

两个 Gd₂配合物的晶体结构及磁制冷性质

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摘要: 使用多齿席夫碱配体(H₂L=pyridine-2-carboxylic acid(3,5-di-*tert*-butyl-2-hydroxy-benzylidene)-hydrazide)分别与 Gd(dbm)₃·2H₂O(Hdbm=二苯甲酰基甲烷)及 Gd(NO₃)₃·6H₂O 反应,通过溶剂热法得到了2个新的 Gd₂配合物[Gd₂(L)₂(dbm)₂(C₂H₅OH)₂] (**1**)和 [Gd₂(L)₂(HL)₂(DMF)]·2CH₃CN (**2**)(DMF=*N,N*-二甲基甲酰胺),并对其结构与磁性进行了系统的研究。单晶结构分析表明配合物**1**中的每个中心 Gd(III)离子均为8配位,其配位几何构型为略微变形的三角十二面体,相邻的中心 Gd(III)离子通过2个 μ₂-O 连接形成了平行四边形的 Gd₂O₂核心;配合物**2**中的每个中心 Gd(III)离子均为9配位,其配位几何构型为扭曲的球形单帽四方反棱柱,相邻的中心 Gd(III)离子通过3个 μ₂-O 连接形成了三角双锥形的 Gd₂O₃核心。磁性测试表明配合物**1**和**2**具有磁制冷性质,其最大磁熵变(-ΔS_m)分别为 20.16 J·K⁻¹·kg⁻¹(T=2.0 K, ΔH=70 kOe)和 17.14 J·K⁻¹·kg⁻¹(T=2.0 K, ΔH=70 kOe)。

关键词: Gd₂配合物; 晶体结构; 磁性; 磁制冷性质

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Crystal Structures and Magnetic Refrigeration Properties of Two Gd₂ Complexes

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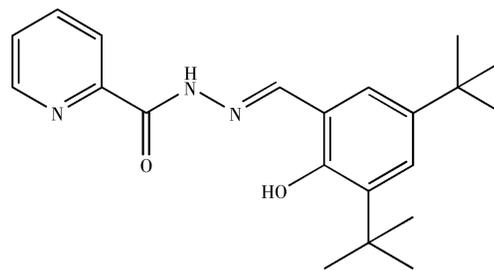
Abstract: By utilizing a polydentate Schiff base ligand (H₂L=pyridine-2-carboxylic acid (3,5-di-*tert*-butyl-2-hydroxy-benzylidene)-hydrazide), reacting with Gd(dbm)₃·2H₂O (Hdbm=dibenzoylmethane) and Gd(NO₃)₃·6H₂O, respectively; two new Gd₂ complexes formulated as [Gd₂(L)₂(dbm)₂(C₂H₅OH)₂] (**1**) and [Gd₂(L)₂(HL)₂(DMF)]·2CH₃CN (**2**) (DMF=*N,N*-dimethylformamide) have been obtained by using solvothermal method. The crystal structures and magnetic properties of the two Gd₂ complexes have been systematically studied. The crystal structures study reveals that each eight-coordinate Gd³⁺ ion in **1** possesses a distorted triangular dodecahedron; the two central Gd(III) ions are connected by two μ₂-O, resulting in a rhombic-shaped Gd₂O₂ core. However, for **2**, each central Gd(III) ion is nine-coordinate and their coordination configurations can be described as distorted spherical capped square antiprism, and the two central Gd(III) ions are connected by three μ₂-O forming a triangular biconical-shaped Gd₂O₃ core. Magnetic investigations showed that the two Gd₂ complexes displayed magnetic refrigeration properties with the magnetic entropy (-ΔS_m) of 20.16 J·K⁻¹·kg⁻¹ for **1** and 17.14 J·K⁻¹·kg⁻¹ for **2** at ΔH=70 kOe and T=2.0 K. CCDC: 2111657, **1**; 2111658, **2**.

