Diverse Lanthanide Coordination Polymers with 3,3′-Dimethylcyclopropane-1,2-dicarboxylate Ligand: Synthesis, Crystal Structure, and Properties

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ABSTRACT: In an attempt to investigate the influence of many variables on the synthesis of lanthanide coordination polymers (Ln-CPs) assembled from the ligand 3,3′-dimethylcyclopropane-1,2-dicarboxylic acid, three different Ln-CPs with formulae \([La_9(\mu_4-dcd)_2(\mu_3-O)_2(H)_n]_\infty\) (1), \([Gd_2(\mu_2-dcd)_3(H_2O)]_n\) (2), and \([Gd_2(\mu-OH)_2(\mu-dcd)(\mu_2-ac)](H_2O)]_n\) (3) (dcd = 3,3′-dimethylcyclopropane-1,2-dicarboxylic acid, ac = acetate) have been hydrothermally synthesized and structurally characterized by elemental analysis, IR spectrum, thermal analysis, powder X-ray diffraction, and single X-ray diffraction techniques. 1 represents the first report of the three-dimensional (3D) Ln-CPs based on nonanuclear lanthanide clusters, although it shows extremely low gas uptakes. 2 exhibits one of the previously reported 3D lanthanide wheel cluster-like frameworks. 3 characterizes a novel one-dimensional ladder-like chain \([Gd_3(\mu-OH)]_\infty\) decorated with mixed ligand ribbons. Variable-temperature magnetic susceptibility measurement reveals that the shortest Gd···Gd distance in 3 induces the antiferromagnetic interactions between adjacent Gd³⁺ cations within the hydroxyl-bridged binuclear unit. Remarkably, magnetic investigation for 2 indicates a unique metamagnetic transition from the antiferromagnet to ferromagnet. Furthermore, magnetic studies for 2 also exhibit the presence of significant magnetocaloric effect with a large magnetic entropy change.

INTRODUCTION

Used as novel porous materials, lanthanide coordination polymers (Ln-CPs) are often composed of lanthanide metal centers or clusters connected with organic ligands. Recently, there has been a growing interest in exploring Ln-CPs because of their unique and interesting physical and chemical properties compared with transition-metal coordination polymers.1,2 Particularly, the highly coordinated lanthanides usually give rise to condensed framework structures in the microporous range, which are beneficial in gas storage and separation.3,4 Apart from the characteristics of microporosity, Ln-CPs also possess unique properties derived from f electrons such as magnetism and luminescence.5,6 Therefore, the synthesis of highly crystalline Ln-CPs with diverse structures is always challenging in chemistry and materials science fields.7–10

From a synthesis perspective, the design and construction of Ln-CPs are based on the judicious selection of ligands and metal ions. Among the different lanthanide cations, the Gd³⁺ ion is the best candidate for constructing magnetic Ln-CPs. Taking this character into account, structural characterization and magnetic studies for gadolinium-based coordination polymers have been widely reported in the recent literature.11–13 However, the exploration of magneto-structural correlations for the gadolinium-based coordination polymers is still unsatisfactory. Many experimental data are also needed in order to assess these aspects adequately.

Comparably, reasonable selection of the ligands as linkers can be viewed as a well-suited way to synthesize Ln-CPs with diverse structures. Numerous Ln-CPs are usually assembled from aromatic carboxylic acids and their derivatives because the oxygen atoms have affinities to lanthanide ions. However, few of the studies focus on the alicyclic carboxylic acid (or its derivative) so far.14 Recently, we have adopted one of the alicyclic carboxylate (3,3′-dimethylcyclopropane-1,2-dicarboxylate, denoted as dcd) ligands as the organic linking ligand to construct lanthanide metal–organic frameworks (MOFs) showing attractive topologies and highly sensitive responses to sodium dodecylbenzene sulfonate.15 The dcd ligand is a favorable organic linker source for the construction of Ln-CPs because of its special clip-like structure. On the other hand, although many Ln-CPs have been synthesized up to now, the targeted syntheses of prospective Ln-CPs are still difficult owing to the subtle synthesis requirements. Many factors influence the final structure, including different ratios and raw materials as well as the variable reaction conditions.

The basic considerations of our synthetic strategy are to study the influence of many variables on the final composition and structures for Ln-CPs assembled from the ligand 3,3′-...
dimethylcyclopropane-1,2-dicarboxylic acid. By blending the reactants 6,6-dimethyl-3-oxabicyclo[3.1.0]hexane-2,4-dione and La₂O₃, the crystal product of [La₉(μ₄-dcd)₁₉(μ₃-O)₁₂(H)₄]ₙ (1) was formed hydrothermally. In order to get other crystal lanthanide products, we selected the same amounts of the mixture of 6,6-dimethyl-3-oxabicyclo[3.1.0]hexane-2,4-dione and Ln₂O₃ (Ln = Nd, Sm, Eu, and Gd) as the starting reactants to further perform this investigation according to the similar synthetic pathway with 1. Unexpectedly, no crystal products isostructural with 1 can be found perhaps because the ion radius of Nd³⁺, Sm³⁺, Eu³⁺, or Gd³⁺ is smaller than that of La³⁺.

