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Gadolinium Oxalate Derivatives with Enhanced Magnetocaloric Effect via Ionothermal Synthesis

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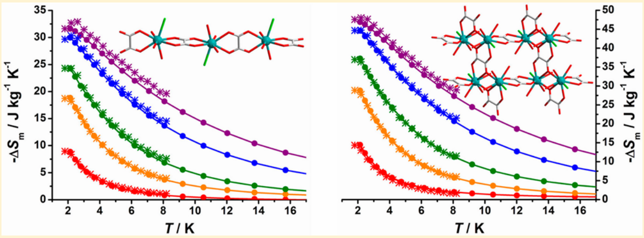
Supporting Information

ABSTRACT: Two new oxalate-bridged Gd(III) coordination polymers, namely, (choline)[Gd(C_2O_4)(H_2O)$_3$Cl]Cl·H_2O (**1**) and [Gd(C_2O_4)(H_2O)$_3$Cl] (**2**), were first obtained ionothermally by using a deep eutectic solvent (DES). The magnetic studies and heat capacity measurements reveal that the two-dimensional Gd(III)-based coordination polymer of **2** has the higher magnetic density and exhibits a larger cryogenic magnetocaloric effect (MCE) (ΔS_m = 48 J kg^{-1} K^{-1} for ΔH = 7 T at 2.2 K).



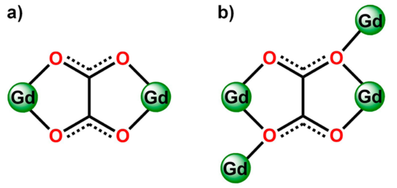
INTRODUCTION

Ionic liquids (ILs), as a class of nonclassical solvents, have attracted considerable attention owing to their special physical and chemical properties.[1] Deep eutectic solvents (DESs) are a new type of ionic solvent that are composed by a mixture of a quaternary salt and a hydrogen bond donor (HBD). Choline chloride (ChCl) has been popularly selected as the salt component for its own advantages, such as the low cost, biodegradability, and low toxicity. Urea, ethylene glycol, and oxalic acid (OA) are popular HBDs for their low cost and easy fusion. In DESs, there is a depression in the freezing point of the mixture compared with either of the individual components.[2] The charge delocalization of the fluid via the formation of hydrogen bonding supramolecular interactions enables DESs to share many characteristics of conventional ILs and, in addition, offers great advantages that surpass many other ionic liquids, for instance, the ease of preparation from easily available feedstock and the relative inertness toward atmosphere moiture.[3−5] DES as a type of alternative and designer solvent has been used widely in materials synthesis.[2a,8] They can act as true solvent-template-reactant systems, where the DESs are at the same time the precursor, the template, and the reactant medium for the fabrication of desired metal-based coordination structure materials.[6,7] The frustrated magnetic solids prepared from ILs by Morris group and Harrison group have been shown among the most interesting examples;[9] nonetheless, there are still very few magnetic materials synthesized by using ILs, especially from DESs.[10,11]

In the area of molecular magnetism, the magnetocaloric effect (MCE) turns out to be one of the most promising applications, especially in the cryogenic region. The two benchmark parameters, isothermal magnetic entropy change (ΔS_m) and adiabatic temperature change (ΔT_{ad}), keep competing in the reported cases.[12−14] Among them, many efforts are toward the increase of ground spin state and the reduction of the ligand-to-metal ratio; most combine the Gd(III) ion (S = 7/2) and small bridging ligands.[15] Although a lot of excellent complexes varying from zero-dimensional (0D) discrete molecules to three-dimensional (3D) frameworks have been reported, the cases regarding one-dimensional (1D) chains or two-dimensional (2D) planes are very limited.[16] Note that the dimensionality seems to be irrelevant for weak-coupling Gd(III) complexes; however, when the variables are controlled, such as using the same ligands, the difference clearly shows up. The essential bridges linking toward higher dimensionality further take up the limited coordination sites of the ligand, then the nonmagnetic guest or solvent molecules are more difficult to be trapped in the structure. Therefore, at the same time, a compact structure with large spin density will be easier to obtain, which is favorable for a large MCE.