Keywords: Gd₂ complexes; crystal structures; magnetic properties; magnetic refrigeration properties

0 Introduction

In recent years, the studies of lanthanide-based compounds have attracted increasing attention of chemists and material scientists not only due to their beauty and fascinating crystal structures^[1] but also because of the potential applications in functional materials, including interesting magnetic properties, luminescence properties, and catalysis^[2-4]. Among these potential applications of lanthanide-based compounds, the molecular-based magnetic material is one of the research hotspots for inorganic chemistry and material chemistry^[5], and magnetic refrigeration and single-molecule magnets (SMMs) are particularly attractive^[6-9]. Key to the potential magnetic refrigeration application of a molecular-based magnetic material is its large magnetocaloric effect (MCE)^[10], and an excellent magnetic refrigeration material featuring large MCE should possess negligible magnetic anisotropy and a large magnetic density^[11]. Hence, the isotropic Gd(III) ion with a high spin state ($S=7/2$) is the best candidate for designing and constructing Gd(III)-based compounds, which would be a promising magnetic refrigerant material to perform significant MCE^[12]. Based on this, lots of poly-nuclear or high-nuclear Gd(III)-based clusters with fascinating structures and larger MCE have been reported over the past decade^[13-16]. It is worth mentioning that Long, Tong, and Zheng's group have conducted outstanding work on the magnetic refrigeration materials of Gd(III)-based clusters^[17-19]. These studies inspire and promote the synthesis of lanthanide-based compounds with outstanding and excellent magnetic refrigeration materials.

It is well-known that the Schiff base ligand is a type of classical ligand. In the past decade, lots of Ln(III)-based compounds with novel topologies and showing outstanding magnetic properties have been constructed by using Schiff base ligands^[20-23]. Considering the advantage of Schiff base ligands, we design and synthesize an organic polydentate Schiff base ligand (H_2L =pyridine-2-carboxylic acid (3,5-di-*tert*-butyl-2-hydroxybenzylidene)-hydrazide, Scheme 1) which possesses abundant coordination sites, strong chelating ability, and various coordination patterns. When H_2L reacted



Scheme 1 Structure of organic polydentate Schiff base H_2L

with $Gd(dbm)_3 \cdot 2H_2O$ ($Hdbm$ =dibenzoylmethane) or $Gd(NO_3)_3 \cdot 6H_2O$, two new Gd_2 complexes with the molecular formulas $[Gd_2(L)_2(dbm)_2(C_2H_5OH)_2]$ (**1**) and $[Gd_2(L)_2(HL)_2(DMF)] \cdot 2CH_3CN$ (**2**) (DMF =*N,N*-dimethylformamide) have been synthesized through a solvothermal method. The structural and magnetic properties of **1** and **2** were deeply investigated and discussed. The magnetic study revealed that complexes **1** and **2** show MCE with $-\Delta S_m$ of $20.16 J \cdot K^{-1} \cdot kg^{-1}$ for **1** and $17.14 J \cdot K^{-1} \cdot kg^{-1}$ for **2** at $\Delta H=70$ kOe and $T=2.0$ K.

1 Experimental

1.1 Materials and measurements

Gadolinium nitrate hexahydrate ($Gd(NO_3)_3 \cdot 6H_2O$) was bought from Energy Chemical Co., Ltd. DMF, ethanol, acetonitrile, and other solvents were purchased from Fuchen chemical corporation. $Hdbm$, picolinohydrazide, and 3,5-di-*tert*-butylsalicylaldehyde were purchased from Aladdin Reagent (Shanghai) Co., Ltd. $Gd(dbm)_3 \cdot 2H_2O$ and polydentate Schiff base ligand H_2L were prepared by using an already reported literature method^[24-25]. The elemental analyses (C, H, and N) of complexes **1** and **2** were performed on a PerkinElmer 240 CHN elemental analyzer. Magnetic properties for complexes **1** and **2** were measured using a Quantum Design MPMS-XL7 and a PPMS-9 ACMS magnetometer. Diamagnetic corrections were estimated with Pascal's constants for all atoms^[26].

1.2 Syntheses of complexes **1** and **2**

$[Gd_2(L)_2(dbm)_2(C_2H_5OH)_2]$ (**1**): H_2L (0.05 mmol), $Gd(dbm)_3 \cdot 2H_2O$ (0.05 mmol), ethanol (6.0 mL), and acetonitrile (5.0 mL) were enclosed in a glass vial (20 mL), and then the mixture was heated to $70^\circ C$ and keep at this temperature for 72 h, and then the temperature was dropped to room temperature slowly. Yellow

block crystals suitable for X-ray diffraction were obtained. Yields based on Gd(dbm)₃·2H₂O: 41%. Elemental analysis Calcd. for C₇₆H₈₄Gd₂N₆O₁₀(%): C 58.61, H 5.40, N 5.40; Found(%): C 58.65, H 5.37, N 5.44.