From the unspecific white precipitates for other lanthanides, only one crystal product of [Gd₆(μ₄-dcd)(H₂O)]ₙ (2) was obtained. This experiment illustrates that the lanthanide contraction effect may play a prominent instructing part in constructing different Ln-CPs. Furthermore, it is known that the ingenious study of Gd-based coordination polymers should contribute to their magneto-structural correlations. Considering all these, we continue to try other synthetic conditions by choosing the same amount of 6,6-dimethyl-3-oxabicyclo[3.1.0]hexane-2,4-dione and Gd(ac)₃·4H₂O together with NaOH to synthesize the crystal lanthanide products similar with 1. Namely, six La₂ ions and dcd ligands adopting two different coordination modes constitute one of the hexagonal-prismatic metal coordination cages (MCCs) and three ligands adopting the 3,3-dimethylcyclopropane-1,2-dicarboxylic acid are variable depending on the different controlled synthetic conditions, which afford us new opportunities for studying various Ln-CPs with interesting structures and properties in future. As a contribution to the elucidation of structures of Ln-CPs, as well as to better understand the nature of the physical property in these systems, we present herein the synthesis, crystal structures, gas adsorption, and magnetic properties of the diverse Ln-CPs built from dcd ligands, [La₉(μ₄-dcd)₁₉(μ₃-O)₁₂(H)]ₙ (1), [Gd₆(μ₄-dcd)(H₂O)]ₙ (2), and [Gd₆(μ₄-OH)₁₉(μ₄-dcd)(μ₂-ac)]ₙ (3) (ac = acetate).

## RESULTS AND DISCUSSION

**Structural Descriptions.** [La₉(μ₄-dcd)₁₉(μ₃-O)₁₂(H)]ₙ (1). Single X-ray diffraction analyses reveal that compound 1 crystallizes in the trigonal space group of R3. It is a neutral three-dimensional (3D) Ln-CP assembled from nanonuclear lanthanum clusters featuring a double-nested trigonal anti-prismatic configuration. Considering the charge balance, the asymmetry unit for 1 contains two crystallographically independent La³⁺ cations, two dcd ligands, one bridge-linking oxygen, and one isolated hydrogen atom. Besides the normal occupancies, it should be noted that the occupancies for La1, O9, and H9 are 1/2, 1/3, and 1/6, respectively.

Figure 1 shows that each of the La1 atoms is 10-coordinated with 10 oxygen atoms from 6 different dcd ligands building a distorted bicapped square antiprism. However, the environment of La2 is best described as a distorted monocapped square antiprism, which is defined by nine O atoms from five different dcd ligands and one oxygen bridge group. The bond lengths of La1–O(carboxylate) and La2–O(carboxylate) are in the ranges of 2.5279(33)–2.7734(27) and 2.4995(31)–2.7548(22) Å, respectively. Compared with the bond lengths of La1–O(carboxylate) and La2–O(carboxylate), it is noticeable that a smaller La2–O(bridge) bond length of 2.3692(11) Å is presented in a trinuclear unit formed by the ligation between one μ₁-O bridge group and three La2 ions. Furthermore, two crystallographically independent dcd ligands can be found in the asymmetry unit of 1. Both of them exhibit μ₄-bridging linkers and adopt the coordination modes of μ₁-Oη¹η²η³η⁴ (for carboxylates with C1 and C2, denoted as L1) and μ₁-Oη¹η²η³η⁴ (for carboxylates with C3 and C4, denoted as L2), as shown in Figure 1.

Structurally speaking, each μ₁-O9 group ligates three La2 ions to form an incipient [La₉(μ₁-O)₁₄]⁴⁺ core with a La₂–La₂ distance of 3.9515(5) Å. By sharing the joints of adjacent La1 ions, three ligands adopting the L1 coordination mode join the [La₉(μ₁-O)₁₄]⁴⁺ core and three additional La1 ions, giving rise to a La₉₋₇ wheel cluster two-dimensional (2D) layer with an entity of [La₉₋₇(μ₁-O(ac))ₖ(μ₁-dcd)]ₖ⁺ (see the Supporting Information, Figure S1). The distance between the two parallel layers is 3.8083(1) Å. At the same time, every two parallel 2D wheel cluster layers are pillared by a bunch of six dcd ligands adopting the L2 coordination mode to give rise to a final microporous 3D lanthanum framework containing an entity of [La₉₋₇(μ₁-O(ac))(μ₁-dcd)]ₖ⁺, as shown in Figures S2 and 2a. On the other hand, by considering the dcd ligands, bridge-linking oxygen atoms and La³⁺ ions as nodes, the microporous 3D lanthanum framework for 1 can also be simplified into an unusual (3,4,4,6,6)-connected 5-nodal network with (4₁²₄₆₆₄)(4₁²₄₆₆₄)(4₁²₄₆₆₄)(4₁²₄₆₆₄)(4₁²₄₆₆₄)(4₁²₄₆₆₄) topology, as shown in Figure 2b.