Herein we report the ionothermal synthesis of two oxalate-bridged Gd(III) coordination polymers, a 1D (choline)[Gd(C_2O_4)(H_2O)$_3$Cl]Cl·H_2O (**1**) and a 2D [Gd(C_2O_4)(H_2O)$_3$Cl] (**2**) with enhanced MCE by using identical choline chloride−oxalic acid DES (ChCl-OA). We improve the magnetic density by means of alternating the bridging modes of the oxalate ligand (Scheme 1) and reducing the nonmagnetic components

Scheme 1. Two Different Bridging Modes of Oxalate in the Crystal Structure: $\mu-\eta^2:\eta^2$ (a) and $\mu_4-\eta^1:\eta^2:\eta^1:\eta^2$ (b)



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in the two polymers. To the best of our knowledge, it is the first case of synthesizing molecule-based magnetic coolants under ionothermal conditions, and complex **2** exhibits larger MCE with the ΔS_m up to 48 J kg^{-1} K^{-1}, which is also the highest MCE value among the 2D molecular coolants.

■ EXPERIMENTAL SECTION

Materials and General Procedures. All reagents for the synthesis were obtained commercially and used without further purification. Powder X-ray diffraction (PXRD) measurements of **1** and **2** were obtained on Bruker D8 Advance Diffractometer (Cu Kα, λ = 1.540 56 Å) by scanning over the range of 5−50° (Supporting Information, Figure S1) with a step of 0.12°/s at 293 K. The simulated PXRD patterns were calculated with Mercury. The IR spectra were recorded from KBr pellets in the range of 4000−400 cm^{-1} on a Bruker-tensor 27 spectrometer (Supporting Information, Figure S2). The C, H, and N microanalyses of the crystal samples were carried out with an Elementar Vario EL elemental analyzer. The magnetic susceptibility data were measured by using a Quantum Design MPMS XL-7 SQUID magnetometer. Diamagnetism was estimated from Pascal constants. Heat capacity measurements were performed with compressed pellets on a Quantum Design PPMS adopting standard relaxation method.

Synthesis. *(choline)[Gd(C_2O_4)(H_2O)$_3$Cl]Cl·H_2O (**1**).* A mixture of $GdCl_3$·$6H_2O$ (0.258 g, 0.69 mmol), choline chloride (0.264 g, 1.9 mmol), and oxalic acid dihydrate (0.225 g, 1.8 mmol) were sealed in a 20 mL Teflon-lined autoclave and heated at 120 °C for 3 d with the heating and cooling rates approximately 40 and 5 °C h^{-1}, respectively. Transparent colorless needle-shaped crystals were collected and washed by ethanol, dried in air, and recovered with 67% yield (based on Gd). IR (KBr, cm^{-1}): 3459 (vs), 3380 (vs), 3309 (vs), 3162 (vs), 2281 (w), 2194 (w), 2083 (w), 1896(w), 1680 (vs), 1637 (vs), 1491 (m), 1475 (s), 1416 (w), 1356 (m), 1313 (s), 1240 (w), 1205 (w), 1144 (w), 1059 (m), 1045 (s), 966 (m), 951 (m), 924 (m), 796 (s), 681(m), 563 (m), 482 (m). Elemental analyses (calc/found) for coordination polymer **1**: C 16.91:17.07, H 4.40:4.50, N 2.83:2.84.

*[Gd(C_2O_4)(H_2O)$_3$Cl] (**2**).* A mixture of $GdCl_3$·$6H_2O$ (0.252 g, 0.68 mmol), Cu(CH_3COO)$_2$·H_2O (0.117 g, 0.59 mmol), choline chloride (0.264 g, 1.9 mmol), and oxalic acid dihydrate (0.225g, 1.8 mmol) were sealed in a 20 mL Teflon-lined autoclave and heated at 120 °C for 3 d with the same heating and cooling rates as for coordination polymer **1**. Transparent colorless diamond-shaped crystals were collected and washed by methanol, dried in air, and recovered with 58% yield (based on Gd). IR (KBr, cm^{-1}): 3516 (vs), 3479 (vs), 3409 (vs), 3369 (vs), 3221 (s), 3182 (s), 1680 (vs), 1647 (vs), 1633 (vs), 1612 (vs), 1583 (vs), 1362 (m), 1329 (s), 808 (s), 629 (m), 580 (m), 517 (s), 465 (s). Elemental analyses (calc: found) for coordination polymer **2**: C 7.23:7.18, H 1.91:1.81.

