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An exceptionally stable 3D Gd^{III}-organic framework towards magnetocaloric refrigerant

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A unexpected 3D Gd^{III}-organic framework containing random Gd^{III}-hydroxy "ladders", {[Gd(OH)(H₂O)(abtc)_{0.5}·H₂O]_n (**1**) (H₄abtc = 3,3',5,5'-azobenzene-tetracarboxylic acid), has been synthesized by an easy solvothermal method with high yield, which is the first lanthanide-based complex including the H₄abtc ligand. It is noteworthy that the H₄abtc used in **1** is the largest ligand compared with all previous reported 3D magnetic refrigerants to date, however, the cryogenic magnetic refrigeration property suggests that **1** possesses a large magnetocaloric effect (MCE) value. More importantly, the superiorly stability of **1** towards air, water, solvents and particularly acid or alkaline conditions, leads it as a promising candidate applied for magnetic refrigerant.

Introduction

The unremitting investigations of novel coordination polymers regarded as magnetocaloric effect (MCE) materials have emerged a rejuvenated and increased attention in recent five years,¹ because not only their structures and properties are controllable, but also they are environmentally friendly and energy-efficiently outperform well-established magnetic refrigerants in ultralow temperature region, as replacements for the rare and expensive He-3.² Several factors are demanded for a molecular refrigerant: large spin ground state *S*, low-lying excited spin states, negligible magnetic anisotropy, dominant ferromagnetic interaction, and high magnetic density,¹⁻³ based on which Gd^{III} as well as high spin Mn^{II} and Fe^{III} ions is ideal candidate to construct large MCE materials. Since the well-known {Mn₁₂} cage with MCE was discovered,⁴ a family of excellent works were documented, breaking the record of $-\Delta S_m$ frequently.¹⁻⁸ However, most of previous reports focused on the various discrete clusters⁵ as well as several 1D⁶ and 2D⁷ examples, the MCE explorations of 3D frameworks have been rarely documented.⁸

Herein, we illustrated the synthesis and fully characterization of a unexpected 3D Gd^{III}-organic framework containing rare Gd^{III}-hydroxy "ladders", {[Gd(OH)(H₂O)(abtc)_{0.5}·H₂O]_n (**1**), which is the first lanthanide-based complex including 3,3',5,5'-azobenzene-tetracarboxylic acid (H₄abtc) ligand, to the best of our knowledge. Complex **1** exhibits a good MCE supported by the magnetic studies and heat capacity measurements, and demonstrates remarkable air, water and chemical stabilities.

Especially, we investigate the first MCE example with high stability towards a vast pH range.

Results and discussion

Structural Descriptions

Complex **1** was obtained with 88% yield by the solvothermal reaction of GdCl₃·6H₂O, H₄abtc, NaOH and H₂O₂ in the mixed solvent of DMA/H₂O. Single crystal X-ray diffraction analysis reveals that **1** crystallizes in the triclinic space group *P*-1. Each asymmetric unit consists of one Gd^{III} ion, one μ₃-OH group, half an H₄abtc ligand, one coordinated water, and one lattice water (Fig. 1a). The free program *SHAPE 2.0*⁹ suggests that the proximate ideal geometry of the eight-coordinated Gd is square antiprism (SAPR) (Table 1), which is defined by four O from the H₄abtc ligand, three μ₃-OH groups and a water molecule with Gd-O distances of 2.336(4) – 2.504(4) Å (2.410 Å in average) (Fig. 1b). In the coordination geometry of Gd^{III} ion, two bottom planes of the square antiprism are constructed by O1, O4, O5, O6 and O2, O3, O4A, O4B with standard deviations of 0.0806 and 0.0139 Å, respectively. The dihedral angle of the two surfaces is 2.2°. The distances between Gd^{III} and two surfaces are 1.404 and 1.192 Å, respectively. Adjacent Gd^{III} ions are bridged by μ₃-OH groups to form a 1D Gd^{III}-hydroxy "ladder" with Gd ⋯ Gd distances ranging from 3.776 to 4.505 Å (Fig. 1c). Adjacent "ladders" are further connected by H₄abtc ligands to generate the 3D framework (Fig. 1d).

