ABSTRACT: Starting from a dinuclear complex {Gd$_2$(L)$_2$(NO$_3$)$_6$(H$_2$O)$_2$}·2(CH$_3$CN) (1) based on 2,6-dimethoxyphenol (HL), a nonanuclear cluster {Gd$_9$(L)$_8$(μ$_4$-OH)$_4$(μ$_4$-OH)$_4$(μ$_2$-OCH$_3$)$_2$(NO$_3$)$_8$(H$_2$O)$_8$}·(OH)-2H$_2$O (2) was obtained via modulating the amount of the ligand and base. Both of them have been structurally and magnetically characterized. Complex 1 decorates the Gd$_2$ core bridged by double μ$_2$-phenoxyl oxygen atoms and coordinated neutral CH$_3$CN molecules, while 2 features the Gd$_9$ core with a sandglass-like topology. Magnetic investigations reveal that the weaker antiferromagnetic interactions between adjacent metal ions exist in complex 2 than in 1, which is in agreement with the theoretical results. Meanwhile, the magnetocaloric effect with a maximum $-\Delta S_m$ value changes from 27.32 to 40.60 J kg$^{-1}$ K$^{-1}$ at 2 K and 7 T.

INTRODUCTION

In the last 2 decades, cryogenic magnetic refrigeration based on the magnetocaloric effect (MCE) has gained much attention due to the energy efficiency, environmental friendliness, and anticipated compactness, which has potential application in replacing increasingly rare and expensive 3$^\text{He}$ as a coolant.$^{1-3}$ The MCE is related to the changes of isothermal magnetic entropy ($\Delta S_m$) and adiabatic temperature ($\Delta T_m$) of the magnetic materials upon application of a magnetic field. Considering the large spin ground state ($S=7/2$) of an isotropic Gd$^{III}$ ion and the weak magnetic couplings between Gd$^{III}$ ions, Gd-clusters are probably the most promising candidates to obtain larger $-\Delta S_m$ as molecular magnetic coolants.$^{4-7}$

Generally speaking, high magnetic density, which guarantees the large metal/ligand mass ratio, is favorable to enhance the MCE. In this sense, a successful approach that has been proposed to obtain the larger MCE is to construct Gd$^{III}$ ions with light and multidentate organic or inorganic ligands.$^{8-10}$ Accordingly, a number of Gd-clusters and coordination polymers with various structures have been constructed and investigated, and the maximum value of $-\Delta S_m$ has been continuously exceeded.$^{11-24}$ Nonanuclear Ln-clusters, especially those with a sandglass topology, were attractively synthesized, but the MCE of Gd complexes was usually neglected.$^{25-29}$ Admittedly, it remains a challenge for researchers to available design and synthesize the limited high nuclearity Gd-clusters that afford interesting structural features and high MCE because of several challenges in synthesizing this type of clusters, such as the coordination modes of the ligands, anion templates, the ratio of raw materials, the pH value, solvents, as well as the temperature. Furthermore, apart from high magnetic density, the large MCE of Gd-clusters is also dependent upon weak magnetic couplings between the metal ions. This is because strong magnetic (ferromagnetic or antiferromagnetic) exchanges that tend to offset the surrounding magnetic moments will fatally cut down the entropy changes.$^5$