[Gd₂(L)₂(HL)₂(DMF)]·2CH₃CN (**2**): H₂L (0.03 mmol), Gd(NO₃)₃·6H₂O (0.03 mmol), ethanol (3.0 mL), DMF (2.0 mL), and acetonitrile (2.0 mL) were added to a three flask and stirred at room temperature for about 3 h. Then the mixture was sealed in a 15 mL glass bottle and heated to 80 °C to react for 48 h and then slowly cooled to room temperature subsequently. Yellow block crystals suitable for X-ray diffraction were obtained. Yields based on Gd(NO₃)₃·6H₂O: 32%. Elemental analysis Calcd. for C₉₁H₁₁₅Gd₂N₁₅O₉(%): C 58.16, H 6.13, N 11.19; Found(%): C 58.11, H 6.17, N 11.25.

1.3 X-ray crystallography

The crystallographic diffraction data for complexes **1** and **2** were collected on a Bruker SMART APEX II CCD diffractometer equipped with graphite monochro-

matized Mo K α radiation ($\lambda=0.071\ 073$ nm) by using φ - ω scan mode. Multi-scan absorption correction was applied to the intensity data using the SADABS program. The structures were solved by direct methods and refined by full-matrix least-squares on F^2 using the SHELXTL (Olex 2) program^[27]. All non-hydrogen atoms were refined anisotropically. All the other H atoms were positioned geometrically and refined using a riding model. Due to the existence of disordered solvent molecules in the crystals of **1** and **2**, we remove the disordered solvent molecules by using PLATON/SQUEEZE program. To determine the specific number of free solvent molecules, the thermogravimetric analysis (TGA) of the crystal samples for **1** and **2** have been measured. Details of the crystal data and structure refinement parameters for complexes **1** and **2** are summarized in Table 1, and selected bond lengths and angles of complexes **1** and **2** are listed in Table S1 and S2 (Supporting information).

CCDC: 2111657, **1**; 2111658, **2**.

Table 1 Crystal data and structure refinement parameters for **1** and **2**

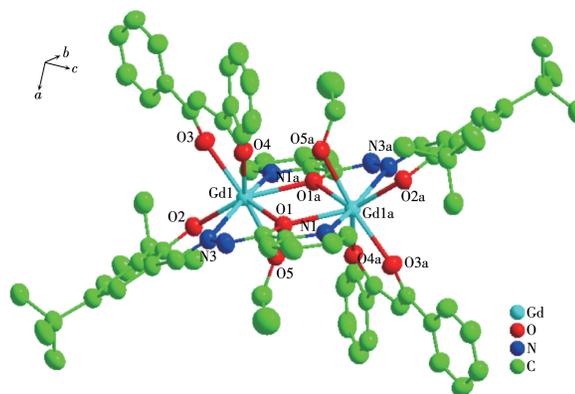
| Parameter | 1 | 2 |
|---------------------------------------|--|---|
| Formula | C ₇₆ H ₈₄ Gd ₂ N ₆ O ₁₀ | C ₉₁ H ₁₁₅ Gd ₂ N ₁₅ O ₉ |
| Formula weight | 1 555.99 | 1 877.42 |
| T / K | 150.0 | 150.0 |
| Crystal system | Monoclinic | Monoclinic |
| Space group | $P2_1/c$ | $P2_1/c$ |
| a / nm | 1.230 26(2) | 2.068 43(6) |
| b / nm | 1.536 69(2) | 1.985 86(5) |
| c / nm | 1.869 93(3) | 2.467 71(8) |
| $\beta / (^\circ)$ | 97.916 1(6) | 91.634 0(11) |
| V / nm^3 | 3.501 47(9) | 10.132 3(5) |
| Z | 2 | 4 |
| Crystal size / mm | 0.36×0.21×0.14 | 0.26×0.13×0.11 |
| $D_c / (\text{g}\cdot\text{cm}^{-3})$ | 1.476 | 1.204 |
| μ / mm^{-1} | 1.940 | 1.353 |
| Limiting indices | $-15 \leq h \leq 14, -19 \leq k \leq 19, -23 \leq l \leq 23$ | $-25 \leq h \leq 25, -24 \leq k \leq 24, -30 \leq l \leq 30$ |
| Reflection collected | 44 308 | 144 368 |
| Unique | 7 178 | 20 725 |
| Parameter | 434 | 1 054 |
| R_{int} | 0.036 5 | 0.084 8 |
| GOF on F^2 | 1.042 | 1.082 |
| $R_1, wR_2 [I > 2\sigma(I)]$ | 0.023 6, 0.056 6 | 0.046 1, 0.108 9 |
| R_1, wR_2 (all data) | 0.030 8, 0.060 9 | 0.068 7, 0.119 9 |

