

## 一维化合物 $[\text{Gd}_2(\text{PDC})_3(\text{phen})(\text{H}_2\text{O}) \cdot \text{H}_2\text{O}]_n$ 的合成、晶体结构及热性质

梁 青 李亚娟 宋会花\* 韩占刚 王继业  
(河北师范大学化学化学与材料科学学院, 石家庄 050016)

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### Synthesis, Crystal Structure and Thermogravimetric Analysis of A 1D Complex: $[\text{Gd}_2(\text{PDC})_3(\text{phen})(\text{H}_2\text{O}) \cdot \text{H}_2\text{O}]_n$

LIANG Qing LI Ya-Juan SONG Hui-Hua\* HAN Zhan-Gang WANG Ji-Ye  
(College of Chemistry and Material Sciences, Hebei Normal University, Shijiazhuang 050016)

**Abstract:** A one-dimensional complex,  $[\text{Gd}_2(\text{PDC})_3(\text{phen})(\text{H}_2\text{O}) \cdot \text{H}_2\text{O}]_n$  ( $\text{H}_2\text{PDC}$ =pyridine-3,4-dicarboxylic acid, phen = 1,10-phenanthroline), has been synthesized under hydrothermal conditions and characterized by elemental analysis, IR, TG analysis, and X-ray single-crystal structure analysis. Crystallographic data for the title complex:  $\text{C}_{33}\text{H}_{21}\text{Gd}_2\text{N}_5\text{O}_{14}$ ,  $M_r=1\,026.05$ , Triclinic, space group  $P\bar{1}$ ,  $a=0.751\,07(15)$  nm,  $b=1.256\,5(3)$  nm,  $c=1.825\,7(4)$  nm,  $\alpha=70.80(3)^\circ$ ,  $\beta=79.00(3)^\circ$ ,  $\gamma=76.05(3)^\circ$ ,  $V=1.567\,4(5)$  nm<sup>3</sup>, the final refinement gave  $R=0.022\,4$  and  $wR=0.047\,5$  for 4 913 observed reflections with  $I>2\sigma(I)$ . The coordination polymer displays a 1D belt-like chain. The 1D chain connected with adjacent chains through  $\pi$ - $\pi$  stacking interaction of phen groups to form 2D layers, which are further extended to a 3D supramolecular network through H-bonds interaction. CCDC: 671430.

**Key words:** gadolinium(III) complex; multicarboxylate; crystal structure

## 0 Introduction

Both the structural and topological novelty of coordination polymers as well as for their potential applications as functional material in catalytic, conductive, luminescent, magnetic, non-linear optical or porous materials have recently attracted great interest<sup>[1-7]</sup>. Thus far carboxylate networks have received a great deal of attention due to their ability of both chelate to

a metal ion and simultaneously bridge an adjacent metal<sup>[8,9]</sup>. As a member of multicarboxylate ligand, pyridine-3,4-dicarboxylic acid contains unique *p*-pyridinedicarboxylate group and *m*-pyridinedicarboxylate group, showing an excellent building block with charge and multi-connecting ability<sup>[10]</sup>. Moreover, much attention has been drawn to the assembly of metal-organic framework (MOF) and significant development has been witnessed in high-dimensional coordination polymers

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\*通讯联系人。E-mail: songhuihua@mail.hebtu.edu.cn

第一作者: 梁 青, 女, 25 岁, 硕士研究生; 研究方向: 配位化学。

containing d-block metals<sup>[5,6,11-20]</sup> such as Mn, Co, and Zn with pyridinedicarboxylic acid ligand<sup>[10,21]</sup>, but those with lanthanide complexes are less reported<sup>[21-24]</sup>. Due to their special abilities such as high coordination number, special magnetic and fluorescence property, lanthanide complexes is likely to bring unprecedented crystal structures and unique properties<sup>[25-28]</sup>. Therefore, a further research in this area is still an attractive target. Herein, we report a new complex of gadolinium with both pyridine-3,4-dicarboxylic acid and 1,10-phenanthroline ligands under hydrothermal synthesis.

## 1 Experimental

### 1.1 General

GdCl<sub>3</sub>·6H<sub>2</sub>O was prepared by dissolving its corresponding oxides in concentrated hydrochloric acid followed by drying. All the other reagents were commercially available and were used as received without further purification. Elemental analyses was determined with an Elemental Vario EL elemental analyzer. IR spectra was (KBr pellets) recorded in the 4 000~400 cm<sup>-1</sup> range with a FTIR-8900 spectrometer. Thermogravimetric analysis (TGA) were performed on a TGA-7 instrument under a static air atmosphere with a heating rate of 15 °C·min<sup>-1</sup>.