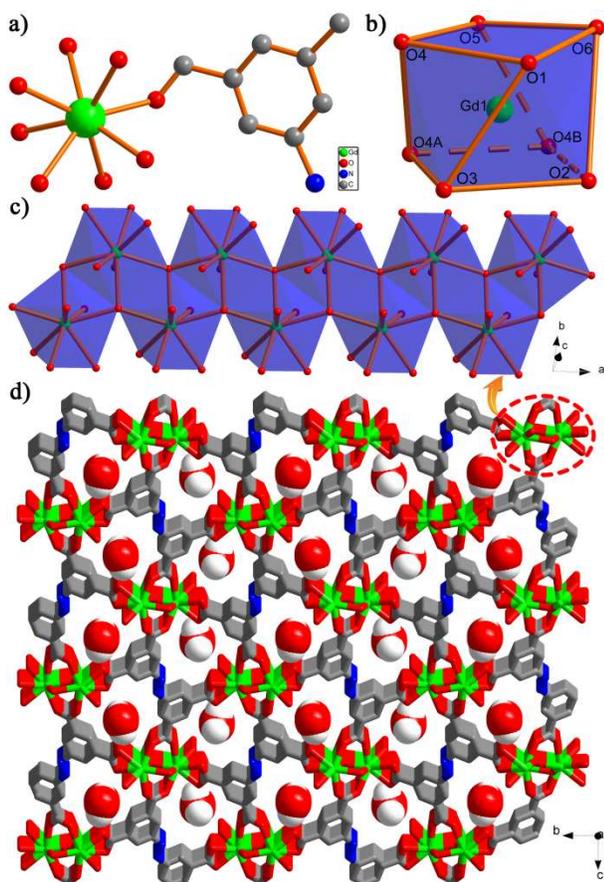


Fig. 1 (a) Ball and stick representation of the asymmetric unit of **1**; (b) The coordination environment of the Gd^{III} ion; (c) The 1D Gd^{III}-hydroxy "ladder" chain; (d) The 3D framework of **1**.

Table 1 SHAPE Analysis of Gd^{III} ion in **1**.

Label	Shape	Symmetry	Distortion
OP-8	Octagon	D_{8h}	29.249
HPY-8	Heptagonal pyramid	C_{7v}	22.165
HBPY-8	Hexagonal bipyramid	D_{6h}	16.706
CU-8	Cube	O_h	10.469
SAPR-8	Square antiprism	D_{4d}	0.330
TDD-8	Triangular dodecahedron	D_{2d}	2.427
JGBF-8	Johnson gyrobifastigium J26	D_{2d}	16.849
JETBPY-8	Johnson elongated triangular bipyramid J14	D_{3h}	28.815
JBTPR-8	Biaugmented trigonal prism J50	C_{2v}	2.759
BTPR-8	Biaugmented trigonal prism	C_{2v}	1.680
JSD-8	Snub diphenoid J84	D_{2d}	5.395
TT-8	Triakis tetrahedron	T_d	11.023
ETBPY-8	Elongated trigonal bipyramid	D_{3h}	24.233

Air and Chemical stabilities

When exposing **1** in the open air, the framework is steady for at least three months, as determined by PXRD patterns (Fig. 2a). **1** exhibits excellent chemical stability in common solvents as well: after immersing **1** in corresponding solvents, such as H₂O, CH₃OH, CH₃CH₂OH, CH₃CN, CH₂Cl₂, DMF, DMA, DMSO, THF, acetone, and *n*-hexane for more than one week, PXRD