2 Results and discussion

2.1 Crystal structures of complexes **1** and **2**

Single-crystal X-ray diffraction analyses reveal that both complexes **1** and **2** crystallize in the monoclinic space group $P2_1/c$ (Table 1). As shown in Fig. 1, the structure of **1** contains two Gd(III) ions, two L^{2-} ions, two dbm^- ions, and two coordinated C_2H_5OH molecules. Each central Gd(III) ion in complex **1** is coordinated by six oxygen atoms (O1, O1a, O2, O3, O4, and O5) and two nitrogen atoms (N1 and N3) forming an O_6N_2 coordination environment (Fig.S1). As shown in Fig.S2, the eight-coordinate Gd1 ion shows a distorted triangular dodecahedron (D_{2h}) coordination geometry. It is also confirmed by using SHAPE 2.0 software (Table 2)^[28]. The coordination modes of L^{2-} and dbm^- are shown in Fig. 2. L^{2-} adopts a quad-dentate chelation model to connect the central Gd(III) ion, and dbm^- adopts a bidentate chelation model to connect the central Gd(III) ion. The Gd1 and Gd1a ions are connected by two μ_2 -O (O1 and O1a) atoms forming a parallelogram Gd_2O_2 core. The Gd1...Gd1a distance is 0.405 2(9) nm, which is slightly larger than those of some reported Gd_2 complexes^[29-32]. In addition, the Gd1—O1—Gd1a angle in the Gd_2O_2 core is 114.90(7)°. In **1**, the Gd—O distances fall in a range of 0.222 3(2)-0.243 1(7) nm, and the

Gd1—N1, Gd1—N3 bond lengths are 0.257 9(2) and 0.247 6(2) nm, respectively. The O—Gd—O bond angles fall in a range of 65.09(7)°-146.46(6)°.



H atoms are omitted for clarity; Symmetry code: a: 1-x, 1-y, 1-z

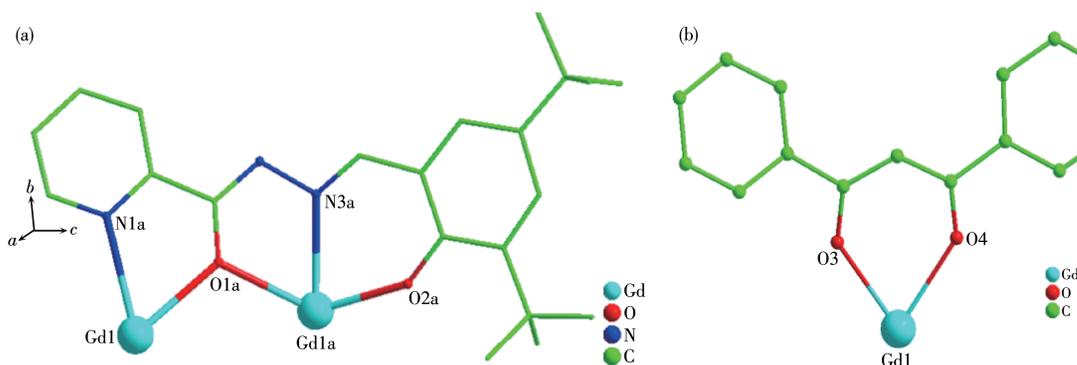
Fig.1 Molecular structure of complex **1** shown with 50% probability displacement ellipsoids

Different from **1**, complex **2** is mainly composed of two Gd(III) ions, two L^{2-} ions, two HL^- ions, and one coordinated DMF molecule (Fig.3). Both Gd1 and Gd2 ions in complex **2** are nine-coordinate, and each Gd(III) ion is coordinated by six oxygen atoms and three nitrogen atoms forming an N_3O_6 coordination environment (Fig.S3). Accordingly, as shown in Fig.S4, both of the nine-coordinate Gd(III) centers lie in a distorted spherical capped square antiprism (C_{4v}) which also can be cal-