X-ray Structure Determination. Single-crystal X-ray diffraction data for **1** were carried out on an Oxford-Diffraction Xcalibur CCD diffractometer using graphite-monochromated Cu Kα radiation (λ = 1.541 78 Å) at 150(2) K. Diffraction data for **2** were recorded on a Rigaku R-AXIS SPIDER Image Plate diffractometer with graphite-monochromated Mo Kα (λ = 0.710 73 Å) radiation at 150(2) K. The structures were solved by direct methods, and all non-hydrogen atoms were refined anisotropically by least-squares on F^2 using the SHELXTL program.[17] Hydrogen atoms on organic ligands were generated by the riding mode. A summary of the crystallographic data and refinement parameters is provided in Supporting Information, Table S1.

■ RESULTS AND DISCUSSION

Synthesis. Both complexes were synthesized from $GdCl_3$·$6H_2O$ in the DES of choline chloride and oxalic acid dihydrate, and X-ray quality crystals were obtained after heating for 3 d. Complex **1** is isostructural with our previously reported 1D dysprosium and erbium chain structures, which were obtained by using the same stoichiometric ratio and experimental

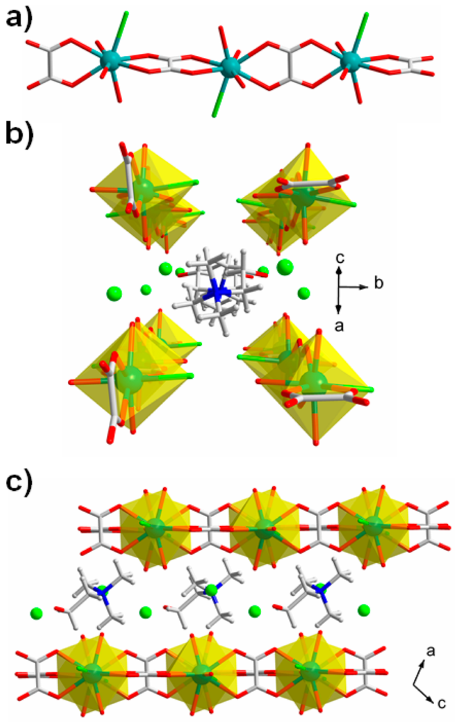

Figure 1. Crystal structure of **1** showing the 1D Gd-oxalate chain (a) and the choline chloride located between the chains (b, c). Color codes: Gd: cyan, Cl: green, C: gray, O: red, N: blue. H: white. Guest water and H atoms on oxygen are omitted for clarity.

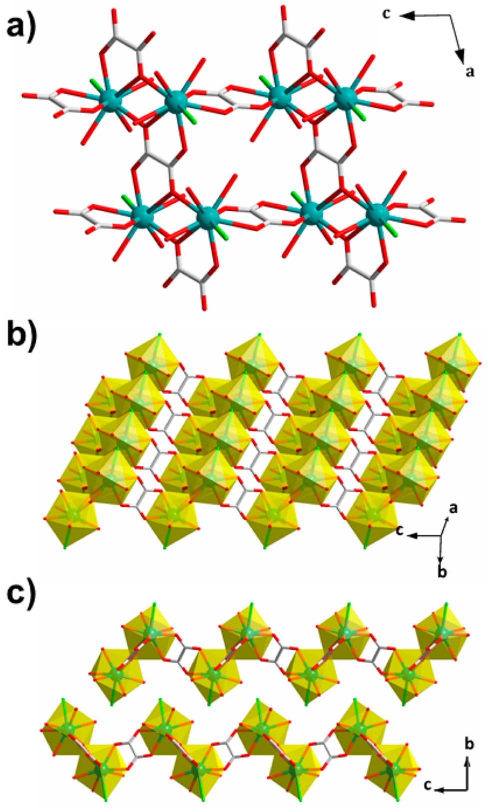

Figure 2. Crystal structure of **2** showing the composition of 2D layer on the *ac* plane (a, b) and their packing along the *b* axis (c). Color codes: Gd: cyan, Cl: green, C: gray, O: red. H atoms are omitted for clarity.

