

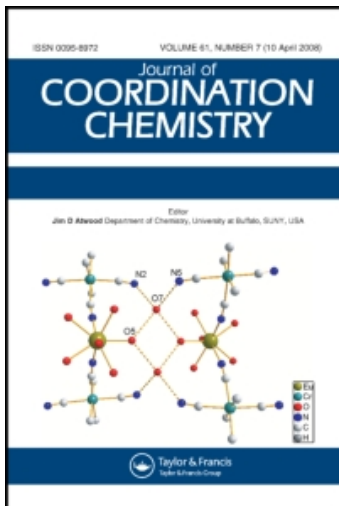
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### Syntheses, structural determination, and binding studies of binuclear eight-coordinate $(enH_2)[Gd^{III}_2(pdta)_2(H_2O)_2] \cdot 8H_2O$ and mononuclear nine-coordinate $(enH_2)[Gd^{III}(egta)(H_2O)]_2 \cdot 6H_2O$

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# Syntheses, structural determination, and binding studies of binuclear eight-coordinate $(\text{enH}_2)[\text{Gd}^{\text{III}}_2(\text{pdta})_2(\text{H}_2\text{O})_2] \cdot 8\text{H}_2\text{O}$ and mononuclear nine-coordinate $(\text{enH}_2)[\text{Gd}^{\text{III}}(\text{egta})(\text{H}_2\text{O})_2] \cdot 6\text{H}_2\text{O}$

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The  $(\text{enH}_2)[\text{Gd}^{\text{III}}_2(\text{pdta})_2(\text{H}_2\text{O})_2] \cdot 8\text{H}_2\text{O}$  (**1**) (en = ethylenediamine and  $\text{H}_4\text{pdta}$  = propylenediamine-*N, N, N', N'*-tetraacetic acid) and  $(\text{enH}_2)[\text{Gd}^{\text{III}}(\text{egta})(\text{H}_2\text{O})_2] \cdot 6\text{H}_2\text{O}$  (**2**) ( $\text{H}_4\text{egta}$  = ethyleneglycol-bis-(2-aminoethylether)-*N, N, N', N'*-tetraacetic acid) complexes were synthesized and characterized by infrared spectrum, thermal analysis, and single-crystal X-ray diffraction. The complex  $(\text{enH}_2)[\text{Gd}^{\text{III}}_2(\text{pdta})_2(\text{H}_2\text{O})_2] \cdot 8\text{H}_2\text{O}$  has a binuclear eight-coordinate structure with pseudo square antiprism and crystallizes in the monoclinic crystal system with  $C2/c$  space group. Through a carboxylate bridge, an infinite 1-D zigzag polymeric binuclear  $[\text{Gd}^{\text{III}}_2(\text{pdta})_2(\text{H}_2\text{O})_2]^{2-}$  complex anion is formed. All infinite zigzag polymeric complex anions link through hydrogen bonds, yielding a layer structure.  $(\text{enH}_2)[\text{Gd}^{\text{III}}(\text{egta})(\text{H}_2\text{O})_2] \cdot 6\text{H}_2\text{O}$  has a mononuclear nine-coordinate structure with pseudo monocapped square antiprism and crystallizes in the monoclinic crystal system with  $P2_1/n$  space group. Each  $\text{enH}_2^{2+}$  cation, through hydrogen bonds, connects two adjacent  $[\text{Gd}^{\text{III}}(\text{egta})(\text{H}_2\text{O})]^-$  complex anions.

**Keywords:** Gadolinium ion ( $\text{Gd}^{\text{III}}$ ); Propylenediamine-*N, N, N', N'*-tetraacetic acid ( $\text{H}_4\text{pdta}$ ); Ethyleneglycol-bis-(2-aminoethylether)-*N, N, N', N'*-tetraacetic acid ( $\text{H}_4\text{egta}$ ); Ethylenediamine; Hydrogen bond

## 1. Introduction

Stable and soluble rare earth metal complexes have intriguing frameworks and wide utilization in many fields [1–3], e.g., luminescent probes in biochemistry [4], shift reagents in nuclear magnetic resonance (NMR) spectroscopy [5], and catalysts in the petrochemical industry [6, 7]. Trivalent gadolinium ( $\text{Gd}^{\text{III}}$ ), with high electron spin and relatively slow electronic relaxation, is widely used as a magnetic resonance imaging (MRI) contrast agent in disease diagnosis [8, 9]. A case in point is  $\text{Gd-DTPA}$ ,

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which has been reported extremely useful in testing abnormalities in blood–brain barrier and gliomas diagnosis [10, 11]. Moreover, Gd–AAZTA could interact with high-affinity ligands and biomolecules to prepare bifunctional targeting probes [12]. Gd<sup>III</sup> could form a co-luminescence system with Tb–ATP–phen (Tb–adenosine triphosphate (ATP)–phenanthroline (phen)) and enhance the fluorescence [13]. Gd<sup>III</sup> sensor, based on *N*-(2-pyridyl)-*N'*-(4-nitrophenyl) thiourea (pyTu4NO<sub>2</sub>), has optimal response time and lifetime [14]. Therefore, it is desirable to conduct a detailed study of Gd<sup>III</sup>.