Table 2 Gd^{III} ion geometry analysis by SHAPE 2.0 for **1***

| Gd ^{III} ion | D_{4d} SAPR-8 | D_{2d} TDD-8 | C_{2v} JBTPR-8 | C_{2v} BTPR-8 | D_{2d} JSD-8 |
|-----------------------|-----------------|----------------|------------------|-----------------|----------------|
| Gd1 | 3.696 | 2.053 | 4.054 | 2.901 | 5.227 |

* SAPR-8=square antiprism; TDD-8=triangular dodecahedron; JBTPR-8=biaugmented trigonal prism J50; BTPR-8=biaugmented trigonal prism; JSD-8=snub diphenoid J84.

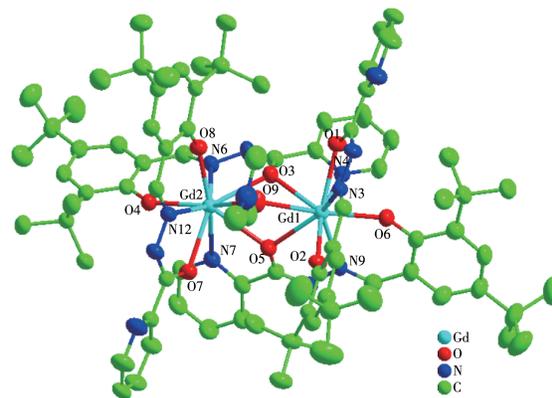


H atoms of C—H bonds are omitted for clarity; Symmetry code: a: 1-x, 1-y, 1-z

Fig.2 Coordination mode of L^{2-} (a) and dbm^- (b) in **1**

culated by using SHAPE 2.0 software (Table 3). There are two coordination modes for L²⁻ and HL⁻ in **2** (Fig.4): quad-dentate or tri-dentate chelation model to connect the central Gd(III) ion, respectively. The two Gd(III) ions are connected by three μ_2 -O (O3, O5, and O9) atoms forming a triangular biconical-shaped Gd₂O₃ core. The distance of the two central Gd(III) ions is 0.392 3(3) nm, which is smaller than that of complex **1**. The Gd1—O3—Gd2, Gd1—O9—Gd2, and Gd1—O9—Gd2 angles in the Gd₂O₃ core are 105.68(3)°, 98.64(6)°, and 106.95(4)°, respectively, which are also smaller than those of complex **1**. The Gd—O bond lengths are in a range of 0.225 3(3)-0.260 7(4) nm, while the average Gd—N distance is 0.261 2(1) nm. The O—Gd—O

bond angles fall in a range of 61.96(10)°-149.73(12)°.



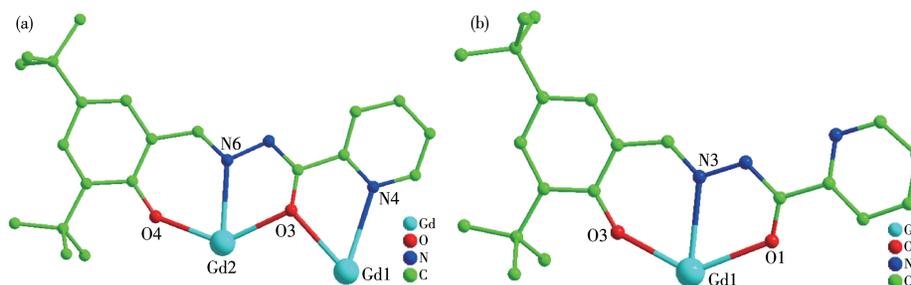
H atoms are omitted for clarity

Fig.3 Molecular structure of the complex **2** shown with 50% probability displacement ellipsoids

Table 3 Gd^{III} ion geometry analysis by SHAPE 2.0 for **2***

| Gd ^{III} ion | C _{4v} JCSAPR-9 | C _{4v} CSAPR-9 | D _{3h} JTCTPR-9 | D _{3h} TCTPR-9 | C _s MFF-9 |
|-----------------------|--------------------------|-------------------------|--------------------------|-------------------------|----------------------|
| Gd1 | 1.93 | 1.301 | 3.129 | 1.611 | 1.588 |
| Gd2 | 2.165 | 1.492 | 3.521 | 1.824 | 1.604 |

*JCSAPR-9=capped square antiprism J10; CSAPR-9=spherical capped square antiprism; JTCTPR-9=tricapped trigonal prism J51; TCTPR-9=spherical tricapped trigonal prism; MFF-9=muffin.



