmol $CuSO_4 \cdot 5H_2O$ (3N, 0.3745 g), 0.75 mmol Gd_2O_3 (3N, 0.3495 g), 0.57 mmol K_2TeO_3 (3N, 0.1446g), and 10 mL deionized water for **1** was sealed in an autoclave equipped with a Teflon liner (28 mL), respectively. Then, the autoclave was put into a furnace which was heated at 210 °C for 4 days under autogenous pressure, and then cooled to room temperature at a rate of ~ 2 °C/h for 4 days.

X-ray crystallographic studies.

The small crystal of **1** (~ 0.15 mm × 0.15 mm × 0.05 mm) is selected and mounted on glassy fiber for single crystal X-ray diffraction (XRD) measurements. Data collections were performed on Rigaku Mercury CCD diffractometer equipped with a graphite-monochromated Mo-Kα radiation ($\lambda = 0.71073$ Å) at 293 K. The data sets were corrected for Lorentz and polarization factors as well as for absorption by Multi-scan method.[1] The structure was solved by direct methods and refined by full-matrix least-squares fitting on F^2 by SHELX-97.[2] All non-hydrogen atoms were refined with anisotropic thermal parameters. The hydrogen atoms were located at calculated positions and refined with isotropic thermal parameters. The final refined structural parameters were checked by the PLATON program.[3] Crystallographic data and structural refinements are summarized in Table S1. The final refined atomic positions and structural parameters are seen in the Supporting Information (Tables S2-4†).

Magnetic Measurements.

Magnetic measurements were performed using a commercial Quantum Design Physical Property Measurement System (PPMS). Powdered sample of 1 (19.440 mg) was placed separately in a gel capsule sample holder which was suspended in a plastic drinking straw. Magnetic susceptibility was measured at 0.1 T from 300 to 2 K (temperature scan of 5 K/min). The isothermal magnetization was measured in the temperature range of 2-8 K in applied field of 0-8 T (field scan of 0.1 T/step).

Thermal Analysis.

Thermogravimetric analysis (TGA) was performed in the NETZSCH STA 449C instruments in a nitrogen atmosphere at a heating rate of 10 °C/min. The sample was placed in Al_2O_3 crucible and heated from room temperature to 1100 °C.

Infrared Spectroscopy.

The infrared spectra of the compounds were recorded on a Vertex 70 FT-IR spectrometer in the range of 4000−400 cm^{-1} at room temperature. The samples and dry KBr were mixed with a mass ratio of about 1:100 and ground into fine powder, then pressed into transparent sheets on the tablet machine. The prepared sheets were put in the sample chamber of the infrared spectrophotometer, and the infrared spectra were measured.

Figure S1. Optical image of single crystals for $Gd_2Cu(SO_4)_2(OH)_4$.

Figure S2. Simulated (Red line) and experimental (Black line) powder X-ray (Cu Kα) diffraction patterns for $Gd_2Cu(SO_4)_2(OH)_4$.

Figure S3. View of the oxygen-coordination environments for (a) Gd, (b) Cu, and (c) S atoms.

Figure S4. *M vs. H/T* curves under the temperatures of 2 - 8 K for $Gd_2Cu(SO_4)_2(OH)_4$.

Figure S5. Powder X-ray (Cu Kα) diffraction patterns for $Gd_2Cu(SO_4)_2(OH)_4$ at room temperature (Black line) and 900 °C (Red line).

Figure S6. The infrared spectrum of $Gd_2Cu(SO_4)_2(OH)_4$.

Table S1. Crystal data and structure refinements for $Gd_2Cu(SO_4)_2(OH)_4$.

Table S2. Atomic coordinates ($\times 10^4$) and equivalent isotropic displacement parameters ($Å^2 \times 10^3$) for $Gd_2Cu(SO_4)_2(OH)_4$. U(eq) is defined as one third of the trace of the orthogonalized Uij tensor.

Table S3. Bond lengths (Å) and angles (deg) for $Gd_2Cu(SO_4)_2(OH)_4$.

Table S4. Anisotropic displacement parameters ($Å^2 \times 10^3$) for $Gd_2Cu(SO_4)_2(OH)_4$. The anisotropic displacement factor exponent takes the form: $-2 \pi^2 [h^2 a^{*2} U11 + ... + 2 h k a^* b^* U12]$.

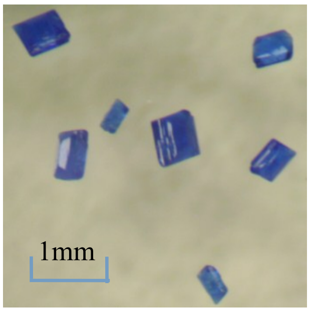

Figure S1. Optical image of single crystals for $Gd_2Cu(SO_4)_2(OH)_4$.