Notably, the entity of [La₉₋₇(μ₁-O(ac))(μ₁-dcd)]ₖ⁺ should be neutral according to the charge-balanced principle. In order to balance the charged entity of [La₉₋₇(μ₁-O(ac))(μ₁-dcd)]ₖ⁺, one resonant hydrogen atom may be encapsulated in the charged entity center.

Furthermore, as mentioned above, the bond length of La2–O(bridge) is 2.3692(11) Å, which is obviously smaller than those of La1–O(carboxylate) [2.5279(33)–2.7734(27) Å] and La2–O(carboxylate) [2.4995(31)–2.7548(22) Å]. Considering the charge balance and relatively short distance, it is reasonable to average one resonant hydrogen atom to two symmetry-related μ₁-O9 bridge-linking groups, resulting in a neutral entity of [La₉₋₇(μ₁-O(ac))(μ₁-dcd)]ₖ⁺ finally.

By closer inspection, two kinds of the holes including hexagonal-prismatic metal coordination cages (MCCs) and close-packed one-dimensional (1D) open trigonal channels can be found in the microporous 3D lanthanum framework containing the entities of [La₉₋₇(μ₁-O(ac))(μ₁-dcd)]ₖ⁺. As shown in Figure 3a, six La2 ions and dcd ligands adopting two coordination modes constitute one of the hexagonal-prismatic MCCs with an inner diameter of 3.81 Å. Namely, six μ₁-dcd ligands (see Figure 3a, labeled mauve color) first hook the...
Figure 2. (a) Microporous 3D lanthanum framework shown in the model of wires/sticks and (b) topology for the equivalent 3D lanthanum framework.

Figure 3. Views of (a) one of the hexagonal-prismatic MCCs with the inner diameter of 3.81 Å and (b) one of the close-packed trigonal channels with the inner diameter of 8.67 Å along the $c$ axis.

Figure 4. (a) Part of the equivalent 3D topology framework, (b) double-nested trigonal antiprismatic configuration, and (c) primitive cubic topology network with the cell length of 14.016 Å. Symmetry codes: A ($1 - y, -1 + x, -y, z$), B ($1.333 - x + y, 1.667 - x, -0.333 + z$), C ($-0.333 + x, -0.333 + y, -0.333 + z$), D ($0.333 - y, -0.333 + x - y, -0.333 + z$), E ($2 - x + y, 1 - x, z$), F ($x - y, -1 + x, -z$), G ($2 - x, -y, -z$), H ($1 + y, 1 - x + y, -z$).
peripheral positions of the Ln₉ core from the top down, giving rise to a primal cage-like framework. Then, the primal cage-like framework is further decorated by six μ₃-dcd ligands (see Figure 3a, labeled green color) through the clamping coordination. Seeing from the coordination sites for the remnant La ions, both La1 and La2 ions are evidently unsaturated. Both of them are finally bridged by other dcd ligands, resulting in one of the close-packed 1D open trigonal channels with an inner diameter of 8.67 Å along the c axis (see Figure 3b).

It is remarkable that the 3D lanthanum framework displays a nonanuclear lanthanum cluster with double-nested trigonal antiprismatic configuration (see Figure 4a,b). As far as we know, although many of the isolated nonanuclear lanthanum clusters are synthesized,16–21 none of the 3D Ln-CPs based on the nonanuclear lanthanum clusters has been reported so far. In order to understand the structure well, topological analysis is further performed to the 3D lanthanum framework. By simply considering [La₉(μ₂-OH)₂(μ₃-dcd)₂(H₂O)]ₙ (3). The single-crystal X-ray diffraction study shows that 3 crystallizes in the triclinic system, and the space group is P1. Evidently, two Gd³⁺ ions bridged by two hydroxyl groups, one dcd ligand, two acetate ligands, and one coordinated water molecule can be found in the asymmetry unit. As illustrated in Figure 6, with a distorted monocapped square antiprism, both of the crystallographically independent Gd³⁺ ions are nine-coordinated. The coordination environment for Gd1 is constituted by nine oxygen atoms from two acetate and two dcd ligands and three hydroxyl groups. However, for Gd2, nine oxygen atoms come from one dcd and two acetate ligands, three hydroxyl groups, and one coordinated water molecule. The bond lengths of Gd–Ocarboxylate, Gd–Oacetate, and Gd–Ohydroxyl are in the range of 2.3567(42)–2.5768(49), 2.3898(50)–2.7250(48), and 2.3917(44)–2.4671(45) Å, respectively.

