

## Research paper

# Synthesis, structures and magnetic refrigeration of two rhombus-shaped Gd<sub>4</sub> cages



Xiao-Fen Guan<sup>a</sup>, Wen-Ying Hou<sup>a</sup>, Xin-Yi Qiao<sup>a</sup>, Zhi-Qing Zhang<sup>a</sup>, Ke-Xin Liu<sup>a</sup>,  
Wen-Ming Wang<sup>a,b,\*</sup>, Ying Shi<sup>c,\*</sup>, Fei Pan<sup>d</sup>

<sup>a</sup> Department of Chemistry, Taiyuan Normal University, Jinzhong 030619, PR China

<sup>b</sup> Key Laboratory of Advanced Energy Materials Chemistry (Ministry of Education), Nankai University, Tianjin 300071, PR China

<sup>c</sup> Department of Biology, Taiyuan Normal University, Jinzhong 030619, PR China

<sup>d</sup> Petro China Pipeline Company, Langfang 065000, PR China

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## ABSTRACT

Two new Gd<sub>4</sub> cages based on 8-hydroxyquinoline Schiff base ligand and β-diketonate auxiliary ligands have been obtained and magnetically characterized. The X-ray structural analysis exhibit that both cages **1** and **2** contain one Gd<sub>4</sub> molecule with a rhombus-shaped arrangement, and each Gd<sup>III</sup> ion of them is located in a distorted square-antiprismatic coordination sphere. Magnetic properties measurement indicate that weak anti-ferromagnetic interactions were existed between the Gd<sup>III</sup> ions in **1** and **2**, and they display magnetic refrigeration with  $-\Delta S_m = 21.95 \text{ J kg}^{-1} \text{ K}^{-1}$  for **1** ( $\Delta H = 7 \text{ T}$  and  $T = 2.0 \text{ K}$ ) and  $-\Delta S_m = 15.02 \text{ J kg}^{-1} \text{ K}^{-1}$  for **2** ( $\Delta H = 7 \text{ T}$  and  $T = 3.0 \text{ K}$ ).

## 1. Introduction

Lanthanide clusters are a current area of research in inorganic chemistry as well as in materials science because of some of their potential applications including magnetic refrigeration, ultra-high-density data storage, fluorescent probes as well as catalysis [1–4]. Among the recent investigation of lanthanide molecular magnets, the study focusing on cryogenic magnetic refrigerant materials was noteworthy. Magnetic refrigeration depends on the magnetocaloric effect (MCE), which represents the change of isothermal magnetic entropy ( $\Delta S_m$ ) and adiabatic temperature ( $\Delta T_{ad}$ ) in change of applied magnetic field. Hence, to achieve larger magnetic entropy ( $\Delta S_m$ ) combination of Gd<sup>III</sup> with smaller multidentate ligands were necessary [5]. In fact, various structures of discrete Gd-clusters have been reported for the past few years, such as Gd<sub>3</sub> [6], Gd<sub>4</sub> [7], Gd<sub>5</sub> [8], Gd<sub>6</sub> [9], Gd<sub>7</sub> [10], Gd<sub>8</sub> [11], Gd<sub>9</sub> [12], Gd<sub>11</sub> [13], Gd<sub>12</sub> [14], Gd<sub>14</sub> [15], Gd<sub>15</sub> [16], Gd<sub>18</sub> [17], Gd<sub>24</sub> [18] and so on. It is worth mentioning that an extremely large  $-\Delta S_m$  value for GdF<sub>3</sub> was observed, up to  $71.6 \text{ J K}^{-1} \text{ kg}^{-1}$ , which was reported by Tong's group in 2012, setting a record in this field [19]. In 2014, a 104-Gd cluster with a large magnetic entropy change of  $-\Delta S_m = 46.9 \text{ J K}^{-1} \text{ kg}^{-1}$  ( $T = 2.0 \text{ K}$  and  $\Delta H = 7 \text{ T}$ ) was reported by Long's group [20]. Although a significant number of polynuclear gadolinium clusters have already been documented in the literature, there

are still a challenge for a logical approach to synthesize this type of cluster.

In our previous work, we successfully obtained series of Gd<sub>2</sub> and Gd<sub>4</sub> clusters through 8-hydroxyquinoline Schiff base ligand [21]. These Gd-based clusters display prominent magnetic refrigeration properties. On the basis of our recent work, in this paper, a bidentate 8-hydroxyquinoline Schiff base ligand (HL) (Scheme 1) and two β-diketonate auxiliary ligands (Hacac and Hdpm) (Scheme 2) have been used to design and construct gadolinium clusters. Two Gd<sub>4</sub> cages, namely [Gd<sub>4</sub>(μ<sub>3</sub>-OH)<sub>2</sub>(L)<sub>6</sub>(acac)<sub>4</sub>] · 2CH<sub>3</sub>CN (**1**) and [Gd<sub>4</sub>(μ<sub>3</sub>-OH)<sub>2</sub>(L)<sub>6</sub>(dpm)<sub>4</sub>] · 5CH<sub>3</sub>CN (**2**), were obtained, and systematic study of the magnetism of the two compounds have been done.