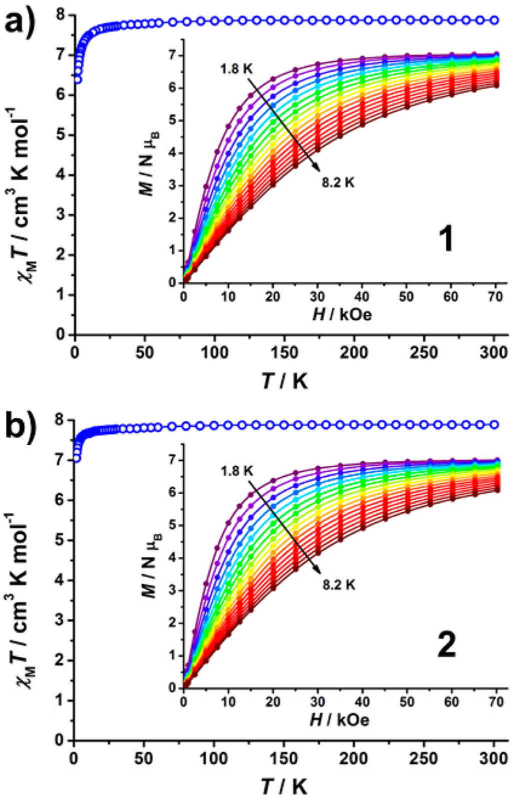

Figure 3. Temperature dependence of the $\chi_M T$ products for **1** (a) and **2** (b) in the field of 1 kOe. (inset) Magnetization vs field for **1** (a) and **2** (b) in the temperature range of 1.8−8.2 K.

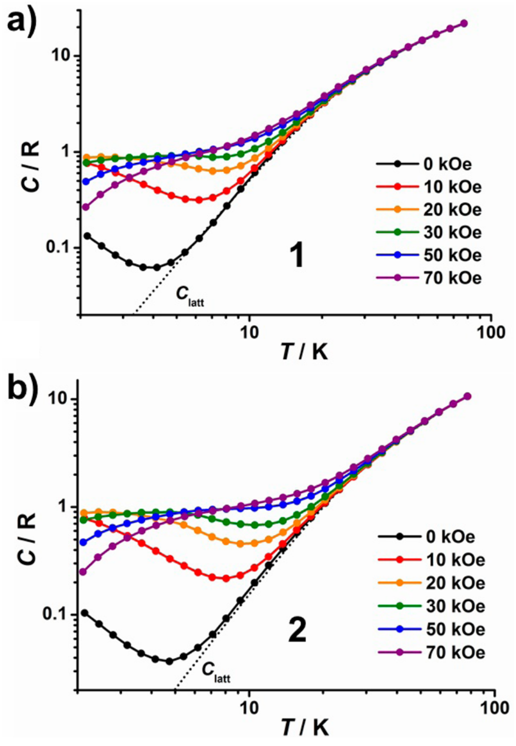

Figure 4. Temperature dependence of the heat capacity normalized to the gas constant in selected fields for **1** (a) and **2** (b). The dotted line represents the lattice contribution.