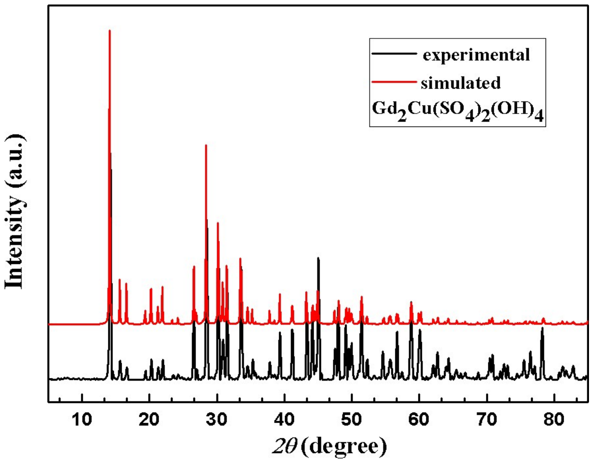

Figure S2. Simulated (Red line) and experimental (Black line) powder X-ray (Cu Kα) diffraction patterns for $Gd_2Cu(SO_4)_2(OH)_4$.

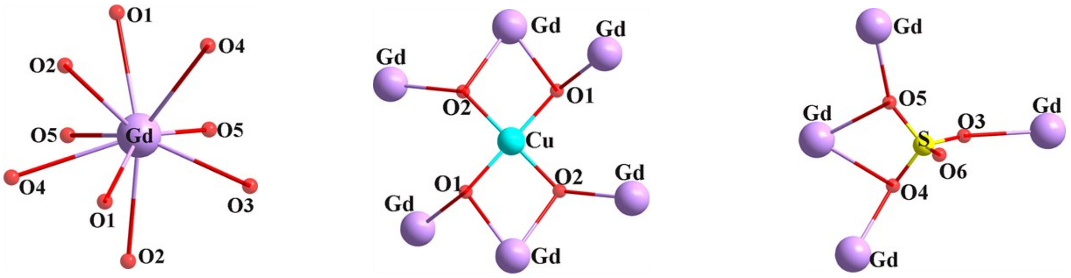

Figure S3. View of the oxygen-coordination environments for (a) Gd, (b) Cu, and (c) S atoms for $Gd_2Cu(SO_4)_2(OH)_4$.

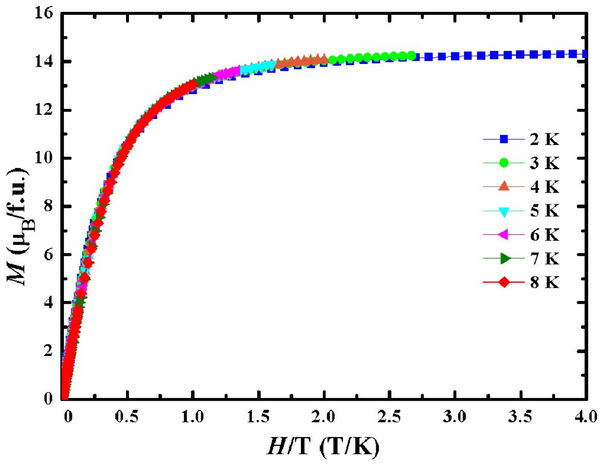

Figure S4. *M vs. H/T* curves under the temperatures of 2 - 8 K for $Gd_2Cu(SO_4)_2(OH)_4$.

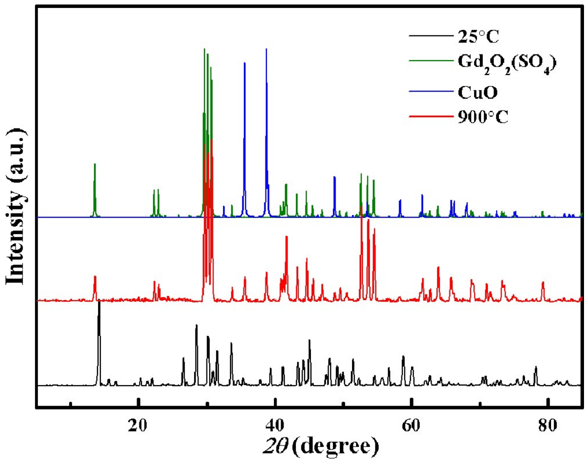

Figure S5. Powder X-ray (Cu Kα) diffraction patterns for $Gd_2Cu(SO_4)_2(OH)_4$ at room temperature (Black line) and 900 °C (Red line). The blue line and green line represent the powder X-ray (Cu Kα) diffraction patterns for CuO and $Gd_2O_2(SO_4)$, respectively.