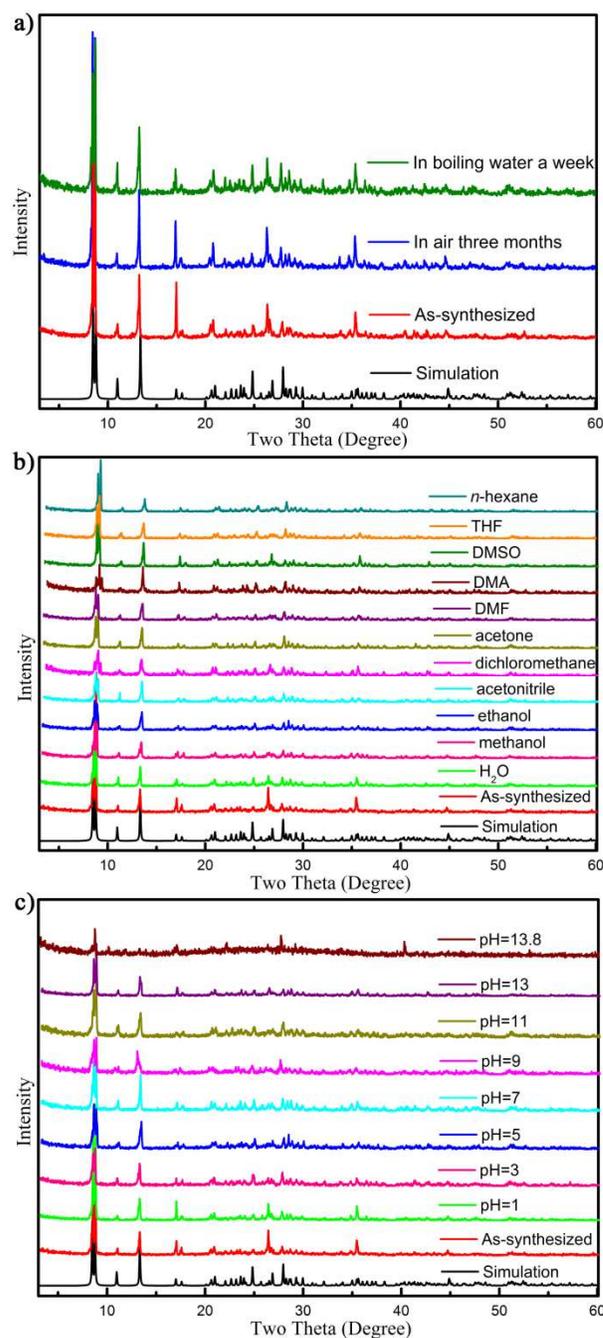


Fig. 2 (a) PXRD patterns of simulated from the X-ray single structure of **1**, as-synthesized **1**, and **1** samples exposed in air for at least three months and soaked in boiling water for more than a week; (b) PXRD patterns of simulated from the X-ray single structure of **1**, as-synthesized **1**, and **1** samples soaked in H₂O, CH₃OH, CH₃CH₂OH, CH₃CN, CH₂Cl₂, DMF, DMA, DMSO, THF, acetone, and *n*-hexane for more than a week; (c) PXRD patterns of simulated from the X-ray single structure of **1**, as-synthesized **1**, and **1** samples immersed in the aqueous solutions ranging from pH = 1 to pH = 13 for more than a week.

patterns are still in accordance with the simulated patterns (Fig. 2b), while PXRD pattern suggests that the framework of **1** is stable after being soaked in boiling water for even one week (Fig. 2a). Especially, we studied concentratedly the stability of **1** with the variation of pH value in a large range. The results

present that the framework of **1** can sustain in the aqueous solutions ranging from pH = 1 to pH = 13 for more than a week (Fig. 2c). In order to further confirm the stabilities of **1**, we took four typical solutions after immersed **1** for a week (CH₃OH, boiling water, pH = 1 and pH = 13 aqueous solutions) to detect the amount of Gd^{III} ions in these solutions by ICP measurements, the ICP results demonstrated that the amount of Gd^{III} ions in these solutions could be almost negligible. The amazing stabilities of **1** could be mainly attributed to the rigid H₄abtc ligand, which has a longer organic backbone with four carboxyl groups, and can be easily partially or completely deprotonated to adopt various metal-oxygen coordination modes to enhance the framework stability and overall rigidity of the framework.

Magnetic properties

Variable-temperature magnetic susceptibility measurement of **1** was executed in the range of 1.8 – 300 K at 1000 Oe. The $\chi_M T$ value is 7.90 cm³·K·mol⁻¹ at ambient temperature, being extremely approximate the theoretical value of one free Gd^{III} ion (7.88 cm³·K·mol⁻¹, ⁸S_{7/2}, *g* = 2).² As the temperature is decreased, $\chi_M T$ almost keeps constant until to *ca.* 100 K, then decreases sharply to a maximum value of 3.58 cm³·K·mol⁻¹ at 1.8 K (Fig. 3), implying the antiferromagnetic interaction among adjacent Gd^{III} ions.