As far as the ligands are concerned, only one crystallographically independent dcd ligand can be found in 3 (see the aubergine parts in Figure 6). It can be used as a μ₃-bridge linking...
ligand with two carboxylate groups adopting the \(\mu_5\eta^2\eta^1\)-chelate-bridging coordination modes. However, there are two crystallographically independent acetate ligands, which exhibit two different coordination modes: \(\mu_3\eta^2\eta^1\)-chelate-bridging mode and \(\mu_2\eta^2\eta^1\)-bis-monodentate mode (see the blue and green parts in Figure 6).

It deserves to be noted that each of the two crystallographically independent hydroxyl oxygen atoms (O9 and O10) adopts the \(\mu_3\)-bridging mode to link three neighboring Gd\(^{3+}\) ions with the distances of 4.0577(5), 3.7115(5), and 3.9328(5) Å for Gd2…Gd2A, Gd2…Gd1, and Gd1…Gd1C, respectively, giving an infinite ladder-like chain with the \([\text{Ln}_4(\text{OH})_4]\) cluster unit (see Figure 7a). Through the bridge-linking ligands \(\mu_3\)-dcd and \(\mu_2\)-ac, these tetranuclear cluster units are further connected by carboxylic groups into a 1D Gd-hydroxyl ladder-like chain decorated with the mixed ligand ribbons, as illustrated in Figures 7b–c and 8a.

![Figure 7](image-url)

**Figure 7.** (a) Infinite ladder-like chain with \([\text{Ln}_4(\text{OH})_4]\) cluster units, (b) ladder-like chain decorated with dcd ligands, and (c) ladder-like chain decorated with ac ligands.

![Figure 8](image-url)

**Figure 8.** (a) 1D ladder-like chain decorated with the mixed ligand ribbons and (b) equivalent topology framework for the 1D ladder-like chain.

Topologically, both dcd and acetate ligands as well as hydroxyl groups could be viewed as the linkers, and each Gd center serves as the connected node. As shown in Figure 8b, the equivalent 1D topology framework for 3 can be simplified as a binodal (4,6)-connected motif, and the Schläfli symbol is \(\{3^4,4^2\}\) \((3^3:4^3:5^3:6^7)\).

**Thermogravimetric Analyses and Powder X-ray Diffraction Patterns.** By using the polycrystalline samples 1 and 3, thermogravimetric analysis (TGA) was performed in order to examine their thermal stabilities (see Figure S3).

The TG curve of the sample 1 shows that there is a plateau of stability from room temperature to 310 °C, and no weight loss is observed before 310 °C, which indicates that 1 was anhydrous and stable up to 310 °C, being in accordance with the single-crystal structure analysis for 1. From 310 to 640 °C, a weight loss of 53.87% should be ascribed to the decomposition of the framework. Evidently, this value is well consistent with the calculated one (53.56%) considering the final product as La\(_3\)O\(_5\). However, for compound 3, the first weight loss of 2.81% (calculated value 2.77%) occurs in the temperature range 100–230 °C, which is due to the escape of the coordinated water molecules. Furthermore, a plateau of stability can also be found before 320 °C, demonstrating that the framework of 3 has the ability to be stable up to 320 °C. Upon heating above 360 °C, the fast weight loss of the framework occurred, giving rise to the final residue weight of 50.6% (calculated value 50.1%) for Gd\(_2\)O\(_3\).

For the as-synthesized samples 1, 2, and 3, their powder X-ray diffraction (PXRD) patterns were measured in the room temperature (see Figures S4–S6). Evidently, all measured PXRD patterns are consistent with those simulated from single-crystal structural data, which indicate that all compounds 1, 2, and 3 are obtained as a single phase, proving the purity of the bulk phases further.

**Gas Adsorption Studies for Compound 1.** Inspired by the microporous structures with hexagonal-prismatic MCCs and close-packed 1D open trigonal channels existed in the novel compound 1, it was selected to perform the gas adsorption tests. The freshly isolated sample was first activated at 210 °C under a dynamic vacuum, and its nearly intact crystal state can be proved by the corresponding PXRD patterns (see Figure S7). Subsequently, different gas adsorption measurements were carried out at a variety of temperatures. As shown in Figures S8–S11, although an obvious adsorption/desorption isotherm with a large hysteresis was observed for N\(_2\) at 77 K, attempts to quantitatively evaluate the mixed gas separation performance at 77 and 298 K were not successful because of the extremely low uptakes of N\(_2\), H\(_2\), CO\(_2\), and CH\(_4\) in compound 1.