The study of aminopolycarboxylic acids is a rapidly growing area, widely exploited in rare earth metal complexes. Containing both O donors and N donors makes it an excellent candidate for synthesizing various rare earth metal complexes for different applications [15]. Previously, rare earth metal complexes with aminopolycarboxylic acid ligands were reported, such as [Pr<sup>III</sup>(nta)(H<sub>2</sub>O)<sub>2</sub>]·H<sub>2</sub>O (H<sub>3</sub>nta = nitrilotriacetic acid) [16], K<sub>4</sub>[Ho<sup>III</sup><sub>2</sub>(dtpa)<sub>2</sub>]·4H<sub>2</sub>O (H<sub>5</sub>dtpa = diethylenetriamine-*N, N, N', N''*, *N'''*-pentaacetic acid) [17], Na[Dy<sup>III</sup>(edta)(H<sub>2</sub>O)]·3.25H<sub>2</sub>O (H<sub>4</sub>edta = ethylenediamine-*N, N, N', N'*-tetraacetic acid) [18], Na[Yb<sup>III</sup>(cydta)(H<sub>2</sub>O)<sub>2</sub>]·5H<sub>2</sub>O (H<sub>4</sub>cydta = trans-1,2-cyclohexanediamine-*N, N, N', N'*-tetraacetic acid) [19] and (NH<sub>4</sub>)[Tb<sup>III</sup>(ttha)]·5H<sub>2</sub>O (H<sub>6</sub>ttha = triethylenetetraamine-*N, N, N', N', N''*-hexaacetic acid) [20]. These aminopolycarboxylic acid ligands coordinate with various rare earth metal ions tightly and form relatively high coordination number complexes. Rare earth metal complexes with different aminopolycarboxylic acid ligands adopt 8-, 9-, and 10-coordinate structures depending on the ionic radius, electronic configuration, and oxidation state of the rare earth metal ions as well as the counter ions [21–25]. For a given trivalent oxidation state, the structure and coordination number should also be related to the framework of the aminopolycarboxylic acid [26, 27]. Gd<sup>III</sup>, with ionic radius of 0.1078 Å and electron configuration of high-spin *f*<sup>7</sup>, may form eight- or nine-coordinate complexes with multidentate aminopolycarboxylates with structure and coordination number decided by the ligand framework. To validate our prediction, herein, we selected pdta (H<sub>4</sub>pdta = 1,3-propylenediamine-*N, N, N', N'*-tetraacetic acid) and egta (H<sub>4</sub>egta = ethyleneglycol-bis-(2-aminoethyl ether)-*N, N, N', N'*-tetraacetic acid) as ligands and protonated ethylenediamine cations (enH<sub>2</sub><sup>2+</sup>) as counter ions, synthesizing (enH<sub>2</sub>)[Gd<sup>III</sup><sub>2</sub>(pdta)<sub>2</sub>(H<sub>2</sub>O)<sub>2</sub>]·8H<sub>2</sub>O and (enH<sub>2</sub>)[Gd<sup>III</sup>(egta)(H<sub>2</sub>O)]<sub>2</sub>·6H<sub>2</sub>O using the hydrothermal method. Crystal and molecular structures were determined by single-crystal X-ray diffraction. Being different from other multidentate aminopolycarboxylate ligands (which only form five-member rings with the central metal), the hexadentate pdta can form a six-member chelating ring owing to the existence of 1,3-propylenediamine. It occupies much space and consequently reduces the coordination number as in (NH<sub>4</sub>)[Eu<sup>III</sup>(pdta)(H<sub>2</sub>O)]·H<sub>2</sub>O [28], while egta, an octadentate ligand, with only five-member chelate rings like nta, edta, dtpa, and ttha, can form a nine-coordinate complex with Gd<sup>III</sup>.

As intended, (enH<sub>2</sub>)[Gd<sup>III</sup><sub>2</sub>(pdta)<sub>2</sub>(H<sub>2</sub>O)<sub>2</sub>]·8H<sub>2</sub>O is a binuclear eight-coordinate complex because of the existence of a six-member chelating ring, while the (enH<sub>2</sub>)[Gd<sup>III</sup>(egta)(H<sub>2</sub>O)]<sub>2</sub>·6H<sub>2</sub>O is a mononuclear nine-coordinate complex since all rings are five-membered ones. Thus, this study confirms that ligand framework has a great effect on coordinate structure and coordination number of rare earth metal complexes.

## 2. Experimental

### 2.1. Syntheses

**2.1.1.  $(\text{enH}_2)[\text{Gd}^{\text{III}}_2(\text{pdta})_2(\text{H}_2\text{O})_2] \cdot 8\text{H}_2\text{O}$  (1).**  $\text{H}_4\text{pdta}$  (=propylenediamine-*N,N,N',N'*-tetraacetic acid) (A.R., Beijing SHLHT Science & Trade Co., Ltd., China) (1.9668 g, 5.0 mmol) was added to 100 mL warm water and  $\text{Gd}_2\text{O}_3$  powder (99.999%, Yuelong Rare Earth Co., Ltd., China) (0.9063 g, 2.5 mmol) was added to the above solution slowly. The solution became transparent after the mixture had been stirred and refluxed for 15.0 h, and then the pH was adjusted to 6.0 by dilute ethylenediamine (en) aqueous solution. Finally, the solution was concentrated to 25 mL on a water bath at 75–80°C. Light yellow crystals appeared on the bottom of the prepared solution after 3 weeks at room temperature (yield ratio = 76.37%).

**2.1.2. Synthesis of  $(\text{enH}_2)[\text{Gd}^{\text{III}}(\text{egta})(\text{H}_2\text{O})]_2 \cdot 6\text{H}_2\text{O}$  (2).** A procedure similar to that of **1** was followed except using  $\text{H}_4\text{egta}$  (=ethyleneglycol-bis-(2-aminoethylether)-*N,N,N',N'*-tetraacetic acid) (A.R., Beijing SHLHT Science & Trade Co., Ltd., China) (1.9017 g, 5.0 mmol) (yield = 73.25%).

