

二维配合物 $\{[\text{Gd}(\text{HEDTA})]\cdot 3\text{H}_2\text{O}\}_n$ 的合成,晶体结构和磁性性质

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摘要: 采用水热法通过 Gd_2O_3 与乙二胺四乙酸为配体的反应合成出 1 个新的具有二维层状结构的钆金属配位聚合物 $\{[\text{Gd}(\text{HEDTA})]\cdot 3\text{H}_2\text{O}\}_n$ (**1**)。X-射线单晶衍射分析表明, 晶体属于正交晶系, $Pbca$ 空间群, 钆金属离子为八配位的方形反棱镜构型, 通过乙二胺四乙酸配体处于相反位置上两个羧基的连接, 形成了尺寸为 $0.666\ 6\ \text{nm}\times 0.669\ 2\ \text{nm}$ 的四核钆金属方形构筑单元。这些构筑单元进一步被乙二胺四乙酸配体连接成(4,4)拓扑网络结构。游离水分子和羧酸氧原子间通过氢键作用进一步将二维结构构筑成 ABAB 顺序的三维超分子网络结构。磁性测试表明该化合物为反铁磁。

关键词: 水热合成; 钆(III)配合物; 晶体结构; 磁性性质

中图分类号: O614.33+9

文献标识码: A

文章编号: 1001-4861(2011)05-0984-05

Hydrothermal Synthesis, Crystal Structure and Magnetic Properties of a New 2D Gadolinium(III) Complex: $\{[\text{Gd}(\text{HEDTA})]\cdot 3\text{H}_2\text{O}\}_n$

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Abstract: One new lanthanide coordination polymer, $\{[\text{Gd}(\text{HEDTA})]\cdot 3\text{H}_2\text{O}\}_n$ (**1**), (H_4EDTA =ethylenediaminetetraacetic acid) with 2D layer structure has been prepared by the hydrothermal synthesis and the structure and magnetic properties were characterized. Complex **1** crystallizes belong to orthorhombic system and has space group $Pbca$. The Gd^{III} ion is eight-coordinated and located at a square-antiprismatic coordination geometry. The $\text{Gd}(\text{III})$ ions are arrayed by two opposite carboxylate groups of EDTA ligand bridges and form a tetranuclear homometallic $\text{Gd}_4(\text{COO})_4$ square units with the dimensions of $0.666\ 6\ \text{nm}\times 0.669\ 2\ \text{nm}$. The square units are further assembled into a highly ordered (4, 4) net through the carboxylate bridges of EDTA ligands. Hydrogen bonds exist between interstitial water molecules and carboxyl oxygen atoms, as a result, the 2D network are further assembled into a 3D supramolecular network in the ABAB sequence. Magnetic studies indicated that complex **1** shows antiferromagnetic coupling between $\text{Gd}(\text{III})$ ions. CCDC: 795952.

Key words: hydrothermal synthesis; gadolinium complex; crystal structure; magnetic properties

The rare earth or radioactive rare earth complexes have attracted a great deal of attention because of their various biologic activities^[1-2]. For examples, the lanthanide (or radioactive rare earth) metal ion $\text{Sm}(\text{III})$

complexes were widely used for tumour therapy of brain, liver, lung, heart and bone tissues^[3], for lanthanide (or rare earth) metal ions $\text{Eu}(\text{III})$ and $\text{Tb}(\text{III})$ emitting unique fluorescence, their compounds were applied for

diagnoses of various diseases^[4], for lanthanide (or rare earth) metal ion Gd (III) containing the most high-spin single electrons, its complexes were usually used for contrast agents of magnetic resonance imaging (MRI) diagnoses^[5]. In order to apply these lanthanide metal ions better, it is necessary to rational design and select ligands with suitable functionalized groups to construct lanthanide complexes and then study the structures and properties. Amongst the synthetic strategies in the context of lanthanide complexes, one of the most fruitful choices is taking advantage of ligand molecule such as aminopolycarboxylic acids. Ethylenediaminetetraacetic acid (H_4EDTA) is such a ligand, which possesses diverse functional groups, may serve as a probe of lanthanide construction. For example, Song^[6] employed 1,2-benzenedicarboxylic acid (H_2BDC) and H_4EDTA as linkers with Nd^{3+} to construct a new lanthanide coordination polymer $\{[\text{Nd}_2(\text{BDC})(\text{EDTA})(\text{H}_2\text{O})_2]\cdot 1.5\text{H}_2\text{O}\}_n$, which performed 2D layer structure. Wang and co-workers used H_4EDTA as a single linker between Dy^{3+} and Na^+ to construct one new heterometallic coordination polymer, $\text{Na}[\text{Dy}(\text{EDTA})(\text{H}_2\text{O})_3]\cdot 3.25\text{H}_2\text{O}$, which showed 1D zigzag type structure^[7]. But so far, there are only two compounds based on Gd(III) ion and H_4EDTA , in which both without discussing the magnetic behavior^[8-9].