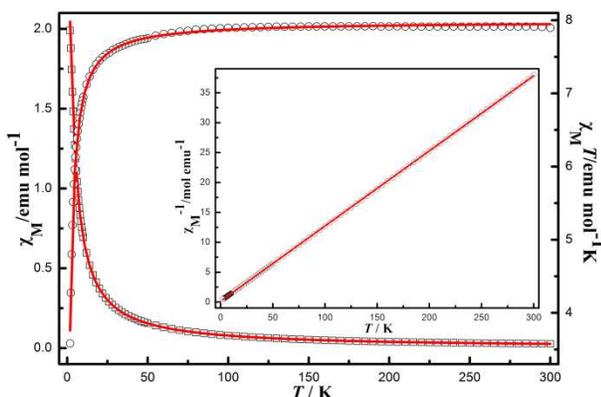


Fig. 3 Temperature dependence of magnetic susceptibility in the forms of $\chi_M T$ and χ_M vs *T* for **1** at 1000 Oe between 1.8 and 300 K. The red solid lines represent the best fitting results. Inset: Temperature dependence of the magnetic susceptibility in the form of χ_M^{-1} vs *T* for **1** at an applied field of 1000 Oe between 1.8 and 300 K. The solid line was generated from the best fit by the Curie-Weiss expression.

From the crystal structure, neighbouring Gd^{III} ions are linked by μ_3 -OH groups to produce a 1D "ladder", and the distances of adjacent Gd^{III} ions ranging from 3.776 to 4.505 Å, much shorter than the distance between adjacent 1D "ladders" (longer than 7.8 Å). As a result, the magnetic interaction among adjacent 1D "ladders" can be ignored and simplifies as the 1D chain model. The expression inferred by Fisher¹⁰ (eq 1) can be used for quantitatively analysis the interaction among adjacent Gd^{III} ions.

$$\chi_{\text{chain}} = \frac{Ng^2\beta^2}{3kT} \frac{S(S+1)(1+u)}{1-u} \quad (1)$$

$$u = \coth(JS(S+1)/kT) - kT / (JS(S+1))$$

In eq (1), *N*, β , *k*, and *g* have their usual meanings, and *J* is the coupling constant between adjacent Gd^{III} ions. The best

least-squares fit parameters are *g* = 2.01, *J* = −0.23 cm⁻¹, and *R* = $\sum[(\chi_M T)_{\text{obsd}} - (\chi_M T)_{\text{calcd}}]^2 / \sum[(\chi_M T)_{\text{obsd}}]^2 = 9.02 \times 10^{-4}$. The result declares antiferromagnetic interaction in **1**. In addition, the curve of χ_M^{-1} vs *T* in 1.8 – 300 K obey the Curie-Weiss law with *C* = 7.96 cm³·K·mol⁻¹ and $\theta = -1.30$ K (inset of Fig. 3), further supporting the antiferromagnetic interaction between adjacent Gd^{III} ions exists in **1**.

The field-dependent magnetization data of **1** is examined at a field of 5 – 70 kOe in the range 2 – 10 K (Fig. 4a), presenting a steady increase with increasing *H* and the saturation value of 6.98 *N* μ_B at 70 kOe and 2 K, which is close to the expected value of 7 *N* μ_B for a Gd^{III} (*S* = 7/2, *g* = 2) ion. The magnetic entropy change ΔS_m can be calculated by the Maxwell equation:^{1b}