### 2.2. Determination of IR spectrum

The  $\text{H}_4\text{pdta}$ ,  $\text{H}_4\text{egta}$ ,  $(\text{enH}_2)[\text{Gd}^{\text{III}}_2(\text{pdta})_2(\text{H}_2\text{O})_2] \cdot 8\text{H}_2\text{O}$  (**1**) and  $(\text{enH}_2)[\text{Gd}^{\text{III}}(\text{egta})(\text{H}_2\text{O})]_2 \cdot 6\text{H}_2\text{O}$  (**2**) were skived and pressed to slices with KBr and their infrared spectra were determined on a Shimadzu-IR 408 spectrograph. The results are shown in figure S1.

### 2.3. Determination of thermogravimetric/differential thermal analysis

Thermogravimetric/differential thermal analysis (TG-DTA) curves of  $(\text{enH}_2)[\text{Gd}^{\text{III}}_2(\text{pdta})_2(\text{H}_2\text{O})_2] \cdot 8\text{H}_2\text{O}$  (**1**) and  $(\text{enH}_2)[\text{Gd}^{\text{III}}(\text{egta})(\text{H}_2\text{O})]_2 \cdot 6\text{H}_2\text{O}$  (**2**) were determined by Mettler Toledo 851° thermogravimetric analyzer in the presence of air (20 mL min<sup>-1</sup>) from room temperature to 800°C at a heating rate of 20°C min<sup>-1</sup>. The results are given in figure S2.

### 2.4. X-ray structure determination

X-ray intensity data were collected on a Bruker SMART CCD X-ray diffractometer system with graphite-monochromated Mo-K $\alpha$  radiation ( $\lambda = 0.71073$  Å). The structure was solved by direct methods. All non-hydrogen atoms were refined anisotropically by full-matrix least-squares methods. All calculations were performed by the SHELXTL-97 program on PDP11/44 and Pentium MMX/166 computers. Figures 1 and 3 illustrate the perspective views of two complexes. Figures 2 and 4 show their coordination polyhedra. Figure S3 gives the extended 1-D zigzag chain structure of **1**. Figures S4 and S6 display their molecular packing in a unit cell. Figures S5 and S7 show the inner hydrogen bonds in **1** and **2**. The crystal data and structure refinement for both complexes are listed in table 1. Final atomic coordinates and equivalent isotropic

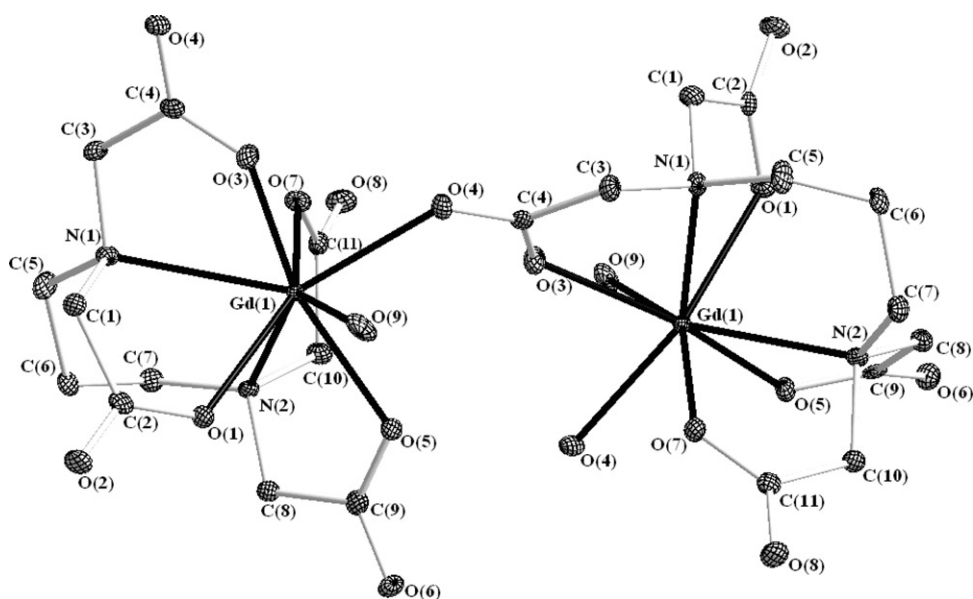


Figure 1. Molecular structure of  $(\text{enH}_2)[\text{Gd}^{\text{III}}_2(\text{pdta})_2(\text{H}_2\text{O})_2] \cdot 8\text{H}_2\text{O}$  (1). (Bond-distance: Gd(1)–O(1): 2.3469(13); Gd(1)–O(3): 2.3593(14); Gd(1)–O(4)#1: 2.3702(14); Gd(1)–O(5): 2.3650(13); Gd(1)–O(7): 2.4015(14); Gd(1)–O(9): 2.3792(14); Gd(1)–N(1): 2.6643(16); Gd(1)–N(2): 2.6086(16). Bond-angle: O(1)–Gd(1)–O(3): 103.00(5); O(1)–Gd(1)–O(4)#1: 143.22(5); O(1)–Gd(1)–O(5): 77.61(5); O(1)–Gd(1)–O(7): 136.78(5); O(1)–Gd(1)–O(9): 72.87(5); O(1)–Gd(1)–N(1): 66.65(5); O(1)–Gd(1)–N(2): 78.53(5); O(3)–Gd(1)–O(4)#1: 77.83(5); O(3)–Gd(1)–O(5): 153.96(5); O(3)–Gd(1)–O(7): 92.24(5); O(3)–Gd(1)–O(9): 78.09(5); O(3)–Gd(1)–N(1): 64.90(5); O(3)–Gd(1)–N(2): 141.11(5); O(4)#1–Gd(1)–O(5): 86.38(5); O(4)#1–Gd(1)–O(7): 79.22(5); O(4)#1–Gd(1)–O(9): 71.39(5); O(4)#1–Gd(1)–N(1): 138.63(5); O(4)#1–Gd(1)–N(2): 123.93(5); O(5)–Gd(1)–O(7): 105.12(5); O(5)–Gd(1)–O(9): 77.29(5); O(5)–Gd(1)–N(1): 134.81(5); O(5)–Gd(1)–N(2): 64.89(5); O(7)–Gd(1)–O(9): 150.35(5); O(7)–Gd(1)–N(1): 84.74(5); O(7)–Gd(1)–N(2): 65.09(5); O(9)–Gd(1)–N(1): 115.00(5); O(9)–Gd(1)–N(2): 136.50(5); N(1)–Gd(1)–N(2): 81.15(5)).