In the search for new magnetic materials, we have introduced the lanthanide metal ions Gd(III), in order to investigate the influence of the change of the organic ligands to magnetic behavior. In this contribution, we report one new 2D coordination polymer with a typical (4, 4) topology, $[\text{Gd}(\text{HEDTA})]\cdot 3\text{H}_2\text{O}$ _n (**1**), which is constructed from Gd(III) ion and H_4EDTA ligand.

1 Experimental

1.1 Materials and measurements

All chemicals purchased were of reagent grade and used without further purification. All syntheses

were carried out in 23 mL Teflon-lined autoclaves under autogenous pressure. Elemental analyses (C, H, and N) were performed on a Perkin-Elmer 240 CHN elemental analyzer. The IR spectra were acquired using Nicolet Avatar 360 FTIR spectrophotometer. Magnetic property was studied under QUANTUM MPMS XL-7 of QUANTUM.

1.2 Synthesis of 1

A mixture of Gd_2O_3 (0.181 g, 0.5 mmol), H_4EDTA (0.292 g, 1 mmol), HClO_4 (0.385 mmol), and water (10 mL) was heated at 160 °C for 60 h. Colorless crystals were obtained when cooling to room temperature at 5 °C $\cdot \text{h}^{-1}$ (yield: 65% based on Gd). Anal. calcd. for $\text{C}_{10}\text{H}_{19}\text{N}_2\text{O}_{11}\text{Gd}(\%)$: C, 23.98; H, 3.80; N, 5.59. Found(%): C, 23.95; H, 3.78; N, 5.63. IR (KBr pellet, cm^{-1}): 3 455, 1 612, 1 573, 1 488, 1 410, 1 335, 1 301, 1 230, 1 100, 925, 861.

1.3 Crystal structure analysis

Single crystal X-ray diffraction data collections for **1** was performed on a Bruker Smart II CCD diffractometer operating at 50 kV and 30 mA using Mo $K\alpha$ radiation ($\lambda=0.071\,073\text{ nm}$) at 293 K. Data collection and reduction were performed using the SMART and SAINT software^[10]. A multi-scan absorption correction was applied using the SADABS program^[10]. The structure was solved by direct methods and refined by full-matrix least squares on F^2 using the SHELXTL program package^[11-12]. All of the non-hydrogen atoms were refined anisotropically^[12]. Water H atoms were tentatively located in difference Fourier maps and were refined with distance restraints of $d(\text{O}-\text{H})=0.086\text{ nm}$ and $d(\text{H}\cdots\text{H})=0.139\text{ nm}$, each within a standard deviation of 0.001 nm, and with $U_{\text{iso}}(\text{H})=1.5U_{\text{eq}}(\text{O})$. Crystal parameters and details of the data collection and refinement are given in Table 1. Selected bond lengths and angles are given in Table 2.

CCDC: 795952.

Table 1 Crystal data and structure refinement information for compound 1

Formula	$\text{C}_{10}\text{H}_{19}\text{N}_2\text{O}_{11}\text{Gd}$	V / nm^3	3.255 7(2)
Formula weight	500.52	Z	8
Temperature / K	293(2)	$D_c / (\text{g}\cdot\text{cm}^{-3})$	2.042
Crystal system	Orthorhombic	μ / mm^{-1}	4.134

Continued Table 1

Size / mm	0.30×0.26×0.22	$F(000)$	1 976
Space group	$Pbca$	θ range / (°)	2.18~25.20
a / nm	1.338 35(5)	Goodness-of-fit	1
b / nm	1.30127(4)	$R_1 [I > 2\sigma(I)]^a$	0.022 3
c / nm	1.869 43(7)	wR_2 (all data) ^b	0.054 5

$$^a R = \sum (|F_o| - |F_c|) / \sum |F_o|, ^b wR_2 = \{ \sum [w(F_o^2 - F_c^2)^2] / \sum (F_o^2)^3 \}^{1/2}.$$

Table 2 Selected bond distances (nm) and angles (°)