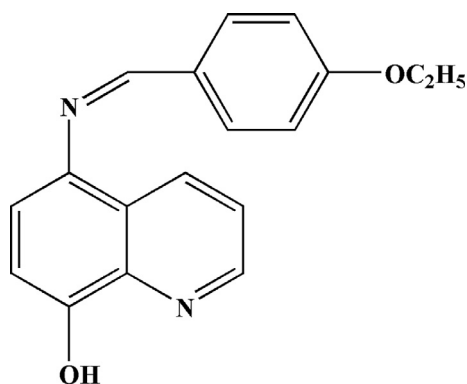
## 2. Experimental section

### 2.1. Materials and instrumentation

All chemicals and solvents used for the syntheses in this paper were reagent grade without further purification. Two β-diketonate salts Gd(acac)<sub>2</sub>·2H<sub>2</sub>O and Gd(dpm)<sub>3</sub>·2H<sub>2</sub>O were synthesized by the reported reference [22] and the Schiff base ligand 5-(4-ethoxybenzylidene)-8-hydroxyquinoline were synthesized according to the method in the earlier literature [23].

\* Corresponding authors at: Department of Chemistry, Taiyuan Normal University, Jinzhong 030619, PR China (W.-M. Wang).

E-mail addresses: [wangwenmin0506@126.com](mailto:wangwenmin0506@126.com) (W.-M. Wang), [lucina0812@163.com](mailto:lucina0812@163.com) (Y. Shi).



Scheme 1. Structure of ligand HL.

Elemental analyses (EA) for C, H and N were performed on a Perkin-Elmer 240 CHN elemental analyzer. The magnetic measurements were performed in the temperature range of 300–2.0 K using a Quantum Design MPMS-XL7 and a PPMS-9 ACMS magnetometer. The diamagnetic corrections for the complexes were estimated using Pascal's constants, and magnetic data were corrected for diamagnetic contributions of the sample holder.

## 2.2. Synthesis of 1 and 2

### 2.2.1. $[Gd_4(\mu_3-OH)_2(L)_6(acac)_4] \cdot 2CH_3CN$ (**1**)

A solution of  $Gd(acac)_3 \cdot 2H_2O$  (0.05 mmol, 0.0247 g) in 20.0 mL of  $CH_3CN$  and a  $CH_2Cl_2$  solution (5.0 mL) containing HL (0.05 mmol; 0.0146 g) were mixed at room temperature. Then the mixture solution was stirred for 4 h at 70 °C and after that cooled to room temperature. After filtration, the resulting solution was kept in the dark and concentrated slowly by evaporation at 4 °C. After about 7 days, block-shaped and pale-yellow crystals were obtained. Yield: 43% (based on Gd). Mp: 210 °C. Anal. Calcd for  $C_{132}H_{124}Gd_4N_{14}O_{22}$  (2887.45): C, 54.86; H, 4.29; N, 6.79. Found: C, 54.69; H, 4.43; N, 6.82. Selected IR data (KBr pellet; 4000–400  $cm^{-1}$ ): 3421 (m), 1596 (m), 1552 (s), 1521 (s), 1405 (m), 1306 (m), 1215 (w), 1103 (w), 752 (w).

### 2.2.2. $[Gd_4(\mu_3-OH)_2(L)_6(dpm)_4] \cdot 5CH_3CN$ (**2**)

The syntheses of cluster **2** is very similar to this of **1**, the only difference being the use of  $Gd(dpm)_3 \cdot 2H_2O$  (0.05 mmol) instead of  $Gd(acac)_3 \cdot 2H_2O$  (0.05 mmol). After about 5 days, block-shaped and deep yellow crystals were obtained. Yield: 47% (based on Gd). Mp: 205 °C. Anal. Calcd for  $C_{162}H_{183}Gd_4N_{17}O_{22}$  (3349.24): C, 58.04; H, 5.46; N, 7.11. Found: C, 57.86; H, 5.57; N, 7.25. Selected IR data (KBr pellet; 4000–400  $cm^{-1}$ ): 3423 (m), 1560 (m), 1523 (s), 1476 (m), 1403 (m), 1216 (w), 1103 (w), 1063 (w), 762 (w).