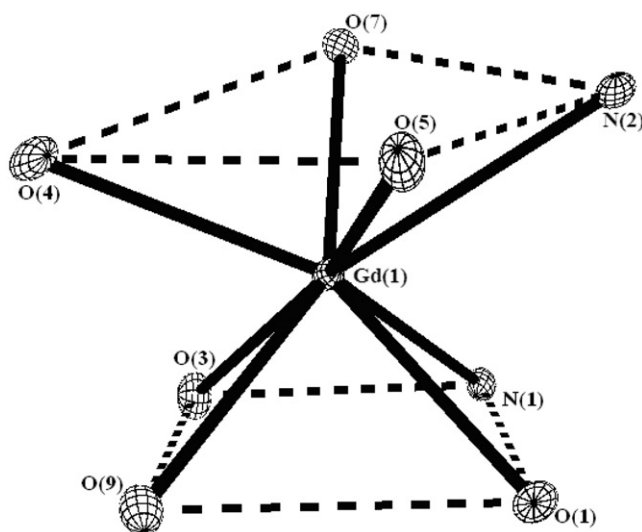


Figure 2. Coordination polyhedron of 1.

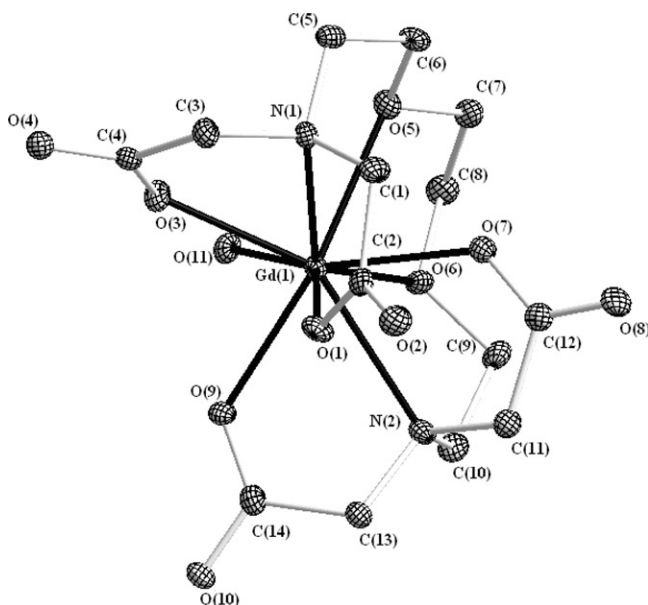


Figure 3. Molecular structure of  $(\text{enH}_2)[\text{Gd}^{\text{III}}(\text{egta})(\text{H}_2\text{O})]_2 \cdot 6\text{H}_2\text{O}$  (**2**). (Bond-distance: Gd(1)–O(1): 2.3773(19); Gd(1)–O(3): 2.3855(19); Gd(1)–O(5): 2.5238(19); Gd(1)–O(6): 2.4780(19); Gd(1)–O(7): 2.3765(19); Gd(1)–O(9): 2.365(2); Gd(1)–O(11): 2.463(2); Gd(1)–N(1): 2.628(2); Gd(1)–N(2): 2.657(2). Bond-angle: O(1)–Gd(1)–O(3): 90.83(7); O(1)–Gd(1)–O(5): 124.88(6); O(1)–Gd(1)–O(6): 137.08(6); O(1)–Gd(1)–O(7): 76.03(7); O(1)–Gd(1)–O(9): 79.01(7); O(1)–Gd(1)–O(11): 148.59(7); O(1)–Gd(1)–N(1): 63.86(7); O(1)–Gd(1)–N(2): 72.83(7); O(3)–Gd(1)–O(5): 91.79(6); O(3)–Gd(1)–O(6): 131.73(7); O(3)–Gd(1)–O(7): 140.87(7); O(3)–Gd(1)–O(9): 82.65(7); O(3)–Gd(1)–O(11): 69.17(7); O(3)–Gd(1)–N(1): 64.52(7); O(3)–Gd(1)–N(2): 146.33(7); O(5)–Gd(1)–O(6): 67.67(6); O(5)–Gd(1)–O(7): 68.04(6); O(5)–Gd(1)–O(9): 155.70(6); O(5)–Gd(1)–O(11): 81.19(7); O(5)–Gd(1)–N(1): 68.06(7); O(5)–Gd(1)–N(2): 121.77(6); O(6)–Gd(1)–O(7): 72.63(6); O(6)–Gd(1)–O(9): 98.63(6); O(6)–Gd(1)–O(11): 64.90(7); O(6)–Gd(1)–N(1): 132.89(7); O(6)–Gd(1)–N(2): 67.54(7); O(7)–Gd(1)–O(9): 128.79(6); O(7)–Gd(1)–O(11): 134.55(7); O(7)–Gd(1)–N(1): 76.70(7); O(7)–Gd(1)–N(2): 64.48(7); O(9)–Gd(1)–O(11): 74.72(7); O(9)–Gd(1)–N(1): 128.48(7); O(9)–Gd(1)–N(2): 65.68(7); O(11)–Gd(1)–N(1): 122.25(7); O(11)–Gd(1)–N(2): 110.45(7); N(1)–Gd(1)–N(2): 127.25(7)).