H atoms of C—H bonds are omitted for clarity

Fig.4 Coordination mode of L²⁻ (a) and HL⁻ (b) in **2**

2.2 TGA of complexes **1** and **2**

To study the thermal stabilities of complexes **1** and **2**, TGA was performed and the curves are shown in Fig.S5 and S6. For **1**, the weight loss of 5.78% (Calcd. 5.91%) between 26 and 285 °C can be attributed to the loss of two coordinated EtOH molecules. After that complex **1** started to decompose. For **2**, the weight loss of 4.11% from 26 to 245 °C is attributed to the loss of two free CH₃CN molecules (Calcd. 4.36%). Thereafter, a weight loss of 3.92% (Calcd. 3.88%) occurred, which is attributed to the loss of a coordinated DMF molecule. Subsequently, complex **2** gradually decomposed in a temperature range of 280-800 °C.

2.3 Magnetic properties of complexes **1** and **2**

Direct current (dc) magnetic susceptibility measurements for the two Gd₂ complexes **1** and **2** were performed on polycrystalline samples during a temperature range of 300.0-2.0 K under an applied field of 1 kOe. The $\chi_M T$ vs T plots for complexes **1** and **2** are shown in Fig.5. The room-temperature $\chi_M T$ products of **1** and **2** were 15.80 and 15.78 cm³·K·mol⁻¹, respectively, which are in good agreement with the expected value (15.76 cm³·K·mol⁻¹) for two uncoupled Gd(III) ions (⁸S_{7/2}, $g=2$). As the temperature decreased, the $\chi_M T$ values of **1** and **2** slowly declined during the temperature range of 300.0-25.0 K. Thereafter, the $\chi_M T$ values

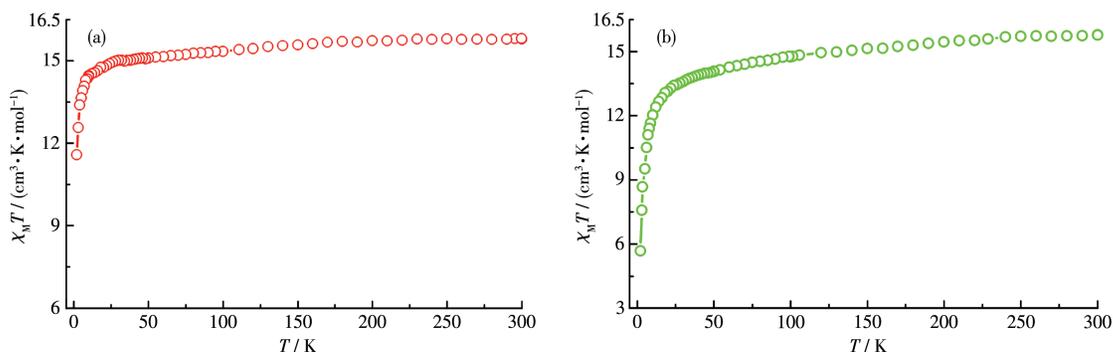


Fig.5 Temperature dependence of $\chi_M T$ products at 1.0 kOe for **1** (a) and **2** (b)

of **1** and **2** quickly dropped to a minimum of 11.58 and 5.68 $\text{cm}^3 \cdot \text{K} \cdot \text{mol}^{-1}$ at 2.0 K. The downward trend of the $\chi_M T$ vs T curves implies that there is an antiferromagnetic (AF) interaction between adjacent Gd(III) ions in the two Gd₂ complexes **1** and **2**^[33].

The Curie-Weiss law was used for fitting the magnetic susceptibility of complexes **1** and **2** (Fig.S7 and S8). The two parameters, $C=15.84 \text{ cm}^3 \cdot \text{K} \cdot \text{mol}^{-1}$ and $\theta=-1.84 \text{ K}$ ($R^2=0.9999$) for **1** and $C=15.91 \text{ cm}^3 \cdot \text{K} \cdot \text{mol}^{-1}$ and $\theta=-5.43 \text{ K}$ ($R^2=0.99951$) for **2** were obtained. The negative θ values of **1** and **2** further suggest that there is an antiferromagnetic interaction between adjacent Gd(III) ions in **1** and **2**^[34].