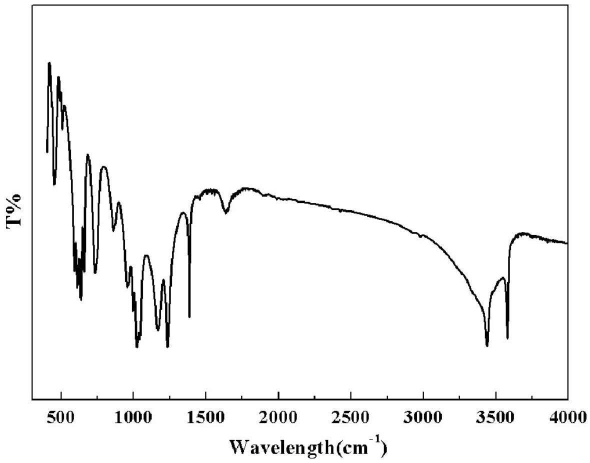

Figure S6. The infrared spectrum of $Gd_2Cu(SO_4)_2(OH)_4$.

Table S1. Crystal data and structure refinements for $Gd_2Cu(SO_4)_2(OH)_4$.

Chemical formula	$Gd_2Cu(SO_4)_2(OH)_4$
Formula mass/g mol^{-1}	638.22
Temperature/K	room temp
λ, Å	0.71073
Space group	$P2_1/c$
a/Å	6.341(6)
b/ Å	6.702(4)
c/Å	10.779(9)
α/deg	90
β/deg	98.37(3)
γ/deg	90
Volume/Å^3	453.2(6)
Z	2
ρ_{calcd}/g cm^{-3}	4.647
μ/cm^{-1}	173.14
F(000)	570
θ range(deg)	3.25 - 27.48°
Limiting indices	$-8 \leq h \leq 8$
	$-8 \leq k \leq 8$
	$-13 \leq l \leq 13$
Reflns collected/unique	3326 / 1032 [R(int) = 0.0429]
Completeness to θ (%)	99.5 %
Refinement method	Full-matrix least-squares on F2
Data/restraints/params	1027/0/79
Max.and Min. transimissions	1.0000, 0.8356
Goodness of fit on F^2	1.115
R1,wR2 [I >2σ(I)]a	0.0285, 0.0709
R1,wR2 (all data)	0.0308, 0.0721
Largest diff. peak and hole	1.227 and -2.928 e.A^{-3}

$^a R1 = \sum||F_o| - |F_c||/\sum|F_o|$, $wR2 = \{\sum w[(F_o)^2 - (F_c)^2]^2/\sum w[(F_o)^2]^2\}^{1/2}$

Table S2. Atomic coordinates ($\times 10^4$) and equivalent isotropic displacement parameters ($Å^2 \times 10^3$) for $Gd_2Cu(SO_4)_2(OH)_4$. U(eq) is defined as one third of the trace of the orthogonalized Uij tensor.

atom	x	y	z	U(eq)
Gd	9204(1)	68(1)	6809(1)	6(1)
Cu	10000	0	10000	10(1)
S	13595(2)	-1713(2)	6283(1)	8(1)
O(1)	11035(5)	1823(5)	11363(3)	9(1)
O(2)	11231(5)	1557(5)	8742(3)	9(1)
O(3)	15492(6)	-491(6)	6598(4)	14(1)
O(4)	12523(5)	-1952(5)	7430(3)	10(1)
O(5)	11973(6)	-569(6)	5411(3)	12(1)
O(6)	14025(6)	-3593(5)	5741(4)	19(1)

Table S3. Bond lengths (Å) and angles (deg) for $Gd_2Cu(SO_4)_2(OH)_4$.