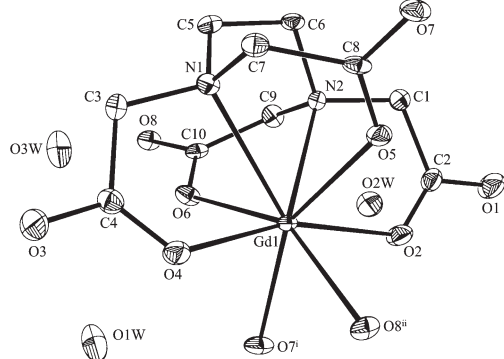
Gd1-O7 ⁱ	0.233 6(3)	Gd1-O2	0.238 8(3)	Gd1-O4	0.233 1(3)
Gd1-O5	0.234 0(3)	Gd1-O6	0.235 2(2)	Gd1-O8 ⁱⁱⁱ	0.237 3(3)
Gd1-N2	0.261 6(3)	Gd1-N1	0.263 4(3)		
O4-Gd1-O5	97.83(11)	O4-Gd1-O2	162.38(11)	O4-Gd1-N2	132.48(10)
N2-Gd1-N1	69.16(10)	O2-Gd1-N2	65.10(10)	O7-Gd1-N1	140.58(10)
O6-Gd1-N1	74.73(11)	O5-Gd1-O8 ⁱⁱⁱ	76.24(10)	O5-Gd1-O6	133.89(10)

ⁱ 0.5-x, -0.5+y, z; ⁱⁱⁱ 0.5+x, y, 0.5-z.

2 Results and discussion

2.1 Structure description

Structural analysis of $\{[Gd(HEDTA)] \cdot 3H_2O\}_n$ (**1**). The asymmetric unit of the compound **1** consists of one Gd(III) ion, one HEDTA³⁻ anion and lattice water molecules. The Gd(III) centre is eight-coordinated by two nitrogen atoms and four oxygen atoms from one EDTA ligand, two oxygen atoms from another two EDTA ligands, and displays a square-antiprismatic coordination geometry (Fig.1). The Gd-EDTA polymer is an eight-coordinate coordination geometry around Gd(III) atom, however, the reported monostructural M-Gd-EDTA (M=Na, K, Cs and NH₄⁺) complexes^[13-16] are nine-coordinate, it's possibly because of the coordination diversity of lanthanide metal ions in different crystal

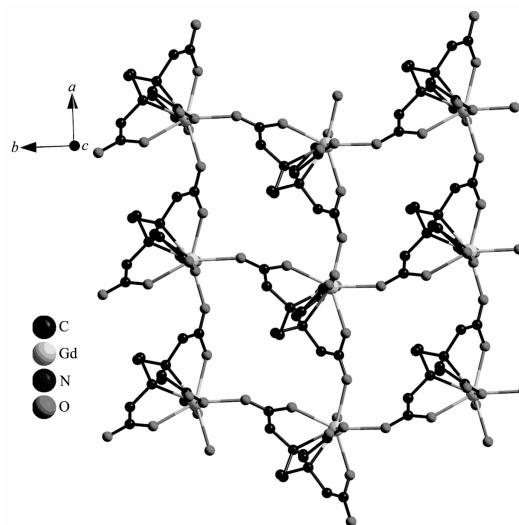


Symmetry codes: ⁱ 1/2-x, -1/2+y, z; ⁱⁱ 1/2+x, y, 1/2-z; All H atoms were omitted for clarity

Fig.1 Asymmetric coordination unit of **1**

environment.

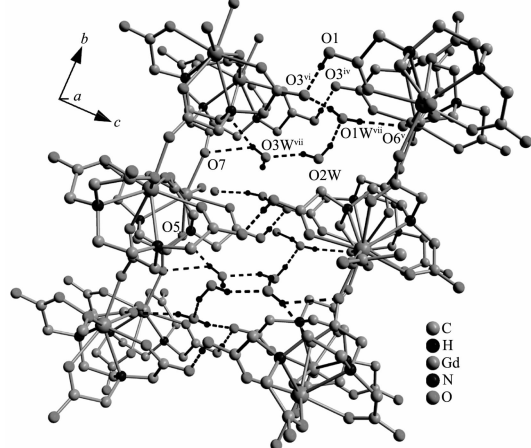
In the coordination polymer **1**, these Gd(III) ions are arrayed by two opposite carboxylate groups of EDTA ligand bridges and form a tetranuclear homometallic Gd₄(COO)₄ square units with the dimensions of 0.666 6 nm×0.669 2 nm. The square units are further assembled into a highly ordered (4, 4) net (Fig.2) through the carboxylate bridges of EDTA ligands. Hydrogen bonds exist between interstitial water molecules and carboxyl oxygen atoms, as a result, the 2D network are further assembled into a 3D supramolecular network in



All H atoms and lattice water molecules were omitted for clarity

Fig.2 2D (4, 4) net linked via carboxylate groups of **1** along the c axis

the ABAB sequence (Fig.3).