Considering the structural analysis above, it is clear that both the hexagonal-prismatic MCCs indwelled in the 3D framework of 1 and channel-like space created by the regular arrangement of the MCCs cannot be served as the main spaces for the gas adsorption, perhaps because the inner spaces in 1 are not completely accessible when the disordered methyl groups, cyclopropane frameworks, and carboxylic groups appended on the open 1D channel partly block the entrance of the gas molecules between the hexagonal-prismatic MCCs and open 1D channels. All of these not only can be inferred from the crystal structure but are also consistent with an extremely small Brunauer–Emmett–Teller surface area.

**Magnetic Properties for Compounds 2 and 3.** It is known that the strong magnetic anisotropy of lanthanide ions is beneficial to the construction of molecular magnetic materials. Considering that the nature of magnetic interaction for Gd\(^{3+}\) ions can be well estimated by the \(\chi_M^T\) versus \(T\) curve, the solid-state magnetic susceptibilities for compounds 2 and 3 were further measured. It should be pointed out that although possessing the same structure with one of the reported lanthanide wheel cluster organic frameworks, the magnetic behavior for 2 was not investigated previously. In order to
confirm the phase purity, the PXRD patterns for the crushed crystalline samples of 2 and 3 were measured (see Figures S5 and S6) before the magnetic measurements. According to the crystal structures described above, four Gd^{3+} cations in 2 are linked by three carboxylate bridges, giving an incipient triangular pyramidal \([\text{Gd}_4(\text{COO})_3]_4\) core with the distances of 4.0851(2), 6.7431(4), and 3.8728(5) Å for Gd1···Gd2, Gd2···Gd3, and Gd3···Gd4, respectively. However, for 3, four Gd^{3+} cations are connected through four hydroxyl bridges into a cluster unit \([\text{Ln}_4(\text{OH})_4]_4\) with the distances of 4.0577(5), 6.7431(4), 3.9115(5), and 3.8728(5) Å for Gd1···Gd2, Gd2···Gd3, Gd3···Gd4, and Gd1···Gd1, respectively. Evidently, the shortest Gd···Gd distance within \([\text{Ln}_4(\text{OH})_4]_4\) units for 3 is smaller than that within \([\text{Ln}_4(\text{COO})_3]_4\) units for 2, which should be of interest for the study of magnetic interactions between the adjacent Gd^{3+} cations. Consequently, compound 3 was first chosen as a representative to study its magnetic susceptibility.

Figure 9 (denoted as red parts) shows the temperature dependence of the \(\chi_M T\) product for 3, where \(\chi_M\) is the magnetic susceptibility per two Gd^{3+} ions. It is evident that the value of \(\chi_M T\) for 3 is equal to 15.69 cm\(^3\) mol\(^{-1}\) K at room temperature, which is as expected for two magnetically isolated Gd^{3+} ions (\(\chi_M T = 15.76\) cm\(^3\) mol\(^{-1}\) K for \(S_{\text{Gd}} = 7/2\) with \(g = 2.0\)). With decrease in the temperature, this value remains invariant until 40 K. Proceeding to the next step, it continually decreases to the value of 9.38 cm\(^3\) mol\(^{-1}\) K at 2.0 K. This feature obviously confirms the weak antiferromagnetic coupling between the Gd^{3+} ions. For the measured magnetic data in the range of 2.0–300 K, the Curie constant \(C = 15.742(3)\) cm\(^3\) mol\(^{-1}\) K and Weiss constant \(\theta = -0.663(3)\) K for 3 (see Figure 9 denoted as blue and green parts) are obtained according to the Curie–Weiss fitting (\(\chi_M = C/T - \theta\)). Similar to the observed \(\chi_M T\) value at room temperature (15.69 cm\(^3\) mol\(^{-1}\) K), the C value for 3 is coincident with the expected value for two Gd^{3+} ions. The profile of the \(\chi_M T\) versus \(T\) together with the small negative \(\theta\) value for 3 indicates weak antiferromagnetic couplings between adjacent Gd^{3+} ions, which is perhaps related with the shortest Gd···Gd distance (3.9115 Å) within \([\text{Ln}_4(\text{OH})_4]_4\) units for 3. All these features are similar to other widely reported gadolinium-based coordination polymers.

Compared with 3, compound 2 displayed a quite different magnetic behavior. Figure 10 shows that the \(\chi_M T\) value at room temperature is 29.2 cm\(^3\) mol\(^{-1}\) K, which is little lower than the expected value (31.52 cm\(^3\) mol\(^{-1}\) K) for four high-spin Gd^{3+} (\(S_{\text{Gd}} = 7/2\) with \(g = 2.0\)) centers, thus indicating weak antiferromagnetic Gd–Gd interactions in the triangular pyramidal Gd\(_4\) unit. The temperature-dependent \(1/\chi_M\) obeys the Curie–Weiss law (\(\chi_M = C/T - \theta\)) with \(\theta = 0.15\) K (inset in Figure 10), and the positive \(\theta\) value suggests the presence of weak ferromagnetic interactions between the Gd\(_{3+}\) ions. Therefore, the weak intermolecular ferro- and antiferromagnetic couplings are synchronously presented in 2, which can be partly confirmed by the temperature-dependent \(\chi_M T\) and \(\chi_M\). We know that if the \(\chi_M T\) value increases with the decreasing temperature, it is certain that the ferromagnetic coupling exists in lanthanide ions. As shown in Figure 10, the \(\chi_M T\) value for 2 slowly increases upon lowering the temperature and reaches a maximum (29.7 cm\(^3\) mol\(^{-1}\) K) at 70 K, determinately indicative of the ferromagnetic Gd···Gd interactions. Then, the \(\chi_M T\) value decreases sharply down to 27.3 cm\(^3\) mol\(^{-1}\) K at 2.0 K, perhaps being the evidence of antiferromagnetic interactions according to Kahn’s model.