Based on the aforementioned considerations, we attempted to further explore the structure–activity relationship between the structural characteristic and the MCE of Gd-clusters. A simple but remarkable ligand, 2,6-dimethoxyphenol (HL), was employed to assemble the corresponding clusters according to the following considerations: (1) Recently, 2,6-dimethoxyphenol that demonstrated to be a good candidate for building 4f clusters with a relatively small molecular weight, in favor of achieving high magnetic density.$^{30-34}$ (2) Phenoxyl donor atoms generally preferred for providing a weak magnetic coupling pathway between Ln$^{III}$ ions. (3) Most of the reported structures consisting of this ligand are dinuclear configurations, and until now, the largest nuclearity was hexa-member Dy$_6$ ring by adopting a mixed-ligand strategy.$^{30}$ It is a promising strategy to construct higher nuclearity Gd-clusters with the enhanced MCE by the utilization of HL via the coordination-driven assembly. In accordance with the reported results, a dinuclear...
cluster \{\text{Gd}_2(L)_2(\text{NO}_3)_4(\text{H}_2\text{O})_2\cdot2(\text{CH}_3\text{CN})\} (1) was first constructed by the utilization of HL and Gd salt under a base condition. The dimer structure exhibits wide coordination sites of Gd ions, which supplies the possibility of introducing more coordination ligands and metal centers to construct the higher cluster structure. In consistent with our assumption, a nonanuclear cluster \{\text{Gd}_8(L)_4(\mu_4-\text{OH})_4(\mu_3-\text{OH})_4(\mu_2-\text{OCH}_3)_4(\text{NO}_3)_4(\text{H}_2\text{O})_4\} (\text{OH})_2\text{H}_2\text{O} (2) had been fabricated by the utilization of the dimer crystal sample as starting materials. Both of these two samples had been magnetically characterized. The \(-\Delta S_{m}^{\text{max}}\) derived from isothermal magnetization is up to 27.32 J kg\(^{-1}\) K\(^{-1}\) for 1 and 40.60 J kg\(^{-1}\) K\(^{-1}\) for 2 at T = 2 K and \(\Delta H = 7 \text{T}\), illustrating the important role of higher cluster for improving MCE property. Furthermore, it is worth noting that the \(-\Delta S_{m}^{\text{max}}\) still achieves 20.4 J kg\(^{-1}\) K\(^{-1}\) for 2 at T = 2 K and \(\Delta H = 3 \text{T}\), which is close to the capacity of commercialized gadolinium gallium garnet Gd\(_3\)Ga\(_2\)O\(_9\) (GGG, about 24 J kg\(^{-1}\) K\(^{-1}\) with \(\Delta H = 3 \text{T}\)). Herein, the synthesis, crystal structures, and magnetic properties of 1–2 are described in detail.

**RESULTS AND DISCUSSION**

**Synthesis.** The reaction of organic ligand and Gd salt under a base condition in the binary solvent mixture MeOH/MeCN (v/v = 1) produced the symmetric dinuclear cluster \{\text{Gd}_2(L)_2(\text{NO}_3)_4(\text{H}_2\text{O})_2\cdot2(\text{CH}_3\text{CN})\} (1). Taking advantage of the crystalline samples of 1 as the starting materials along with the addition of more ligand and base, a sandglass-like topology nonanuclear cluster \{\text{Gd}_8(L)_4(\mu_4-\text{OH})_4(\mu_3-\text{OH})_4(\mu_2-\text{OCH}_3)_4(\text{NO}_3)_4(\text{H}_2\text{O})_4\} (\text{OH})_2\text{H}_2\text{O} (2) had been subsequently obtained. The structural transition could be validated by SCXRD and PXRD (see Table S1 and Figure S5 in the Supporting Information).

**Crystal Structure Description.** For cluster 1, the molecular structure exhibiting the symmetric dinuclear core, as shown in Figures 1a and S1 (with partial labeling), crystalizes in the triclinic space group P\(\bar{1}\). The asymmetric unit comprises one crystallographically independent Gd ion, one deprotonated L ligand, one coordinated water, two nitrate anions, and a free acetonitrile solvent. The central metal ions adopt nine-coordinated spheres [Gd\(_{\text{O}}\)], which are occupied by four oxygen atoms from two deprotonated L ligands, one oxygen atom from water molecules, and two bidentate-chelating nitrate anions. The local coordination configuration of the Gd ion could be seen as spherical-capped square antiprism \((C_{4h})\) that was evaluated by employing SHAPE software \(^{35,36}\) (Figure 2a and Table S4). The two crystallographically unique Gd ions are bonded together via two doubly bridged phenoxido atoms of L, which also adapt bidentate chelating fashion by O2·—O1 and O2·—O3 atoms. The intramolecular Gd–Gd distance is 3.848(8) Å along with the Gd1–O2–Gd1A angle of 113.68°, and the Gd–O bond lengths are in the normal range of 2.281(5)–2.528(5) Å. The two symmetric ligands run parallel to each other, causing the relative displacement of two Gd ions.