Symmetry codes: ^{iv} $-x, 1-y, -1-z$; ^v $1+x, y, z$; ^{vi} $1-x, 1.5+y, 1.5-z$; ^{vii} $-0.5+x, 1+y, -0.5-z$; ^{viii} $2.5-x, -y, 0.5+z$; H atoms bonding of C were omitted for clarity

Fig.3 Packing diagram of the complex **1** through hydrogen bonding interaction

2.2 IR and magnetic properties

The infrared spectra of the complex **1** are consistent with the structural data presented above. The broad band in the region of $3\,455\text{ cm}^{-1}$ may be assigned to the $\nu(\text{O-H})$ stretching vibrations of the water molecules. The features at $1\,612, 1\,488\text{ cm}^{-1}$ are associated with the asymmetric (COO) and symmetric (COO) stretching vibrations^[17].

The variable temperature magnetic susceptibilities of complex **1** were studied in the temperature range 2~300 K under 1 000 Oe. Fig.4a shows the data of the $\chi_{\text{M}}T$ versus T . For the complex **1**, the $\chi_{\text{M}}T$ of Gd(III) at 300 K is $8.05\text{ cm}^3\cdot\text{mol}^{-1}\cdot\text{K}$, slightly higher than the value of $7.88\text{ cm}^3\cdot\text{mol}^{-1}\cdot\text{K}$ of free Gd(III) ion ($S_{\text{A}}=7/2, g=2.00$)^[18]. The $\chi_{\text{M}}T$ data seems to be constant in the temperature range 300~10 K, but dramatically decreases from $7.639\text{ cm}^3\cdot\text{mol}^{-1}\cdot\text{K}$ at 10 K to $7.106\text{ cm}^3\cdot\text{mol}^{-1}\cdot\text{K}$ at 2 K. This behavior mainly caused by the weak antiferromagnetic coupling between Gd^{3+} ions^[19]. The plots of χ_{M}^{-1} versus T obeys the Curie-Weiss rule from 2~300 K (Fig.4b), giving the $C=8.03, \theta=-0.86$. Fisher has derived simple

uniform chain model with $H=-\sum_{i<j} J_{ij}S_iS_j$, that is

$$\chi = \frac{Ng^2\beta^2S(S+1)}{3kT} \frac{1+u}{1-u} \quad (1)$$

Where $u = \coth\left[\frac{JS(S+1)}{kT}\right] - \frac{kT}{JS(S+1)}$, other symbols

has their usual meaning in magnetism^[20]. Actually, this Eq.(1) seems good for $S_{\text{A}}=5/2$ and above in the chain model in practice^[21]. So the best fit by MAGMUN4.1 process with the Eq.(1) gives $g=2.004(2), J=-0.016\,8(8)\text{ cm}^{-1}$, and $R=1.13\times 10^{-4}$. The magnetic behavior of **1** is different from those of a trinuclear gadolinium complex reported by Aspinall et al.^[22]. However, it is similar to the observation of Benelli et al.^[23], Orvig and coworkers^[24], and Li et al.^[25], who observed weak antiferromagnetic coupling interactions for Gd(III) complexes.

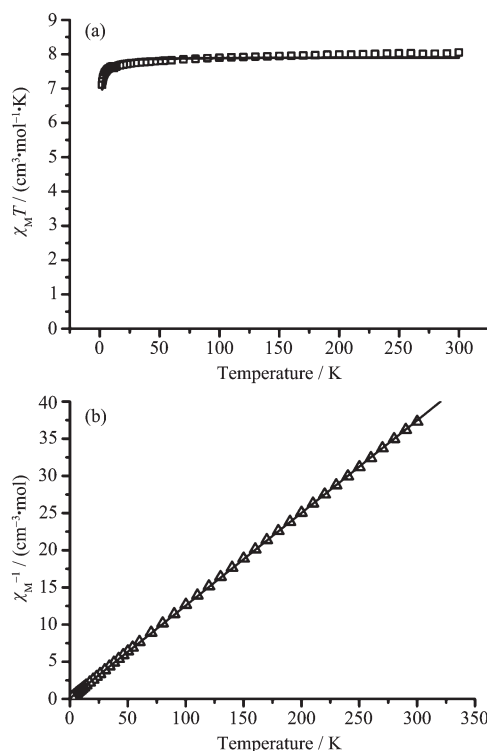


Fig.4 (a) Plot of $\chi_{\text{M}}T$ vs T in the range of 2~300 K for complex **1** measured under 1 000 Oe; (b) Plot of χ_{M}^{-1} vs T in the range of 2~300 K for complex **1**

In summary, based on a facile hydrothermal method, one new lanthanide coordination polymer $\{[\text{Gd}(\text{HEDTA})]\cdot 3\text{H}_2\text{O}\}_n$ containing the EDTA ligands have been synthesized and structurally characterized. **1** feature a 2D layer structure of a typical (4, 4) topology. Magnetic studies indicate that the interactions between Gd(III) ions is antiferromagnetic. This successful synthetic idea can be used to prepare other lanthanide coordination polymer materials with particular function.

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