Evidently, the ferromagnetic interactions are tempered by the antiferromagnetic interactions at low temperatures. On the other hand, the structural analysis reveals that a triangular pyramidal Gd\(_4\) unit can be found in compound 2. Therefore, the magnetic interactions for the whole molecule can be simplified as the isotropic Hamilton equation (eq 1) considering the magnetic coupling in the Gd\(_4\) unit (inset in Figure 10).

\[
\hat{H} = -2 J_1(\mathbf{S}_{\mathbf{1}} \cdot \mathbf{S}_{\mathbf{2}} + \mathbf{S}_{\mathbf{3}} \cdot \mathbf{S}_{\mathbf{4}} + \mathbf{S}_{\mathbf{5}} \cdot \mathbf{S}_{\mathbf{6}}) - 2 J_2(\mathbf{S}_{\mathbf{2}} \cdot \mathbf{S}_{\mathbf{3}} + \mathbf{S}_{\mathbf{4}} \cdot \mathbf{S}_{\mathbf{5}} + \mathbf{S}_{\mathbf{6}} \cdot \mathbf{S}_{\mathbf{1}})
\]

(1)

\(J_1\) and \(J_2\) represent the equivalent neighboring exchange parameters between two corresponding Gd\(_{3+}\) ions in the Gd\(_4\) unit. On the basis of the bond angle/distance between the adjacent Gd\(_{3+}\) ions, the fitting of the \(\chi_M T\) plot was further carried out using the Origin 8.5 software package. The best fitting result is \(g = 1.93, J_1 = -0.14\) cm\(^{-1}\), \(J_2 = 0.14\) cm\(^{-1}\) (\(T = 2.0–70\) K) and \(g = 2.02, J_1 = -2.07\) cm\(^{-1}\), \(J_2 = 1.78\) cm\(^{-1}\) (\(T = 70–300\) K). This result further confirms the coexistence of weak ferro- and antiferromagnetic interactions between the Gd\(_{3+}\) ions. Structural determination for 2 has confirmed the existence of the Gd\(_4\) units with the triangular pyramidal configuration and two crystallographically independent dcd ligands. According to the related reference,\(^{32}\) the bridging ligands between the Gd\(_4\) units might play an important role in the magnetic Gd···Gd interactions, being responsible for this ferro- antiferromagnetic coupling behavior. Quantitative analyses for the
coexistence of weak ferro- and antiferromagnetic Gd⋯Gd interactions in 2 still need more examples in future.

In the range of 0.0−7.0 T at 2.0−10.0 K, the field dependence of the magnetic measurements for 2 was also carried out (Figure 11a). It can be seen that the plot of $M$ versus $H$ shows a gradual increase with the increasing field, showing a saturation value of 30 $N\beta$ for $M$ at 2.0 K and 7.0 T, where $N$ and $\beta$ represent the Avogadro constant and Bohr magneton, respectively. Considering the weak ferro- and antiferromagnetic coupling, the saturation value for $M$ is slightly larger than the expected theoretical value of 28 $N\beta$ for four uncorrelated Gd$^{3+}$ ions.

Furthermore, the Ln-CPs containing high nuclear gadolinium clusters have recently attracted immense interest because they can be used as good candidates for designing efficient magnetic refrigerant materials based on the Maxwell equation.

Figure 11. (a) Field-dependent experimental magnetization plots at different temperatures for 2 and (b) calculated changes of magnetic entropy for 2.