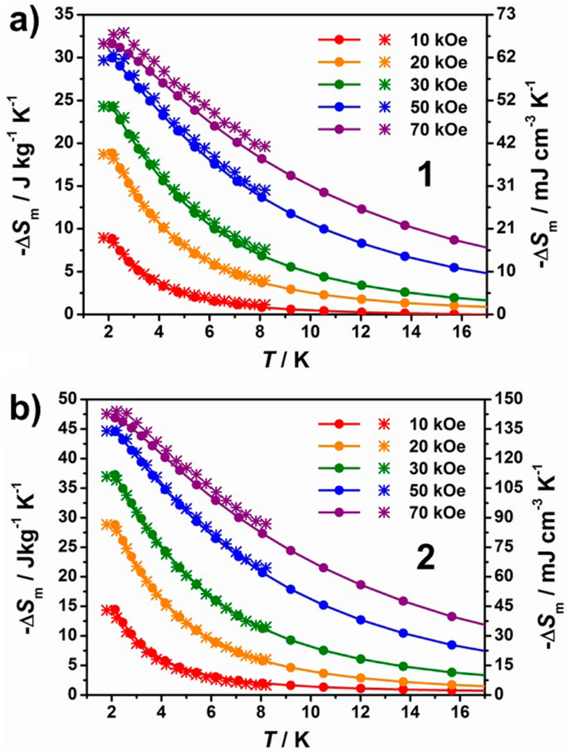

Figure 5. Temperature dependence of $-\Delta S_m$ obtained from magnetization (∗) and heat capacity (●) corresponding to selected ΔH for **1** (a) and **2** (b).

conditions.[18] The 2D complex **2** is formed in the similar structure with La and Pr analogues synthesized by recrystallizing rare earth oxalate from hot concentrated hydrochloric acid.[19] The addition of acetate anions into the reacting system is crucial in our experiments, but the cations can vary from copper to sodium, nickel, magnesium, and zinc, while the copper acetate gives the best crystal quality and yield.

Crystal Structures. Single crystal X-ray crystallography reveals that complex **1** crystallizes in the monoclinic space group $P2_1/n$ and that the asymmetric unit cell contains one formula unit. Each Gd ion in **1** is eight-coordinated by one chlorine atom and seven oxygen atoms in triangular dodecahedron geometry. Four of the oxygen atoms are from three water molecules, while the others are from two oxalate anions (Figure 1a).

The Gd−O bond lengths range from 2.313(6) to 2.431(5) Å, which falls in the range of Gd−O bond lengths typical of Gd(III) complexes. And the Gd−Cl bond length is 2.700(2) Å. The adjacent Gd(III) ions are bridged by one $\mu-\eta^2:\eta^2$ oxalate anion, and each oxalate anion forms two Gd−O−C−C−O five-membered chelating rings (Scheme 1a), resulting in a Gd···Gd distance of 6.2690(7) Å. The chains are slightly away from linearity with Gd−Gd−Gd angles of 174.07(1)°. Choline cations and chloride anions are located in the voids between the chains (Figure 1b,c) along with guest water molecules, resulting in an interchain Gd···Gd separation as small as 7.592(1) Å. Multiple hydrogen-bonds including the O_{water}−H···Cl^- and the $O_{choline}$−H···$O_{oxalate}$ ones help stabilize the 1D structure (Supporting Information, Figure S3).

Complex **2** crystallizes in the monoclinic space group $P2_1/n$ with one formula unit in the asymmetric unit cell. Each Gd ion in **2** is nine-coordinated in capped square antiprism geometry by one chlorine atom, three oxygen atoms from water

Table 1. Magnetic Entropy Change for Selected Molecule-Based Magnetic Coolants Classified by Dimensionality

complex[ref a]	ΔH (kOe)	$-\Delta S_{m,\,max}$ (J kg^{-1} K^{-1})	$-\Delta S_{m,\,max}$ (mJ cm^{-3} K^{-1})
0D			
$\{Co_{10}Gd_{42}\}$[13h]	70	41.3	113
$\{Gd_{48}\}$[14h]	70	43.6	121
$\{Gd_{24}\}$[14d]	70	46.1	89.9
$[Mn(glc)_2(H_2O)_2]$[12g]	70	60.3	112
1D			
$[GdNa(C_5O_5)_2(H_2O)_7]_n$[16b]	70	31.0	70.2
$[Gd_2(piv)_5(OH)(H_2O)]_n$[16f]	70	37.5	61.1
$[Gd(OAc)_3(H_2O)_{0.5}]_n$[16a]	70	47.7	106
1 in this work	70	32.9	68.3
2D			
$\{Gd_{36}O_6(OH)_{49}\}_n$[16e]	70	39.7	91.3
$[Gd(cit)(H_2O)]_n$[16f]	70	43.6	115
$[Gd(HCOO)(OAc)_2(H_2O)_2]_n$[16c]	70	45.9	110
$[Gd(C_4O_4)(OH)(H_2O)_4]_n$[16d]	90	47.3	113
2 in this work	70	48.0	144
3D			
$[Mn(Meip)(DMF)]_n$[12f]	80	42.4	66.7
$\{Gd_6O(OH)_8\}_n$[14e]	70	46.6	207
$[Gd_6(OH)_8(suc)_5(H_2O)_2]_n$[14g]	70	48.0	144
$\{Mn_3Gd_2\}_n$[14h]	70	50.1	114
$[Gd(HCOO)_3]_n$[14f]	70	55.9	216
$[Gd(OH)CO_3]_n$[14i]	70	66.4	355