The magnetization data for the two Gd₂ complexes **1** and **2** were collected at 2.0-10.0 K in the 0-70 kOe field. As depicted in Fig.S9, the M values for complexes **1** and **2** rapidly increased below 20 kOe and then steadily increased to $14.13N\beta$ for **1** and $14.07N\beta$ for **2** at 70 kOe, which are very close to the saturation value of $14N\beta$ for two isolated Gd(III) ($S=7/2$, $g=2$) ions.

According to the previously reported literature^[35-37], because of the larger isotropic and high-spin ground state of Gd(III) ion, the MCE of both **1** and **2** was studied. The maximum magnetic entropy change ($-\Delta S_m$) of **1** and **2** were calculated by using the Maxwell equation: $\Delta S_m(T) = \int [\partial M(T, H) / \partial T]_H dH$ ^[38]. The $-\Delta S_m$ vs T curves of **1** and **2** are shown in Fig.6. The observed $-\Delta S_m$ values of **1** and **2** were 20.16 and 17.14 $\text{J} \cdot \text{K}^{-1} \cdot \text{kg}^{-1}$ at $\Delta H=70 \text{ kOe}$ and $T=2.0 \text{ K}$, which were smaller than the theoretical values of 22.22 $\text{J} \cdot \text{K}^{-1} \cdot \text{kg}^{-1}$ for **1** and 18.83 $\text{J} \cdot \text{K}^{-1} \cdot \text{kg}^{-1}$ for **2** (based on the equation $-\Delta S_m = 2R \ln(2S+1)/M$, $S_{\text{Gd}}=7/2$, and $R=8.314 \text{ J} \cdot \text{mol}^{-1} \cdot \text{K}^{-1}$). The difference between experimental and theoretical $-\Delta S_m$ values may be due to the antiferromagnetic interaction between Gd(III) ions in **1** and **2**^[39]. To better compare and display the $-\Delta S_m$ values of Gd₂ complexes, the $-\Delta S_m$ values of recently reported dinuclear Gd(III)-based complexes are listed in Table 4^[40-49]. The $-\Delta S_m$ of **2** was smaller than some reported Gd₂ complexes, however, it is worth mentioning that the $-\Delta S_m$ of complex **1**

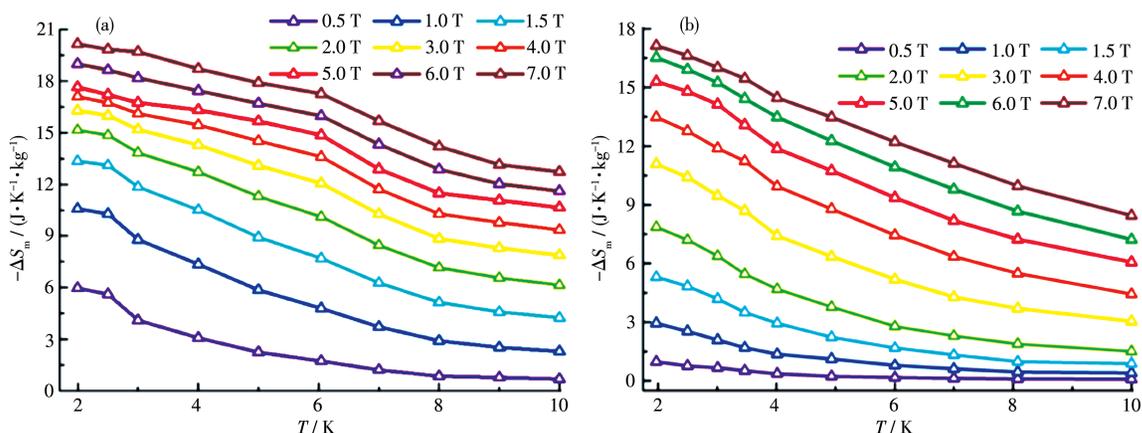


Fig.6 Plots of $-\Delta S_m$ vs T for **1** (a) and **2** (b)