**CONCLUSIONS**

Through rationally employing one of the alicyclic dicarboxylic acids as the ligand, three different Ln-CPs [L$\alpha_3$(μ$_3$-dcd)$_2$(μ$_2$-O)$_2$(H$_2$O)]$_n$ (1), [Gd$_4$(μ$_3$-dcd)$_2$(H$_2$O)]$_n$ (2), and [Gd$_3$(μ$_2$-OH)$_2$(μ$_4$-dcd)(μ$_3$-3c)(H$_2$O)]$_n$ (3) have been synthesized by the hydrothermal reaction. The single-crystal X-ray diffraction analysis reveals that 1 presents a microporous 3D lanthanum framework with hexagonal-prismatic MCCs, and the regular arrangement of each three MCCs also creates many close-packed 1D open trigonal channels. The 3D lanthanum framework for 1 also displays a nonanuclear lanthanum cluster with double-nested trigonal antiprismatic configuration. This is the first report of the 3D Ln-CPs based on the nonanuclear lanthanide clusters, although attempts to quantitatively evaluate the mixed gas separation performance were not successful because of its extremely low gas uptakes. Compound 2 presents a 3D lanthanide wheel cluster-like framework, which was previously synthesized by us through the different synthetic route. Compound 3 displays a novel 1D decorated ladder-like chain with the dcd and acetate ligands. Magnetic investigations indicate that the antiferromagnetic interactions exist in compound 3, which may be due to the short Gd⋯Gd separation between adjacent Gd$^{3+}$ cations within the ladder-like chain [Gd$_4$(OH)$_6$]$\alpha$. Remarkably, magnetic investigation for compound 2 indicates a unique metamagnetic transformation. Furthermore, 2 also presents a significant MCE with a large magnetic entropy change ($-\Delta S_m = 36.1$ J kg$^{-1}$ K$^{-1}$ with $H = 2.0$ K and $\Delta H = 7.0$ T). The study presented here demonstrates that the diverse synthesized Ln-CPs from the ligand 3,3-dimethylcyclopropane-1,2-dicarboxylic acid are variable depending on the different controlled synthetic conditions, affording us new opportunities for studying various Ln-CPs with interesting structures and properties in future. At the same time, the related study should be of interest in the design of new Ln-CPs based on other alicyclic dicarboxylic acids, as well as in correlation studies including geometric structures, gas adsorption properties, and magnetic interaction mechanisms.

**EXPERIMENTAL SECTION**

**General Remarks.** The compounds were synthesized in poly(tetrafluoroethylene)-lined stainless steel autoclaves. All available reagents were of commercial origin with high-purity grade, and ultrapure water was used in all experiments.

**Physical Techniques.** The elemental carbon and hydrogen analysis was carried out on a PerkinElmer 2400 series. IR spectra were recorded with a PerkinElmer Fourier transform infrared (FT-IR) spectrometer. The PerkinElmer Diamond TG/differential thermal analysis instrument was used for the thermogravimetric thermal analysis. A Bruker D8 Focus Bragg–Brentano X-ray powder diffractometer (Cu $K\alpha$, $\lambda = 1.54184$ Å) was used to measure the PXRD patterns. A fully automated gas sorption analyzer Autosorb-iQ2-MP (Quantachrome Instruments) was used to perform the gas sorption measurements. A Quantum Design MPMS3 instrument was used to determine the magnetic susceptibility.
Table 1. Crystal Data and Refinement Parameters for 1, 2, and 3

| Compound | 1 | 2 | 3 |
|----------|---|---|---|
| Empirical formula | $\text{C}_{316}\text{H}_{197}\text{O}_{50}\text{La}_{9}$ | $\text{C}_{316}\text{H}_{197}\text{O}_{50}\text{Gd}_{4}$ | $\text{C}_{316}\text{H}_{197}\text{O}_{50}\text{Gd}_{4}$ |
| Formula weight | 3156.80 | 1583.82 | 640.75 |
| Crystal system | trigonal | trigonal | triclinic |
| Space group | P3 | P3 | P1 |
| $a$/Å | 19.380(4) | 18.2451(6) | 7.3427(6) |
| $b$/Å | 19.380(4) | 18.2451(6) | 9.8733(6) |
| $c$/Å | 25.3246(6) | 19.8036(7) | 13.2382(10) |
| $\alpha$/deg | 90 | 90 | 90 |
| $\beta$/deg | 90 | 90 | 90 |
| $\gamma$/deg | 120 | 120 | 120 |
| Volume/Å$^3$ | 82373.4(4) | 57097.3(3) | 82322.12(3) |
| $Z$ | 3 | 4 | 2 |
| $\rho_{calc}$/g·cm$^{-3}$ | 1.909 | 1.842 | 2.497 |
| $\mu$/mm$^{-1}$ | 3.505 | 4.661 | 7.766 |
| $I$(000) | 45420 | 3032 | 600.0 |
| Reflected | 12214 | 21758 | 10442 |
| Unique refl. | 3740 | 3906 | 3480 |
| $R_{int}$ | 0.0326 | 0.0361 | 0.0487 |
| GOF | 1.062 | 1.104 | 1.075 |
| $R_1$ (I $> 2\sigma(I)$) | 0.0251 | 0.0219 | 0.0313 |
| $wR_1$ (I $> 2\sigma(I)$) | 0.0543 | 0.046 | 0.0792 |
| $R_{int}$ (all data) | 0.0320 | 0.0287 | 0.0427 |
| $wR_1$ (all data) | 0.0577 | 0.0491 | 0.0877 |