$$\Delta S_m(T) = \int [\partial M(T, H) / \partial T]_H dH \quad (2)$$

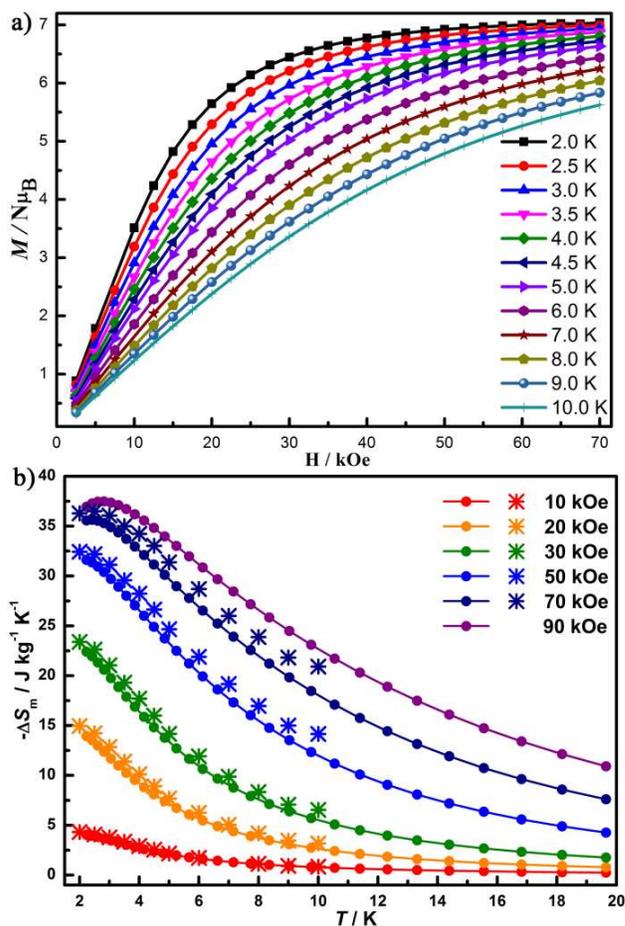


Fig. 4 (a) Field dependencies of isothermal normalized magnetizations for **1** at *T* = 2 – 10 K and 5 – 70 kOe; (b) Temperature dependence of $-\Delta S_m$ obtained from magnetization (*) and heat capacity (●) corresponding to selected ΔH for **1**.

Theoretically, the entropy value of per Gd^{III} ion calculated as $R \ln(2S+1)$ is 17.29 J·mol⁻¹·K⁻¹. Therefore, the theoretical entropy change value of **1** is 44.6 J·kg⁻¹·K⁻¹. The $-\Delta S_m$ value counted by magnetizations is 36.6 J·kg⁻¹·K⁻¹ at 2.5 K for $\Delta H = 70$ kOe, corresponding to 97.5 mJ·cm⁻¹·K⁻¹ (*D*_c = 2.665 g·m⁻³) (Fig. 4b and Fig. S1). The experimental value is smaller than the expected one ascribing to the presence of antiferromagnetic interactions among Gd^{III} ions.⁸

The heat capacity (C) for **1** was measured from zero fields up to 90 kOe, which exhibit typical temperature- and field-dependencies with the Shottky-type magnetic contribution in the low-temperature region and the lattice contribution dominating the high-temperature region (Fig. 5a). According to the inverse integration method applied by Tong *et al.*,^{1c} we obtained a relatively large Debye¹¹ temperature (θ_D) as 354(5) K, indicating a rigid crystal structure that is beneficial for larger ΔT_{ad} . Meanwhile, we calculated the $-\Delta S_m$ and ΔT_{ad} by neglecting the magnetic contribution that quickly converging toward zero by T^{-2} law above the experimental region,¹² which has been proven effective and successful.^{1c,13} The results are in nice consistent with those calculated from the magnetization (Fig. 4b), with just a tiny and expectable underestimation only for the larger ΔH . The maximum $-\Delta S_m$ for $\Delta H = 90$ kOe turns out to be $37.5 \text{ J}\cdot\text{kg}^{-1}\cdot\text{K}^{-1}$ at 2.6 K, and the maximum ΔT_{ad} is 17.1 K (Fig. 5b), which are relatively large among the molecular magnetic coolants.^{1c}