[a] piv = pivalate, cit = citrate, Meip =5-methylisophthalate, bdc = benzenedicarboxylate, suc = succinate.

molecules, and five oxygen atoms from three oxalate anions (Figure 2a). The structure of **2** consists of 2D layers packing along the *b* axis. Each layer can be regarded as the assembly of $\{Gd_2\}$ units by oxalate ions adopting two different bridging modes (Scheme 1): Half of them are in $\mu_4{-}\eta^1{:}\eta^2{:}\eta^1{:}\eta^2$ mode to connect the $\{Gd_2\}$ units into parallel chains along the *a* axis. The others are in $\mu{-}\eta^2{:}\eta^2$ mode, linking the adjacent chains along the *c* axis and thus forming the 2D layered structure. The Gd−O bond lengths range from 2.387(6) to 2.661(5) Å, and the Gd−Cl bond length is 2.820(2) Å. The distances between neighboring Gd(III) ions in $\{Gd_2\}$ units is 4.4169(5), while the Gd−Gd separation between the adjacent $\{Gd_2\}$ units is 5.8391(5) Å along the *a* axis and 6.3105(5) Å along the *c* axis. Likewise, there are abundant hydrogen bonds in the structure (Supporting Information, Figure S4): the $O_{water}{-}H\cdots O_{oxalate}$ ones are established inside the layers, while the $O_{water}{-}H\cdots O_{water}$ and $O_{water}{-}H\cdots Cl^-$ ones are formed between the layers. The compact 2D layer and their dense packing along the *b* axis (Figure 2b,c) in the crystal structure of **2** leave no space for other guest or solvent molecules, which turns out to be the most significant difference between **1** and **2**.

Magnetic Properties. Variable-temperature magnetic susceptibility measurement was performed on polycrystalline sample of both complexes in the field of 1 kOe (Figure 3). At room temperature, the $\chi_m T$ values are 7.88 cm^3 K mol^{-1} for **1** and 7.90 cm^3 K mol^{-1} for **2**, which are in good agreement with the spin-only value (7.875 cm^3 K mol^{-1}) for a free Gd^{3+} ion with $g = 2$. Upon cooling, $\chi_m T$ values only undergo gradual decrease to the minimum value at 1.8 K as 6.39 cm^3 K mol^{-1} for **1** and 7.05 cm^3 K mol^{-1} for **2**. The paramagnetic behavior of both complexes can be described by nice fits of the magnetic susceptibility to the Curie−Weiss law (Supporting Information, Figure S5) with $C = 7.89$ cm^3 K mol^{-1} and $\theta = -0.53$ K for **1** and $C = 7.90$ cm^3 K mol^{-1} and $\theta = -0.35$ K for **2**, indicating weak antiferromagnetic coupling.

The isothermal magnetization was measured from 1.8 to 8.2 K (insets of Figure 3). The magnetization increases steadily with the applied field and reach the expected saturation value (7 $N\mu_B$ per Gd^{3+} ion with $S = {}^7/_2$ and $g = 2$) at 1.8 K and 70 kOe. The large magnetization values and significant temperature-dependency indicate that they may be promising candidates for cryogenic magnetic refrigeration.