Cluster 2 could be prepared via modulating the concentration of ligand and base amount in the solution of cluster 1. As shown in Figures 1 and S2, compound 2 features the Gd\(_3\) core with a
sandglass-like topology, which crystallizes in the orthorhombic I222 space group, and the asymmetric unit consists of one deprotonated L ligand, three independent Gd(III) ions, two nitrate anions, two coordinated water, one methoxy group, and \( \mu_4\)-, \( \mu_3\)-hydroxyl groups. The Gd(1) ion is located in a special Wyckoff position connected by eight \( \mu_3\)-bridging hydroxyl groups and adapts an almost perfect square antiprism coordination geometry, which was also determined by the SHAPE software with a very small deviation value of 0.319 (Figure 2b and Table S4). Each \( \mu_3\)-hydroxo group connects the other two Gd ions (Gd(2) and Gd(3) ions) together, forming the nonanuclear molecular structure with the Gd···Gd distances of 3.807(8) and 3.817(8) Å. The \( \mu_4\)-hydroxyl or methoxy groups further interconnect two sets of symmetric Gd(2) and Gd(3) ions to constitute the basal plane with the Gd···Gd distances of 3.605(2) and 3.521(1) Å, giving rise to a slightly distorted square antiprism geometry of Gd(1) ion. Two vertex-sharing square pyramids stack over each other with the basal planes rotated by 45°. The Gd−O bond lengths are in the range of 2.294(1)−2.654(1) Å, in agreement with the related distances of other similar Gd clusters.

**Magnetic Properties of 1−2.** The direct-current (dc) magnetic susceptibility data for polycrystalline powders 1 and 2 were measured in the temperature range of 1.8−300 K under an applied field of 1000 Oe, as shown in Figure 3. The observed \( \chi_M T \) product of 15.52 cm\(^3\) K mol\(^{-1}\) for 1 and 69.31 cm\(^3\) K mol\(^{-1}\) for 2 at 300 K is close to the expected values of 15.76 cm\(^3\) K mol\(^{-1}\) for two free Gd(III) ions and 70.92 cm\(^3\) K mol\(^{-1}\) for nine isolated Gd(III) ions. As temperature decreases, the \( \chi_M T \) values gradually decrease above 50 K for both complexes and then rapidly drop to minimum values of 5.46 and 22.09 cm\(^3\) K mol\(^{-1}\) for 1 and 2 at 1.8 K, respectively. The decrease of the \( \chi_M T \) value below 50 K could be attributed to the occurrence of weak antiferromagnetic exchange between the Gd(III) centers. Meanwhile, the \( \chi_M T \) vs T plots obeying the Curie−Weiss law lead to Weiss constants of −5.44 and −4.58 K for 1 and 2, respectively. The negative Weiss parameters further prove the presence of weak antiferromagnetic interactions between the Gd(III) centers.

In order to illustrate the magnetic coupling mechanism of compounds 1 and 2, magnetic fitting was carried out following the Hamilton operators (Figure 4). The coupling parameter \( J \)
was used to represent the magnetic exchange between adjacent Gd$^{3+}$ ions. For 1, the magnetic propagation is dominated by two $\mu_2$-O bridges ($J_1$). However, it is impossible to perform the irreducible tensor methods owing to the great large matrix of $8^4 \times 8^2$ for 2. Thus, a combination of Genetic Algorithm$^{39}$ with the Quantum Monte Carlo (QMC) method of ALPS$^{40}$ software is used to simulate magnetic parameters.$^{3,41,42}$ Inspection of the whole structure of 2 can unveil that the magnetic property is originated from the mixed bridges ($J_1$) of $\mu_2$-O and $\mu_2$-OH, pure bridge ($J_2$) of $\mu_2$-OH, and the bridge ($J_3$) of $\mu_2$-OH. The related coupling parameters could be defined based on eqs 1 and 2, respectively.

$$H = -JS_S S_2$$  \hspace{1cm} (1)

$$H = -J_1(S_S S_2 + S_S S_3 + S_S S_4 + S_S S_5 + S_S S_7 + S_S S_8$$
$$+ S_S S_9) - J_2(S_S S_1 + S_S S_2 + S_S S_7 + S_S S_9)$$
$$- J_3(S_S S_1 + S_S S_2 + S_S S_3 + S_S S_4 + S_S S_5 + S_S S_6$$
$$+ S_S S_7 + S_S S_8)$$  \hspace{1cm} (2)