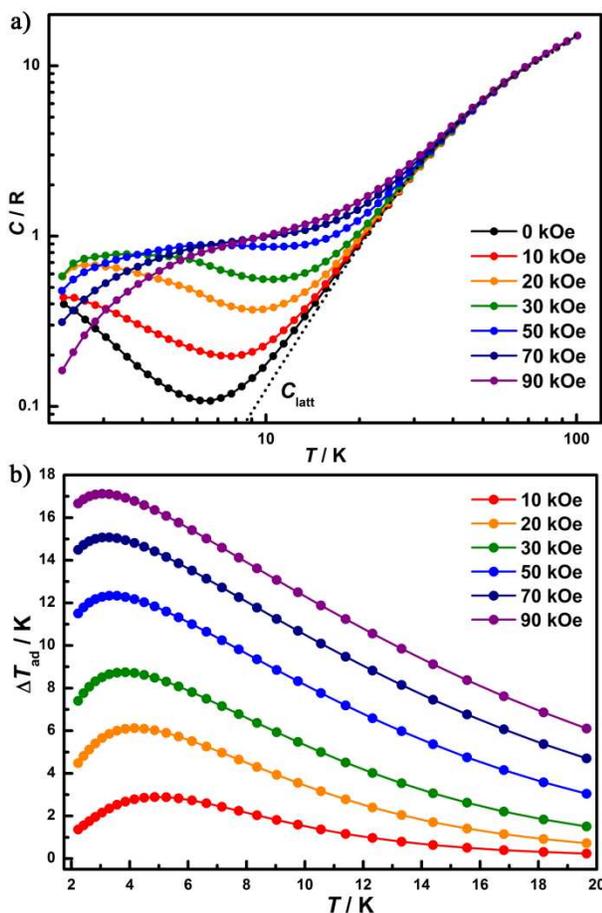


Fig. 5 (a) Temperature dependence of the heat capacity normalized to the gas constant in selected fields for **1**. The dotted line represents the lattice contribution; (b) Temperature dependence of ΔT_{ad} corresponding to selected ΔH for **1**.

It is noteworthy that the ligand used in **1** is the largest one compared with all previous reported 3D magnetic refrigerants to date (Table S1), however, the cryogenic magnetic refrigeration property suggests that **1** possesses a large MCE value, clearly larger than most of reported 3D Gd^{III}-containing magnetic refrigerants^{2,8} although the big H₄abtc ligand has a significant negative contribution to the MCE value.

Furthermore, the $-\Delta S_m$ values per unit mass still reach the values of 15.0 and $23.4 \text{ J}\cdot\text{kg}^{-1}\cdot\text{K}^{-1}$ at 2.0 K for $\Delta H = 20$ and 30 kOe, respectively, which is very close to the commercial GGG whose $-\Delta S_m$ value of $24 \text{ J}\cdot\text{kg}^{-1}\cdot\text{K}^{-1}$ ($173 \text{ mJ}\cdot\text{cm}^{-1}\cdot\text{K}^{-1}$) for $\Delta H = 30$ kOe.¹⁴

Experimental Section

General Methods and Materials

The H₄abtc ligand was prepared according to the previous literature developed by Ameerunisha *et al.* for 4,4'-azobenzoic acid.¹⁵ and further determined by ¹H-NMR. Other chemical reagents were all purchased and used as they were. Elemental analyses (C, H and N) were measured on a Perkin-Elmer 2400-II CHNS/O analyzer. Inductively coupled plasma (ICP) analyses were performed on a Thermo IRIS Advantage spectrometer. Thermogravimetric analyses (TGA) were obtained under a N₂ atmosphere on a Labsys NETZSCH TG 209 Setaram apparatus with the heating rate of $10 \text{ }^\circ\text{C}\cdot\text{min}^{-1}$ from 25 to 800 $^\circ\text{C}$. PXRD were measured on a Rigaku Ultima IV instrument with Cu K α radiation ($\lambda = 1.54056 \text{ \AA}$), with a scan speed of $10^\circ \text{ min}^{-1}$ in the range $2\theta = 3 - 60^\circ$. The temperature-variable in-situ PXRD pattern was examined on the Pt sample platform under N₂ atmosphere with the heating rate of $10 \text{ }^\circ\text{C}\cdot\text{min}^{-1}$ from 25 to 650 $^\circ\text{C}$, with a scan speed of 5° min^{-1} in the range $2\theta = 3 - 60^\circ$. Magnetic data were obtained using a Quantum Design SQUID VSM magnetometer. Diamagnetic corrections were made with both Pascal's constants and sample holder. Heat capacity measurements were studied with compressed pellets on a Quantum Design PPMS using the standard relaxation technique. The ¹H-NMR spectrum was tested on a Mercury Vx-300 NMR spectrometer.