Synthesis of Compounds. [La$_2$(μ$_4$-dcd)$_6$(μ$_2$-O)$_2$(H$_2$O)$_n$]$_n$ (1). A mixture of 2.5 mmol La$_2$O$_3$, 5.0 mmol 6,6-dimethyl-3-oxabicyclo[3.1.0]hexane-2,4-dione, and 20.0 mL H$_2$O was first stirred in a beaker for 30 min. Then, the obtained aqueous suspension was transferred into a 40 mL Teflon-lined stainless-steel vessel and heated at 180 °C for 5 days. After the reactant mixture was slowly cooled to room temperature, the colorless stick-like single crystals of 1 can be found in the bottom of the vessel. Through filtering and washing with ultrapure water, the crystals were finally dried in air (yields: 85%). Elemental analysis (%) calcd for C$_{316}$H$_{197}$O$_{50}$La$_{9}$ (3156.80): C, 31.96; H, 3.10. Found: C, 31.42; H, 3.07. IR (KBr pellet, cm$^{-1}$): 3854 w, 3738 w, 3438 m, 2931 w, 2357 m, 1571 s, 1497 s, 1417 s, 1296 w, 1116 w, 1065 w, 954 w, 823 w, 651 w, 561 w. [Gd$_2$(μ$_4$-dcd)$_6$(H$_2$O)$_n$]$_n$ (2). Although compound 2 can be synthesized through the synthetic route described by us, we here adopted an additional synthetic method similar to that described for 1. Yellowish block-like single crystals of 2 were filtered off, washed with ultrapure water, and dried in air (yields: 80%). [Gd$_2$(μ$_2$-OH)$_2$(μ$_2$-dcd)]$_2$(μ$_2$-ac)$_2$(H$_2$O)$_n$ (3). A mixture of 10.0 mmol Gd(ac)$_3$, 4H$_2$O, 5.0 mmol 6,6-dimethyl-3-oxabicyclo[3.1.0]hexane-2,4-dione, 10.0 mmol NaOH, and 20.0 mL H$_2$O was first stirred in a beaker for 30 min. Then, the obtained aqueous suspension was transferred into a 40 mL Teflon-lined stainless-steel vessel and heated at 180 °C for 5 days. After the reactant mixture was slowly cooled to room temperature, the colorless stick-like single crystals of 3 can be found in the bottom of the vessel. Through filtering and washing with ultrapure water, the crystals were finally dried in air (yields: 75%). Elemental analysis (%) calcd for C$_{11}$H$_{18}$O$_{11}$Gd$_2$ (640.75): C, 20.62; H, 2.83. Found: C, 20.58; H, 2.78. IR (KBr pellet, cm$^{-1}$): 3744 w, 3638 w, 3239 m, 2952 m, 2374 w, 1585 vs, 1438 vs, 1284 w, 1126 w, 1116 w, 1035 w, 968 w, 753 w, 667 m, 541 w.

Single-Crystal X-ray Crystallography. Appropriate crystals of 1, 2, and 3 were picked for single-crystal X-ray diffraction analysis. Crystal data were gathered at 296 K with Mo Kα radiation ($\lambda = 0.70736$ nm) using an Xcalibur Eos Gemini diffractometer. Decreasing data were completed by the CrysAlisPro program. The direct method was used to handle the construction by the SHELXL 97 program. The crystal structures were refined with the full matrix least-squares method based on $F^2$. By using the software Diamond, the structural images for all compounds were obtained. Furthermore, crystallographic data for crystals 1, 2, and 3 were stored in the Cambridge Crystallographic Data Centre. CCDC 1857980 (1), 1484198 (2), and 1857981 (3) contain the supplementary crystallographic data for this paper. These data are able to be acquired from the Cambridge Crystallographic Data Centre for free www.ccdc.cam.ac.uk/data_request/cif. The data and structure details of all crystals are indicated in Table 1. The coordination modes for carboxylate groups in dcd and ac ligands can also be displayed in Chart 1.

ASSOCIATED CONTENT

Supporting Information

The Supporting Information is available free of charge on the ACS Publications website at DOI: 10.1021/acsomega.8b01963.

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La$_{27}$ wheel cluster, 2D layered structure containing La$_{27}$ wheel clusters, structural assembly process from two parallel 2D layers to a final porous 3D lanthanum framework, TG curves, experimental and simulated PXRD patterns, experimental PXRD patterns for compound 1 sintered at 210 °C under a dynamic vacuum, N$_2$ adsorption/desorption isotherm, H$_2$ adsorption/desorption isotherm, CO$_2$ adsorption/desorption isotherm, CH$_4$ adsorption/desorption isotherm, and FT-IR spectra (PDF) Crystal data for compounds 1, 2, and 3 (TXT)

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