Magnetocaloric Effect. The MCE of both complexes was evaluated using two independent ways: from heat capacity and from magnetization. The heat capacity (C) measured in zero field and in applied fields up to 70 kOe show typical temperature- and field-dependencies (Figure 4). More specifically, the low-temperature region is dominated by field-sensitive Shottky-type magnetic contribution, while the lattice contribution gradually rises with the increase of temperature. The lattice contribution can be fitted to the Debye model:[20]

$$\frac{C_{latt}}{R} = \frac{234 r_D T^3}{(\theta_D + \varepsilon T^2 + \delta T^4)^3}$$

where the number of vibration modes r_D are fixed equal to the total number of atoms in the formula (52 for complex **1** and 16 for complex **2**) and the other parameters are left free as suggested in the literature. The fitting yields relatively large Debye temperatures (θ_D) as 279(2) K for **1** and 282(3) K for **2**, indicating rigid crystal structures.

From the heat capacity, the entropy should be obtained by numerical integration according to eq 1:[21]

$$S(T) = \int_0^T C(T)/T \,dT \qquad (1)$$

However, the lack of experimental C to absolute zero can lead to large error during the extrapolation. Therefore, we adopt a different approach to calculate the $-\Delta S_m$ and ΔT_{ad} by simply neglecting the magnetic contribution above the experimental region, which is quickly converging toward zero by T^{-2} law with increasing temperature.[22] Although there is not any other assumption or correction involved, the result depicted in Figure 5 turns out to be nicely consistent with that calculated from the magnetization by applying the Maxwell eq 2:[21]

$$\Delta S_m(T) = \int_0^H [\partial M(T, H)/\partial T]_H \mathrm{d}H \tag{2}$$

The temperature dependence of $-\Delta S_m$ values also shows typical features like other weak-coupling Gd(III) system, growing gradually with decreasing temperature and increasing fields. The maximum $-\Delta S_m$ value experimentally obtained for complex **1** is 32.9 J kg^{-1} K^{-1} (68.3 mJ cm^{-3} K^{-1}) at $T = 2.6$ K and $\Delta H = 7$ T, which is close to the theoretical limiting value of 35.1 J kg^{-1} K^{-1} (72.9 mJ cm^{-3} K^{-1}) calculated from $R \ln(2S + 1)/M_w$ with $S = {}^7/_2$ and $M_w = 492.41$ g mol^{-1}. For complex **2**, the more compact structure can be regarded as "squeezing out" the nonmagnetic components, resulting in a much lower $M_w = 334.77$ g mol^{-1} corresponding to an upper limit of 51.6 J kg^{-1} K^{-1} (155 mJ cm^{-3} K^{-1}). The experimental $-\Delta S_m$ is approaching the limit, reaching 48.0 J kg^{-1} K^{-1} (144 mJ cm^{-3} K^{-1}) at $T = 2.2$ K and $\Delta H = 7$ T. Both complexes can compare favorably with the recently reported molecule-based magnetic coolants (Table 1), and **2** exhibits the largest MCE value in 2D complexes especially when considered from the volumetric aspect.[23] Their MCE values are further demonstrated by the ΔT_{ad} (Supporting Information, Figure S6), namely, up to 12.4 K for **1** and 16.9 K for **2**, respectively, showing the promising efficiency toward cryogenic applications.

CONCLUSION

In this study, two new oxalate-bridged Gd(III) coordination polymers, namely, (choline)[Gd(C_2O_4)(H_2O)$_3$Cl]Cl·H_2O (**1**) and [Gd(C_2O_4)(H_2O)$_3$Cl] (**2**), were ionothermally obtained in a DES. The magnetic studies reveal that there are weak antiferromagnetic interactions in both complexes **1** and **2**, and **2** with a higher magnetic density exhibits larger MCE relative to that of **1**, ranking among the highest ones. Our finding enrich the few 1D/2D systems in the molecule-based magnetic coolants. Furthermore, the work here demonstrates that DESs not only allow the design of eco-efficient processes but also open a straightforward access to new chemicals and materials.

ASSOCIATED CONTENT

Supporting Information

Crystallographic data, powder X-ray diffraction patterns, IR spectra, additional structural figures, and magnetic properties for **1** and **2**. This material is available free of charge via the Internet at http://pubs.acs.org. CCDC 999029 (**1**) and 999030 (**2**) contain the supplementary crystallographic data for this paper. These data can be obtained free of charge from the Cambridge Crystallographic Data Center via www.ccdc.cam.ac.uk/data_request/cif.

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Notes

The authors declare no competing financial interest.

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