Synthesis of $\{[\text{Gd}(\text{OH})(\text{H}_2\text{O})(\text{abtc})_{0.5}]\cdot\text{H}_2\text{O}\}_n$ (1**):** A mixture of GdCl₃·6H₂O (0.0743 g, 0.20 mmol), H₄abtc (0.0358 g, 0.10 mmol), 4 mol·L⁻¹ NaOH (10 μL), H₂O₂ (500 μL), DMA (2 mL) and H₂O (4 mL) was magnetic stirred for 10 min at room temperature. The resulting mixture was transferred into a 25 mL Teflon-lined stainless steel autoclave and kept at 160 $^\circ\text{C}$ for 72 h, and then slowly cooled to ambient temperature in 48 h. Yellow strip crystals were harvested. Yield: ca. 88% (based on H₄abtc). The amount of solvent molecules contained in the crystal was determined by elemental analyses and TGA result. Elemental analyses calcd. (%) for C₈H₈NO₇Gd: C 24.80, H 2.08, N 3.62. Found: C 24.91, H 2.17, N 3.65.

Crystal data for **1:** C₈H₈NO₇Gd, $M_r = 387.40 \text{ g}\cdot\text{mol}^{-1}$, triclinic space group $P\bar{1}$, $a = 4.5054(3) \text{ \AA}$, $b = 10.3354(7) \text{ \AA}$, $c = 10.8017(9) \text{ \AA}$, $\alpha = 77.933(6)^\circ$, $\beta = 79.230(6)^\circ$, $\gamma = 83.148(5)^\circ$, $V = 481.52(6) \text{ \AA}^3$, $T = 128(1) \text{ K}$, $Z = 2$, $D_c = 2.665 \text{ g}\cdot\text{m}^{-3}$, $\mu = 6.913 \text{ mm}^{-1}$, $F(000) = 364$, $R_{int} = 0.0424$, 2808 reflections, 1698 with $I > 2\sigma(I)$ for 158 parameters, GOF = 1.041, $R_1 = 0.0267$, $wR_2 = 0.0572$ [$I > 2\sigma(I)$] and $R_1 = 0.0288$, $wR_2 = 0.0593$ (all data).

X-ray Crystallography

Crystallographic data of **1** was collected on an Oxford SuperNova diffractometer with a graphite monochromatic Mo K α radiation ($\lambda = 0.71073 \text{ \AA}$) at 128 K. Routine Lorentz polarization and empirical absorption corrections were used. All the structures were solved by direct methods and refined by full-matrix least-squares methods on F^2 with the SHELXTL-97 program package.¹⁶ Anisotropic thermal parameters were assigned to all non-hydrogen atoms. Positions of H atoms attached to C and N atoms were geometrically added. The final formula was determined through single-crystal structures,

element analyses and TGA. CCDC no. 1023444 for **1**. The data can be obtained free of charge from The Cambridge Crystallographic Data Centre via www.ccdc.cam.ac.uk/data_request/cif.

Conclusions

In conclusion, a 3D Gd^{III}-organic framework including scarce Gd^{III}-hydroxy "ladders" has been successfully prepared and structurally characterized, which represents the first lanthanide-based coordination polymer containing the H₄abc ligand. Although the ligand used in **1** is the largest one for all known 3D magnetic refrigerants to date, it still exhibits a large MCE value of 36.6 J·kg⁻¹·K⁻¹, which satisfactorily supplements the family of 3D Gd^{III}-containing magnetic refrigerants. The superior stability of **1** towards air, water, solvents and particularly acid or alkaline conditions, leads it as a promising candidate applied for magnetic refrigerant.

Acknowledgements

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Notes and references

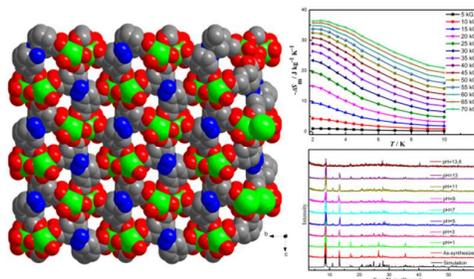
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Electronic Supplementary Information (ESI) available: The TG analyses and temperature-variable *in situ* PXRD sections, as well as crystallographic data in CIF see DOI: 10.1039/b000000x/

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An exceptionally stable 3D Gd^{III}-organic framework towards magnetocaloric refrigerant

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The first example of 3D Gd^{III}-H₄abtc framework was successfully prepared, exhibiting a large cryogenic magnetocaloric effect and exceptionally air and chemical stabilities, especially in water and under acidic/alkaline conditions.