Gd-O(3)#1	2.362(4)	Gd-O(1)#2	2.366(4)
Gd-O(5)#3	2.424(4)	Gd-O(2)#4	2.433(4)
Gd-O(1)#5	2.466(3)	Gd-O(4)#6	2.475(4)
Gd-O(2)	2.492(4)	Gd-O(4)	2.510(4)
Gd-O(5)	2.511(4)	Cu-O(1)	1.949(3)
Cu-O(1)#2	1.949(3)	Cu-O(2)	1.961(3)
Cu-O(2)#2	1.961(3)	S-O(6)	1.432(4)
S-O(3)	1.454(4)	S-O(5)	1.499(4)
S-O(4)	1.504(4)	O(3)#1-Gd-O(1)#2	79.13(1)
O(3)#1-Gd-O(5)#3	76.57(1)	O(1)#2-Gd-O(5)#3	148.05(1)
O(3)#1-Gd-O(2)#4	75.34(1)	O(1)#2-Gd-O(2)#4	70.51(1)
O(5)#3-Gd-O(2)#4	83.43(1)	O(3)#1-Gd-O(1)#5	127.30(1)
O(1)#2-Gd-O(1)#5	134.73(7)	O(5)#3-Gd-O(1)#5	77.09(1)
O(2)#4-Gd-O(1)#5	144.06(1)	O(3)#1-Gd-O(4)#6	71.14(1)
O(1)#2-Gd-O(4)#6	94.07(1)	O(5)#3-Gd-O(4)#6	97.35(1)
O(2)#4-Gd-O(4)#6	145.24(1)	O(1)#5-Gd-O(4)#6	68.06(1)
O(3)#1-Gd-O(2)	121.97(1)	O(1)#2-Gd-O(2)	66.79(1)
O(5)#3-Gd-O(2)	144.80(1)	O(2)#4-Gd-O(2)	128.15(1)
O(1)#5-Gd-O(2)	67.95(1)	O(4)#6-Gd-O(2)	66.35(1)
O(3)#1-Gd-O(4)	136.50(1)	O(1)#2-Gd-O(4)	69.01(1)
O(5)#3-Gd-O(4)	117.63(1)	O(2)#4-Gd-O(4)	66.69(1)
O(1)#5-Gd-O(4)	96.18(1)	O(4)#6-Gd-O(4)	137.84(7)
O(2)-Gd-O(4)	71.49(1)	O(3)#1-Gd-O(5)	133.60(1)
O(1)#2-Gd-O(5)	122.93(1)	O(5)#3-Gd-O(5)	64.72(1)
O(2)#4-Gd-O(5)	75.73(1)	O(1)#5-Gd-O(5)	68.70(1)
O(4)#6-Gd-O(5)	135.91(1)	O(2)-Gd-O(5)	104.43(1)
O(4)-Gd-O(5)	55.66(1)	O(1)-Cu-O(1)#2	180.000(1)
O(1)-Cu-O(2)	93.64(1)	O(1)#2-Cu-O(2)	86.36(1)

O(6)-S-O(3)	113.0(2)	O(6)-S-O(5)	110.4(2)
O(3)-S-O(5)	109.1(2)	O(6)-S-O(4)	112.1(2)
O(3)-S-O(4)	109.0(2)	O(5)-S-O(4)	102.6(2)

Symmetry transformations used to generate equivalent atoms: #1 x-1,y,z; #2 -x+2,-y,-z+2; #3 -x+2,-y,-z+1; #4 -x+2,y-1/2,-z+3/2; #5 x,-y+1/2,z-1/2; #6 -x+2,y+1/2,-z+3/2.

Table S4. Anisotropic displacement parameters ($Å^2 \times 10^3$) for $Gd_2Cu(SO_4)_2(OH)_4$. The anisotropic displacement factor exponent takes the form: $-2 \pi^2 [h^2 a^{*2} U11 + ... + 2 h k a^* b^* U12]$.

atom	U11	U22	U33	U23	U13	U12
Gd	8(1)	5(1)	6(1)	0(1)	-1(1)	0(1)
Cu	17(1)	6(1)	6(1)	0(1)	0(1)	-1(1)
S	7(1)	7(1)	8(1)	1(1)	-1(1)	-1(1)
O(1)	16(2)	5(2)	5(2)	-2(1)	-2(2)	2(1)
O(2)	13(2)	8(2)	6(2)	1(1)	-1(1)	-4(1)
O(3)	8(2)	15(2)	16(2)	1(2)	-3(2)	-5(2)
O(4)	11(2)	11(2)	8(2)	0(2)	-1(2)	-2(1)
O(5)	12(2)	11(2)	10(2)	1(2)	-3(2)	1(2)
O(6)	26(2)	8(2)	24(2)	-5(2)	8(2)	3(2)

REFERENCES

1*CrystalClear*, Version 1.3.5; Rigaku Corp.: The Woodlands, TX, 1999.

2 G. M. Sheldrick, *Crystallographic Software Package*, SHELXTL, version 5.1; Bruker-AXS: Madison, WI, 1998.

3 A. L. Spek, *J. Appl. Crystallogr.*, 2003, **36**, 7.