According to least reliability factor $R (\sum[(\chi M)_\text{obs} - (\chi M)\text{calcd}]^2/\sum[(\chi M)_\text{obs}]^2)$, the best set of optimal parameters: $J_1 = -0.26 \text{ cm}^{-1}, J_2 = -0.266 \text{ cm}^{-1}, J_3 = -0.146 \text{ cm}^{-1}, g = 1.95$, and $R = 1.17 \times 10^{-3}$ for 1; $J_1 = 0.0108 \text{ cm}^{-1}, J_2 = -0.266 \text{ cm}^{-1}, J_3 = -0.146 \text{ cm}^{-1}, g = 1.95$, and $R = 3.83 \times 10^{-4}$ for 2. It is concluded that (1) the mixed bridges ($J_1 = 0.0108$) of $\mu_2$-O and $\mu_2$-OH indicate very weak ferromagnetic coupling, while the rest of bridges feature weak antiferromagnetic couplings; (2) generally, the antiferromagnetic property of 1 is slightly larger than that of 2. To prove the results, spin-polarized density functional theory calculation with PBE functional was carried out by using VASP program.$^{43}$ To reduce the effect of self-interaction error, DFT + $U$ with the $U_{eff}$ (10.0 eV)$^{44}$ is used to correct the strongly correlated interaction of 4f electrons of Gd$^{3+}$ ions. We combined the broken-symmetry techniques of Noodleman and the non-spin projected strategy of Ruiz to estimate magnetic exchange parameters (see Supporting Information). The obtained coupling parameters are $J = -0.65 \text{ cm}^{-1}$ for 1 and $J_1 = 0.52 \text{ cm}^{-1}, J_2 = -1.49 \text{ cm}^{-1}, J_3 = -0.62 \text{ cm}^{-1}$ for 2. Despite the values from DFT calculation are larger than those of QMC simulation because of the energy-difference overestimation of DFT methods, both of them feature the same magnetic coupling characteristics.

The field dependence of the magnetization was carried out at $1.8-15 \text{ K}$ and $0-7 \text{ T}$, as shown in Figure 5. The magnetization values rise gradually accompanying the increasing fields and attain the saturated value of $12.87 \text{ N} / \beta$ and $60.77 \text{ N} / \beta$ at 7 T and 1.8 K for 1 and 2, respectively, which are slightly smaller than the theoretical ones of 14 N/β for two non-interacting Gd$^{3+}$ ions and 63 N/β for nine non-interacting Gd$^{3+}$ ions. It also indicates that the intramolecular antiferromagnetic interactions in the above-mentioned compounds are very weak.

As well known, a magnetic system with larger isolated spins without zero-field splitting, spin–orbit coupling, and hyperfine interaction constantly manifests a larger MCE.$^{45}$ The values of magnetic entropy change ($-\Delta S_m$) have been calculated using

![Figure 5](https://doi.org/10.1021/acsomega.2c04412)

Figure 5. Isothermal magnetization plots for 1 (left) and 2 (right). The solid lines are a guide for the eye.

![Figure 6](https://doi.org/10.1021/acsomega.2c04412)

Figure 6. Temperature-dependent $-\Delta S_m$ value obtained from magnetization for 1 (left) and 2 (right). The solid lines are a guide for the eye.
the Maxwell thermodynamic relation of \(\Delta S_m(\Delta H) = \int \left( \frac{\partial M(T, H)}{\partial T} \right)_H dH\) based on the experimental magnetization data, as shown in Figure 5, where \(T\) is the applied temperature, \(H\) is the applied magnetic field, and \(M\) is magnetization. The \(-\Delta S_m\) values of both complexes are tardily increased along with the increasing applied magnetic field and the decreasing temperature. The maximum values of \(-\Delta S_m\) reach 27.32 J kg\(^{-1}\) K\(^{-1}\) for 1 and 40.60 J kg\(^{-1}\) K\(^{-1}\) for 2 at 2 K with a field change of 7 T (Figure 6). The experimental values are smaller than the corresponding calculated ones based on the equation \(-\Delta S_m = nR \ln(S^2 + 1)\) (\(R\) is the gas constant and \(S\) is the spin state), which are attributable to the presence of weak antiferromagnetic interactions between spin centers. Nevertheless, the observed \(-\Delta S_m\) value of 2 is still comparable to those of the reported higher nuclear metal clusters due to the weaker magnetic interaction, such as Gd\(^{III}\) (\(-\Delta S_m = 39.66\) J kg\(^{-1}\) K\(^{-1}\) with \(\Delta H = 7\) T),\(^{16}\) Gd\(^{III}\) (\(-\Delta S_m = 38.71\) J kg\(^{-1}\) K\(^{-1}\) with \(\Delta H = 7\) T),\(^{19}\) and Gd\(^{III}\) (\(-\Delta S_m = 37.9\) J kg\(^{-1}\) K\(^{-1}\) with \(\Delta H = 7\) T).\(^{47}\) Furthermore, in terms of the lack of anisotropy and orbit contribution on Gd\(^{III}\) ions, the interaction between Gd\(^{III}\) ions plays a significant role in the great MCE. It is clear that the \(-\Delta S_m\) value of 2 is larger than that of 1 at the same temperature and applied field. Meanwhile, the absolute value of Weiss temperature of 2 is smaller than the value of 1. These indicate that the antiferromagnetic interaction in 2 is weaker, which is in good agreement with the theoretical calculation, in combination with greater magnetic density leads to the larger MCE.