displacement parameters for all non-hydrogen fractions are given in table S1 for both complexes.

### 3. Results and discussion

#### 3.1. FT-IR spectra

In figure S1, the  $\nu(\text{C}-\text{N})$  band of **1** at  $933\text{ cm}^{-1}$  red-shifts  $58\text{ cm}^{-1}$  compared with that of  $\text{H}_4\text{pdta}$  ( $991\text{ cm}^{-1}$ ), indicating that the amine nitrogens of the pdta are coordinated to  $\text{Gd}^{\text{III}}$ . The  $\nu_{\text{as}}(\text{COOH})$  band of  $\text{H}_4\text{pdta}$  at  $1654\text{ cm}^{-1}$  disappears in the spectrum of **1**. The  $\nu_{\text{as}}(\text{COO})$  band at  $1611\text{ cm}^{-1}$  blue-shifts  $52\text{ cm}^{-1}$  compared with that ( $1559\text{ cm}^{-1}$ ) of  $\text{H}_4\text{pdta}$ ;  $\nu_{\text{s}}(\text{COO})$  of **1** at  $1403\text{ cm}^{-1}$  red-shifts  $11\text{ cm}^{-1}$  compared with that ( $1414\text{ cm}^{-1}$ ) of  $\text{H}_4\text{pdta}$ . These changes confirm that oxygens from carboxylates are also coordinated to  $\text{Gd}^{\text{III}}$ . A broad  $\nu(\text{OH})$  band near  $3450\text{ cm}^{-1}$  reveals the presence of  $\text{H}_2\text{O}$  in **1**. For **2**, the  $\nu(\text{C}-\text{N})$  at  $1039\text{ cm}^{-1}$  red-shifts  $60\text{ cm}^{-1}$  compared with

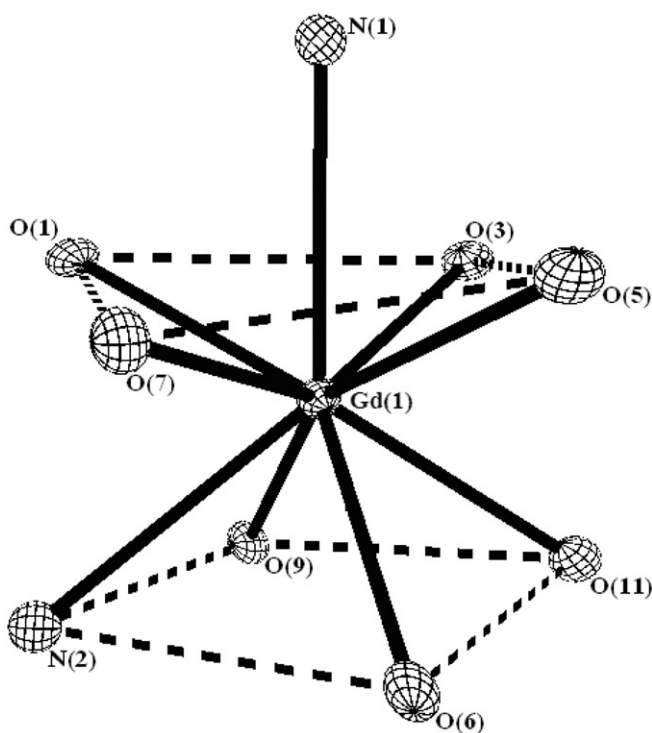


Figure 4. Coordination polyhedron of **2**.

that ( $1099\text{ cm}^{-1}$ ) of  $\text{H}_4\text{egta}$ , indicating that amine nitrogens of  $\text{egta}$  are coordinated to  $\text{Gd}^{\text{III}}$ . The  $\nu_{\text{as}}(\text{COOH})$  band of  $\text{H}_4\text{egta}$  at  $1739\text{ cm}^{-1}$  disappears in **2**. The  $\nu_{\text{s}}(\text{COO})$  of **2** at  $1415\text{ cm}^{-1}$  blue-shifts  $12\text{ cm}^{-1}$  compared with that ( $1403\text{ cm}^{-1}$ ) of  $\text{H}_4\text{egta}$  and  $\nu_{\text{as}}(\text{COO})$  at  $1595\text{ cm}^{-1}$  red-shifts  $42\text{ cm}^{-1}$  compared with that ( $1637\text{ cm}^{-1}$ ) of  $\text{H}_4\text{egta}$ . These changes demonstrate that oxygens from carboxylates are also coordinated to  $\text{Gd}^{\text{III}}$ . The broad  $\nu(\text{OH})$  near  $3467\text{ cm}^{-1}$  reveals the presence of  $\text{H}_2\text{O}$  in **2**.