Table 4 Comparison of $-\Delta S_m$ values for complexes **1**, **2** and some reported Gd₂ complexes

| Dinuclear Gd(III)-based complex | M_r | Magnetic interaction | $-\Delta S_m / (J \cdot K^{-1} \cdot kg^{-1})$ | $\Delta H / kOe$ | Ref. |
|--|----------|------------------------------------|--|------------------|-----------|
| [Gd ₂ (bfa) ₄ (L) ₂]·CH ₂ Cl ₂ ^a | 1 747.16 | AF (no J value reported) | 18.5 | 70 | [40] |
| [Gd ₂ (hfac) ₄ (L) ₂] ^b | 1 795.07 | AF ($J=-0.07$ cm ⁻¹) | 15.00 | 80 | [41] |
| [Gd(hfac) ₂ (L) ₂] ^c | 1 693.37 | AF ($J=-0.04$ cm ⁻¹) | 19.94 | 70 | [42] |
| [Gd ₂ (dbm) ₄ (L) ₂] ^d | 1791.99 | AF (no J value reported) | 14.36 | 70 | [43] |
| [Gd ₂ (hfac) ₄ (L1) ₂] ^e | 1 665.32 | AF ($J=-0.13$ cm ⁻¹) | 17.66 | 70 | [44] |
| [Gd ₂ (hfac) ₄ (L2) ₂] ^f | 1 693.37 | AF ($J=-0.10$ cm ⁻¹) | 14.81 | 70 | [44] |
| [Gd ₂ (L1) ₂ (tmhd) ₂ (CH ₃ O) ₂] ^g | 1 670.21 | AF (no J value reported) | 18.59 | 70 | [45] |
| [Gd(bfa) ₂ (L) ₂] ^h | 1 681.61 | AF (no J value reported) | 17.78 | 70 | [46] |
| [Gd ₂ (L) ₂ (dbm) ₂ (H ₂ O) ₂]·CH ₃ OH ⁱ | 1 395.57 | AF ($J=-0.045$ cm ⁻¹) | 23.2 | 70 | [47] |
| [Gd ₂ (dbm) ₂ (L) ₂ (CH ₃ OH) ₂] ^j | 1 445.76 | AF (no J value reported) | 21.1 | 70 | [48] |
| [Gd(OAc) ₃ (H ₂ O) ₂]·4H ₂ O | 2 474.95 | F ($J/k_B=0.068(2)$ K) | 40 | 70 | [49] |
| Complex 1 | 1 555.99 | AF (no J value reported) | 20.16 | 70 | This work |
| Complex 2 | 1 836.42 | AF (no J value reported) | 17.14 | 70 | This work |

^a HL=2-(((4-methylphenyl)imino)methyl)-8-hydroxyquinoline; ^b HL=2-((4-bromo-phenylimino)-methyl)-quinolin-8-ol; ^c HL=2-((4-ethylphenyl)imino)methyl-8-hydroxyquinoline; ^d HL=2-((4-nitrophenyl)imino)methyl-8-hydroxyquinoline; ^e HL1=2-(4-methylaniline-imino)methyl)-8-hydroxyquinoline; ^f HL2=2-((3,4-dimethylaniline)-imino)methyl)-8-hydroxyquinoline; ^g HL1=bis-Schiff base ligand; ^h HL=2-(5-methyl-1,2-oxazol-imino)methyl)-8-hydroxyquinoline; ⁱ HL=2-((1E)-((pyridin-2-yl)formamido)imino)methyl)benzoic acid; ^j HL=N'-(4-(diethylamino)salicylaldehyde)pyridyl-2-carbohydrazide.

was larger than those of some dinuclear Gd(III)-based complexes. The reason for the larger $-\Delta S_m$ of complex **1** may be due to the weak antiferromagnetic interaction and the smaller M_r/N_{Gd} ratio of **1**.

3 Conclusions

In summary, we have synthesized two new Gd₂ complexes [Gd₂(L)₂(dbm)₂(C₂H₅OH)₂] (**1**) and [Gd₂(L)₂(HL)₂(DMF)]·2CH₃CN (**2**). Both complexes **1** and **2** are binuclear structures with different coordination environments of central Gd(III) ions. Magnetic measurements imply that the two Gd₂ complexes display magnetic refrigeration properties. Our present work provides a new approach to design and construct Gd(III)-based magnetic refrigeration materials. Magnetic refrigeration studies of other poly-nuclear or high-nuclear Gd(III)-based clusters are underway in our group.

Supporting information is available at <http://www.wjhxsb.cn>

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