**CONCLUSIONS**

In summary, two different nuclearity Gd-clusters had been synthesized under the guidance of the specific synthesis strategy, whose crystal structures and magnetic properties had been fully characterized. Importantly, the nonanuclear cluster 2 with sandglass-like topology can be obtained via modulating the concentration of ligand and base amount in the solution of 1. Both magnetization experimental and theoretical calculations demonstrate the existence of weak antiferromagnetic interactions in adjacent Gd\(^{III}\) ions of both 1 and 2. Due to the high spin density and the dominant weak antiferromagnetic coupling, both of them display a large MCE, with the maximum \(-\Delta S_m\) values of 27.32 and 40.60 J kg\(^{-1}\) K\(^{-1}\) \(-\Delta S_m\) for 2 at 2 K and 7 T, respectively. Caused by the structural conversion from 1 to 2, the presence of higher magnetic density and weaker exchange interaction contribute to a significantly increased MCE. Notably, the \(-\Delta S_m\) still achieves 20.4 J kg\(^{-1}\) K\(^{-1}\) at \(T = 2\) K and \(\Delta H = 3\) T, making cluster 2 a promising candidate for cryo-magnetic refrigerants at low temperature and external fields. As observed in the present work, the proper modulation of the cluster structure may afford a feasible strategy for tuning the MCE of polynuclear gadolinium systems.

**ASSOCIATED CONTENT**

- **Supporting Information**
  The Supporting Information is available free of charge at https://pubs.acs.org/doi/10.1021/acsomega.2c04412.

  Materials and general methods; X-ray structural determination; crystal data and structure refinements; selected bond lengths and bond angles; evaluated local coordination geometry analysis; spin magnetic moment; perspective view of the asymmetric unit and ORTEP representation; FT-IR spectra; TG curves; PXRD patterns; and computational details (PDF)

- **Crystal structure of 1 (CIF)**
- **Crystal structure of 2 (CIF)**

**Accession Codes**

CCDC 1577366 and 2103547 contain the supplementary crystallographic data for this paper. These data can be obtained free of charge via www.ccdc.cam.ac.uk/data_request/cif, or by emailing data_request@ccdc.cam.ac.uk, or by contacting The Cambridge Crystallographic Data Centre, 12 Union Road, Cambridge CB2 1EZ, UK; fax: +44 1223 336033.

**AUTHOR INFORMATION**

**Corresponding Authors**

Ludi Ji — Hubei Key Laboratory of Radiation Chemistry and Functional Materials, Non-power Nuclear Technology Collaborative Innovation Center, Hubei University of Science and Technology, Xianning, Hubei 437100, China; Email: jiludi@126.com

Bao Li — Hubei Key Laboratory of Bioinorganic Chemistry & Materia Medica, School of Chemistry and Chemical Engineering, Huazhong University of Science and Technology, Wuhan, Hubei 430074, China; Email: libao@hust.edu.cn

**Authors**

Peng Hu — Hubei Key Laboratory of Radiation Chemistry and Functional Materials, Non-power Nuclear Technology Collaborative Innovation Center, Hubei University of Science and Technology, Xianning, Hubei 437100, China

Shanghua Li — Hubei Key Laboratory of Radiation Chemistry and Functional Materials, Non-power Nuclear Technology Collaborative Innovation Center, Hubei University of Science and Technology, Xianning, Hubei 437100, China

Linghui Cao — Hubei Key Laboratory of Bioinorganic Chemistry & Materia Medica, School of Chemistry and Chemical Engineering, Huazhong University of Science and Technology, Wuhan, Hubei 430074, China

Aogang Liu — Hubei Key Laboratory of Bioinorganic Chemistry & Materia Medica, School of Chemistry and Chemical Engineering, Huazhong University of Science and Technology, Wuhan, Hubei 430074, China

Gui-Lin Zhuang — Institute of Industrial Catalysis, College of Chemical Engineering, Zhejiang University of Technology, Hangzhou, Zhejiang 310023, China; orcid.org/0000-0002-4763-7397

Complete contact information is available at: https://pubs.acs.org/doi/10.1021/acsomega.2c04412

**Notes**

The authors declare no competing financial interest.

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