### 3.2. Thermal analysis

Shown in figure S2, the TG curve of  $(\text{enH}_2)[\text{Gd}^{\text{III}}_2(\text{pdta})_2(\text{H}_2\text{O})_2] \cdot 8\text{H}_2\text{O}$  has a three-stage decomposition. The first-stage weight loss of 10.24% from room temperature to  $237^\circ\text{C}$  corresponds to the release of eight crystal waters and two coordinated waters, with an endothermic peak at  $193^\circ\text{C}$  in the DTA curve. The second weight loss of 23.92% from  $237^\circ\text{C}$  to  $387^\circ\text{C}$  corresponds to oxidation of ethylenediamine, with an exothermic peak at  $367^\circ\text{C}$ . The last weight loss of 18.78% from  $387^\circ\text{C}$  to  $800^\circ\text{C}$  corresponds to decomposition and combustion of carboxylate. The total weight loss is 52.94%. For  $(\text{enH}_2)[\text{Gd}^{\text{III}}(\text{egta})(\text{H}_2\text{O})_2] \cdot 6\text{H}_2\text{O}$ , the first-stage weight loss is 9.23% from room temperature to  $155^\circ\text{C}$ , which corresponds to expulsion of crystal waters with a marked endothermic peak in the DTA curve at  $135^\circ\text{C}$ . The weight loss of 2.21% from  $155^\circ\text{C}$  to  $217^\circ\text{C}$  corresponds to release of two coordinated waters, producing a DTA



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

Complex	<b>1</b>	<b>2</b>
Formula weight	1161.26	636.69
Temperature (K)	93(2)	93(2)
Wavelength (Å)	0.71073	0.71073
Crystal system	Monoclinic	Monoclinic
Space group	<i>C2/c</i>	<i>P2<sub>1</sub>/n</i>
Unit cell dimensions (Å, °)		
<i>a</i>	18.171(3)	12.9242(18)
<i>b</i>	9.2651(13)	12.5978(19)
<i>c</i>	25.200(4)	14.843(2)
$\beta$	100.569(2)	105.731(3)
Volume (Å <sup>3</sup> ), <i>Z</i>	4170.7(10), 4	2326.2(6), 4
Calculated density (Mg m <sup>-3</sup> )	1.849	1.818
Absorption coefficient (mm <sup>-1</sup> )	3.249	2.924
<i>F</i> (000)	2320	1280
Crystal size (mm <sup>3</sup> )	0.30 × 0.27 × 0.27	0.40 × 0.37 × 0.30
$\theta$ range for data collection (°)	3.05–27.47	3.23–27.49
Limiting indices	$-19 \leq h \leq 23$ ; $-11 \leq k \leq 12$ ; $-32 \leq l \leq 32$	$-16 \leq h \leq 16$ ; $-15 \leq k \leq 16$ ; $-18 \leq l \leq 19$
Reflections collected	16455	18483
Independent reflections	4775 [ <i>R</i> (int) = 0.0215]	5263 [ <i>R</i> (int) = 0.0408]
Completeness to $\theta_{\max}$ (%)	99.7	98.4
Absorption correction	Empirical	Empirical
Max. and min. transmission	0.4775 and 0.4423	0.4741 and 0.3875
Refinement method	Full-matrix least-squares on <i>F</i> <sup>2</sup>	Full-matrix least-squares on <i>F</i> <sup>2</sup>
Goodness-of-fit on <i>F</i> <sup>2</sup>	1.004	1.002
Final <i>R</i> indices [ <i>I</i> > 2 $\sigma$ ( <i>I</i> )]	<i>R</i> <sub>1</sub> = 0.0178, <i>wR</i> <sub>2</sub> = 0.0390	<i>R</i> <sub>1</sub> = 0.0260, <i>wR</i> <sub>2</sub> = 0.0594
<i>R</i> indices (all data)	<i>R</i> <sub>1</sub> = 0.0199, <i>wR</i> <sub>2</sub> = 0.0399	<i>R</i> <sub>1</sub> = 0.0314, <i>wR</i> <sub>2</sub> = 0.0621
Largest difference peak and hole (e Å <sup>-3</sup> )	1.231 and -0.369	1.755 and -0.835

peak at 169°C. The second weight loss of 26.56% is attributed to expulsion of ethylenediamine from 217°C to 381°C with an endothermic peak at 267°C. The last weight loss of 24.70% from 381°C to 800°C is attributed to the decomposition and combustion of carboxylate, with an exothermic peak at 399°C. The total weight loss is 62.70%.

### 3.3. Molecular and crystal structures

A bridging carboxylate (O(3)–C(4)–O(4)) links two neighboring Gd<sup>III</sup> ions along the *a*-axis with Gd<sup>III</sup>...Gd<sup>III</sup> distance of 5.819 Å (figure 1). The central Gd<sup>III</sup> is eight-coordinate with two amine nitrogens and four carboxylate oxygens of one hexadentate pdta, one oxygen (O(9)) from coordinated water, and one bridging carboxylate oxygen (O(4)) from a neighboring pdta. Therefore (figure S3), an infinite 1-D zigzag polymeric binuclear [Gd<sup>III</sup><sub>2</sub>(pdta)<sub>2</sub>(H<sub>2</sub>O)<sub>2</sub>]<sup>2-</sup> complex anion is formed through this carboxylate bridge. O(9) from coordinated water and O(4) from a carboxylate of neighboring pdta are coordinated *cis* to Gd<sup>III</sup> with the  $\angle$ O(9)–Gd(1)–O(4) angle of 71.39°. The Gd<sup>III</sup> takes part in four five-membered rings which are almost coplanar and one six-membered ring which is not coplanar.