## 2.3. Single-crystal X-ray diffraction measurements

Single crystal X-ray diffraction data of clusters **1** and **2** were collected on a computer-controlled Rigaku Saturn CCD area detector diffractometer, equipped with confocal monochromatized Mo  $K\alpha$

**Table 1**  
Crystallographic Data and Structure Refinements for **1** and **2**.

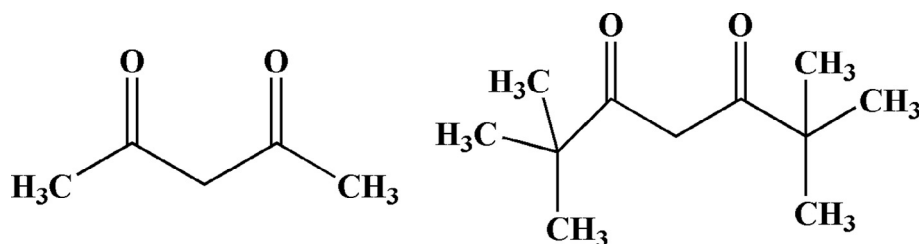
	<b>1</b>	<b>2</b>
Formula $M_r$	$C_{132}H_{124}Gd_4N_{14}O_{22}$ 2887.45	$C_{162}H_{183}Gd_4N_{17}O_{22}$ 3349.24
Cryst syst	Triclinic	Triclinic
Space group	<i>P</i> -1	<i>P</i> -1
<i>a</i> (Å)	12.7011(4)	16.8315(9)
<i>b</i> (Å)	14.0672(5)	23.2791(12)
<i>c</i> (Å)	17.7992(6)	24.4251(13)
$\alpha$ (°)	81.5360(10)	66.323(7)
$\beta$ (°)	87.2710(10)	73.054(8)
$\gamma$ (°)	81.1160(10)	70.166(7)
<i>V</i> (Å <sup>3</sup> )	3106.78(18)	8109.9(7)
<i>Z</i>	1	2
$D_c$ (g cm <sup>-3</sup> )	1.543	1.372
$\mu$ (mm <sup>-1</sup> )	2.182	1.683
$\theta$ °	3.16–28.36	3.02–25.02
<i>F</i> (0 0 0)	1446	3412
Reflns collected	55,257	27,427
Unique reflns	15,338	14,534
GOF on $F^2$	1.017	1.157
$R_i$ , $wR_2$ [ $I > 2\sigma(I)$ ]	0.0457, 0.0951	0.0935, 0.1911
$R_i$ , $wR_2$ (all data)	0.0833, 0.1103	0.1920, 0.2252

radiation with a radiation wavelength of 0.71073 Å using the  $\omega$ - $\phi$  scan technique. The structures were solved by direct methods and refined with a full-matrix least-squares technique based on  $F^2$  using the SHELXS-97 and SHELXL-97 programs [24]. Anisotropic thermal parameters were assigned to all non-hydrogen atoms. Crystallographic data and structural refinement parameters for **1** and **2** are listed in Table 1. CCDC (1840924 for **1** and 1840925 for **2**) contain the supplementary crystallographic data for this paper. These data can be obtained free of charge from The Cambridge Crystallographic Data Centre.

## 3. Results and discussion

### 3.1. Structure descriptions of 1 and 2

The reaction of 8-hydroxyquinoline Schiff base ligand (HL) with Gd(acac) $_3$ ·2H $_2$ O or Gd(dpm) $_3$ ·2H $_2$ O in 1:1 ratio in the mixture solution of  $CH_3CN$  and  $CH_2Cl_2$  afforded the tetranuclear complexes **1** and **2**. Single-crystal X-ray diffraction analysis reveals that cage **1** crystallized in the triclinic space group *P*-1 (Fig. 1). **1** is mainly containing four Gd<sup>III</sup> ions, six L<sup>-</sup>, four acac<sup>-</sup> and two  $\mu_3$ -OH. The core structure of **1** has a tetranuclear arrangement of Gd<sup>III</sup> ions with crystallographic inversion symmetry. In the centrosymmetric unit, both the Gd1 and Gd2 ions are eight coordinated, and their coordination polyhedrons can be described as being a distorted square-antiprismatic geometry with a quasi- $D_{4d}$  symmetry, which are calculated by using the SHAPE 2.0 program (Table S1). The central Gd1 ion is coordinated by seven oxygen atoms and one nitrogen atom; while Gd2 ion is coordinated by six oxygen atoms and two nitrogen atoms. The two adjacent Gd1 and Gd2 ions connected by a  $\mu_3$ -OH and a  $\mu_2$ -O which is from a Schiff base ligand (L<sup>-</sup>). The four 8-coordinated Gd<sup>III</sup> ions in **1** from formation of an approximate parallelogram. In **1**, the O–Gd–O angles are in the range of

Scheme 2. Structures of  $\beta$ -diketonate auxiliary ligands Hacac (left) and Hdpm (right).

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