The coordination around Gd<sup>III</sup> can be considered as eight-coordinate pseudo square antiprismatic (figure 2). The upper square plane is formed by one amine N(2) and three carboxylates (O(4), O(5), and O(7)); the other square plane is formed by one amine (N(1)), one coordinated water (O(9)), and two carboxylates (O(1) and O(3)). The torsion angle of the two quadrilateral planes is about 45°.

Gd(1)–O bond distances vary from 2.3469(13) Å (Gd(1)–O(1)) to 2.4015(14) Å (Gd(1)–O(7)), with an average value of 2.3704(14) Å. The longest Gd(1)–O(7) bond distance may be relevant to the hydrogen bond formed between coordinated O(7) and ethylenediamine N(3). The Gd(1)–N bond distances are 2.6643(16) Å (Gd(1)–N(1)) and 2.6086(16) Å (Gd(1)–N(2)) (average 2.6365(16) Å). From figure 2, it can be calculated that, to the top plane, the value of the dihedral angle between  $\Delta(\text{O}(4)\text{O}(5)\text{O}(7))$  and  $\Delta(\text{N}(2)\text{O}(5)\text{O}(7))$  is about 11.58°, and that between  $\Delta(\text{O}(4)\text{O}(5)\text{N}(2))$  and  $\Delta(\text{O}(4)\text{O}(7)\text{N}(2))$  is about 13.21°. To the bottom plane, the value of the dihedral angle between  $\Delta(\text{O}(1)\text{O}(9)\text{N}(1))$  and  $\Delta(\text{O}(3)\text{O}(9)\text{N}(1))$  is about 5.60°, and between  $\Delta(\text{O}(1)\text{O}(3)\text{N}(1))$  and  $\Delta(\text{O}(1)\text{O}(3)\text{O}(9))$  is about 4.86°. In view of these calculated data and on the basis of Guggenberger and Muetterties' method [29], we conclude that the conformation of Gd(1)N<sub>2</sub>O<sub>6</sub> in [Gd<sup>III</sup>(pdta)(H<sub>2</sub>O)]<sup>−</sup> is an eight-coordinate square antiprismatic polyhedron. We speculate that the decrease (from nine to eight) of coordination number is from one six-membered ring in the coordinate geometry.

In one unit cell, (figure S4), there are four (enH<sub>2</sub>)[Gd<sup>III</sup><sub>2</sub>(pdta)<sub>2</sub>(H<sub>2</sub>O)<sub>2</sub>]·8H<sub>2</sub>O molecules, connected through hydrogen bonds and electrostatic forces with crystal water molecules and protonated ethylenediamine cations (enH<sub>2</sub><sup>2+</sup>). As seen from figure S5, one enH<sub>2</sub><sup>2+</sup> cation connects two [Gd<sup>III</sup>(pdta)(H<sub>2</sub>O)]<sup>−</sup> through hydrogen bonds of N(3) with a coordinated carboxylate (O(7)) from one adjacent [Gd<sup>III</sup>(pdta)(H<sub>2</sub>O)]<sup>−</sup> complex anion and an uncoordinated carboxylate (O(8)) from the other neighboring one. The distances of N(3)–O(7) and N(3)–O(8) are 2.890 and 2.847 Å, respectively. Hence, all catenulate complex anions link through hydrogen bonds with crystal water and protonated enH<sub>2</sub><sup>2+</sup>, yielding a layer structure.

For complex **2** (figure 3), the central Gd<sup>III</sup> is nine-coordinate with two amine nitrogens and seven oxygens with O(11) a coordinated water. The remaining two amine nitrogens, four carboxylate oxygens, and two ethyleneglycol oxygens come from one octadentate egta. The octadentate egta has seven five-membered rings with Gd<sup>III</sup> in **2**, with each five-membered ring almost coplanar.

The coordination geometry around Gd<sup>III</sup> in [Gd<sup>III</sup>(egta)(H<sub>2</sub>O)]<sup>−</sup> (figure 4) is a nine-coordinate pseudo monocapped square antiprism, with the capping position occupied by N(1). The quadrilateral plane of the antiprism is formed by one ethyleneglycol (O(5)), and three carboxylates (O(1), O(3), and O(7)), the bottom quadrilateral plane is one amine N(2), one coordinated water (O(11)), one ethyleneglycol (O(6)), and one carboxylate (O(9)). The twist angle of the quadrilateral planes is 38.06°, consistent with the geometry.

As shown in figure 3, Gd(1)–O bond distances are considerably different, ranging from 2.365(2) Å (Gd(1)–O(9)) to 2.5238(19) Å (Gd(1)–O(5)). Gd(1)–N bond distances are 2.628(2) Å (Gd(1)–N(1)) and 2.657(2) Å (Gd(1)–N(2)), average 2.6425(2) Å.

Figure 4 shows that to the top square plane, the value of the trigonal dihedral angle between  $\Delta(\text{O}(1)\text{O}(3)\text{O}(5))$  and  $\Delta(\text{O}(1)\text{O}(5)\text{O}(7))$  is 13.56°, and between  $\Delta(\text{O}(1)\text{O}(3)\text{O}(7))$  and  $\Delta(\text{O}(3)\text{O}(5)\text{O}(7))$  is 13.47°. To the bottom square plane, the value of the trigonal dihedral angle between  $\Delta(\text{O}(6)\text{O}(11)\text{N}(2))$  and  $\Delta(\text{O}(9)\text{O}(11)\text{N}(2))$  is 7.63° and between

$\Delta(\text{O}(6)\text{O}(9)\text{N}(2))$  and  $\Delta(\text{O}(6)\text{O}(9)\text{O}(11))$  is  $6.66^\circ$ . According to Guggenberger and Muettterties' method [28], we conclude that the conformation of  $\text{Gd}(\text{I})\text{N}_2\text{O}_7$  in  $[\text{Gd}^{\text{III}}(\text{egta})(\text{H}_2\text{O})]^-$  complex anion is a slightly distorted pseudo monocapped square antiprismatic polyhedron, in agreement with other  $\text{Gd}^{\text{III}}$  complexes with aminocarboxylic acid ligands, e.g.,  $\text{K}_3[\text{Gd}^{\text{III}}(\text{nta})_2(\text{H}_2\text{O})] \cdot 6\text{H}_2\text{O}$  [30],  $\text{Na}[\text{Gd}^{\text{III}}(\text{edta})(\text{H}_2\text{O})_3] \cdot 5\text{H}_2\text{O}$  [31],  $\text{Na}_4[\text{Gd}^{\text{III}}(\text{dtpa})(\text{H}_2\text{O})_2] \cdot 14\text{H}_2\text{O}$  [31], and  $(\text{py})[\text{Gd}^{\text{III}}(\text{Hnta})(\text{nta})(\text{H}_2\text{O})] \cdot 5\text{H}_2\text{O}$  [32].  $\text{Gd}^{\text{III}}$  forms nine-coordinate complexes with aminopolycarboxylic acids if the coordinated rings are all five-membered. If some biomolecules such as peptide or amino acid interact with these  $\text{Gd}^{\text{III}}$  complexes, we could also obtain a nine-coordinate monocapped square antiprism.

There are four  $(\text{enH}_2)[\text{Gd}^{\text{III}}(\text{egta})(\text{H}_2\text{O})_2] \cdot 6\text{H}_2\text{O}$  molecules in a unit cell (figure S6). The complex molecules connect with one another through hydrogen bonds and electrostatic forces with crystal water and protonated ethylenediamine cations ( $\text{enH}_2^{2+}$ ). Each  $\text{enH}_2^{2+}$  forms hydrogen bonds with two adjacent  $[\text{Gd}^{\text{III}}(\text{egta})(\text{H}_2\text{O})]^-$  anions (figure S7). Every N(3) connects three oxygens, in which O(3) and O(4) come from the same carboxylate of one  $[\text{Gd}^{\text{III}}(\text{egta})(\text{H}_2\text{O})]^-$  and O(10) comes from the other  $[\text{Gd}^{\text{III}}(\text{egta})(\text{H}_2\text{O})]^-$ . The N(3)–O(3), N(3)–O(4) and N(3)–O(10) distances are 3.030, 2.777, and 2.754 Å, respectively. Owing to this special coordination environment, the Newman' pattern dihedral angle of ethylenediamine is exactly  $180^\circ$ . Thus, four atoms of ethylenediamine all locate in the same plane.

#### 4. Conclusions

Two  $\text{Gd}^{\text{III}}$  complexes with aminopolycarboxylic acid ( $\text{H}_4\text{pdta} = \text{propylenediamine-N,N,N',N'}$ -tetraacetic acid and  $\text{H}_4\text{egta} = \text{ethyleneglycol-bis-(2-aminoethylether)-N,N,N',N'}$ -tetraacetic acid) ligands,  $(\text{enH}_2)[\text{Gd}^{\text{III}}_2(\text{pdta})_2(\text{H}_2\text{O})_2] \cdot 8\text{H}_2\text{O}$  and  $(\text{enH}_2)[\text{Gd}^{\text{III}}(\text{egta})(\text{H}_2\text{O})_2] \cdot 6\text{H}_2\text{O}$ , were synthesized and characterized by infrared spectrum method, thermal analysis, and single crystal X-ray diffraction method.  $(\text{enH}_2)[\text{Gd}^{\text{III}}_2(\text{pdta})_2(\text{H}_2\text{O})_2] \cdot 8\text{H}_2\text{O}$  adopts a binuclear molecular structure with an eight-coordinate square antiprism and crystallizes in the monoclinic crystal system with space group  $C2/c$ .  $(\text{enH}_2)[\text{Gd}^{\text{III}}(\text{egta})(\text{H}_2\text{O})_2] \cdot 6\text{H}_2\text{O}$  is mononuclear with a nine-coordinate monocapped square antiprism crystallizing in the monoclinic crystal system with space group  $P2_1/n$ . The structure and composition of aminopolycarboxylic acids decide the molecular structure, coordination number, and conformation of rare earth metal complexes.  $[\text{Gd}^{\text{III}}(\text{pdta})(\text{H}_2\text{O})]^-$  and  $[\text{Gd}^{\text{III}}(\text{egta})(\text{H}_2\text{O})]^-$  interact with ethylenediamine cations ( $\text{enH}_2^{2+}$ ) through hydrogen bonds and electrostatic forces.

#### Supplementary material

CCDC 753741  $(\text{enH}_2)[\text{Gd}^{\text{III}}_2(\text{pdta})_2(\text{H}_2\text{O})_2] \cdot 8\text{H}_2\text{O}$  and CCDC 753742  $(\text{enH}_2)[\text{Gd}^{\text{III}}(\text{egta})(\text{H}_2\text{O})_2] \cdot 6\text{H}_2\text{O}$  contain the supplementary crystallographic data for this article. These data can be obtained free of charge via [www.ccdc.cam.ac.uk/data\\_request/cif](http://www.ccdc.cam.ac.uk/data_request/cif), by e-mailing [data\\_request@ccdc.cam.ac.uk](mailto:data_request@ccdc.cam.ac.uk), or by contacting

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