### 1.2 Preparation of [Gd<sub>2</sub>(PDC)<sub>3</sub>(phen)(H<sub>2</sub>O)·H<sub>2</sub>O]<sub>n</sub>

A mixture of GdCl<sub>3</sub>·6H<sub>2</sub>O (0.2 mmol, 0.074 3 g), pyridine-3,4-dicarboxylic acid (0.3 mmol, 0.050 2 g),

phen (0.3 mmol, 0.059 5 g) and NaOH (0.6 mmol, 0.2 mol·L<sup>-1</sup>, 3 mL) and H<sub>2</sub>O (8.0 mL) was sealed in a 23mL Teflon reactor, which was heated to 180 °C for 3 days and then slowly cooled to room temperature at a rate of 10 °C·h<sup>-1</sup>. Colorless needle-like single crystal of the title compound suitable for X-ray single crystal diffraction was obtained. Yield 49.4% (based on Gd). Anal. Calcd. for C<sub>33</sub>H<sub>21</sub>Gd<sub>2</sub>N<sub>5</sub>O<sub>14</sub>(%): C 38.63, H 1.37, N 6.83; found (%): C 38.64, H 1.385, N 6.87. IR (KBr, cm<sup>-1</sup>): 3 435m(ν<sub>OH</sub>), 1 646s(ν<sub>C=N(phen)</sub>), 1 602s(ν<sub>as</sub><sup>COO</sup>), 1 542s(ν<sub>as</sub><sup>COO</sup>), 1 425s(ν<sub>s</sub><sup>COO</sup>), 1 395s(ν<sub>s</sub><sup>COO</sup>), 845m(δ<sub>C-H(phen)</sub>), 729m(δ<sub>C-H(phen)</sub>).

### 1.3 Crystal structure determination

A suitable needle-like crystal with dimensions of 0.08 mm×0.06 mm×0.02 mm was selected for data collection on a rigaku saturn area detector diffractometer with Mo Kα radiation (λ=0.071 073 nm) at 113(2) K. The Lp factor and Semiempirical absorption corrections were applied to the intensity data. The structure was solved by direct methods. All non-hydrogen atoms were refined anisotropically by full-matrix least-squares methods. The hydrogen atoms were added geometrically and not refined. All calculations were performed using SHELX-97<sup>[29]</sup>. A summary of the crystallographic data and refinement parameters are given in Table 1. The selected bond lengths and angles are given in Table 2.

CCDC: 671430.

Table 1 Crystallographic data for the title complex

Empirical formula	C <sub>33</sub> H <sub>21</sub> Gd <sub>2</sub> N <sub>5</sub> O <sub>14</sub>	Calculated density / (Mg·m <sup>-3</sup> )	2.174
Formula weight	1 026.05	<i>F</i> (000)	988
Temperature / K	113(2)	Absorption coefficient / mm <sup>-1</sup>	4.281
Wavelength / nm	0.071 073	θ range for data collection / (°)	1.75~25.02
Crystal system	Triclinic	Limiting indices	-8 ≤ <i>h</i> ≤ 8, -14 ≤ <i>k</i> ≤ 14, -21 ≤ <i>l</i> ≤ 21
Space group	<i>P</i> $\bar{1}$	Reflections collected / unique ( <i>R</i> <sub>int</sub> )	16 021 / 5 501 (0.030 4)
<i>a</i> / nm	0.751 07(15)	Completeness to θ=25.02° / %	99.80
<i>b</i> / nm	1.256 5(3)	Maximum and minimum transmission	0.919 3 and 0.725 8
<i>c</i> / nm	1.825 7(4)	Data / restraints / parameters	5 501 / 3 / 487
α / (°)	70.80(3)	Goodness-of-fit on <i>F</i> <sup>2</sup>	1.054
β / (°)	79.00(3)	Final <i>R</i> indices [ <i>I</i> >2σ( <i>I</i> )]	<i>R</i> <sub>1</sub> =0.022 3, <i>wR</i> <sub>2</sub> =0.0470
γ / (°)	76.05(3)	<i>R</i> indices (all data)	<i>R</i> <sub>1</sub> =0.026 2, <i>wR</i> <sub>2</sub> =0.049 0
<i>V</i> / nm <sup>3</sup>	1.567 4(5)	Largest differences in peak and hole / (e·nm <sup>-3</sup> )	907 and -510
<i>Z</i>	2		

**Table 2** Selected bond lengths (nm) and bond angles ( $^{\circ}$ )

Gd(1)-O(1)	0.230 1(2)	Gd(1)-O(4)#3	0.250 6(3)	Gd(1)-O(11)#1	0.235 2(2)
Gd(1)-O(2)#2	0.238 8(2)	Gd(1)-O(5)	0.235 5(2)	Gd(1)-O(13)	0.260 6(2)
Gd(1)-O(3)#3	0.260 0(2)	Gd(1)-O(7)	0.235 7(2)	Gd(1)-O(13)#4	0.255 0(2)
Gd(2)-O(3)#3	0.246 5(2)	Gd(2)-O(8)	0.254 9(3)	Gd(2)-O(12)#1	0.232 8(2)
Gd(2)-O(6)#3	0.239 6(2)	Gd(2)-O(9)	0.241 2(3)	Gd(2)-N(5)	0.258 4(3)
Gd(2)-O(7)	0.254 9(2)	Gd(2)-O(10)	0.243 9(2)	Gd(2)-N(4)	0.259 1(3)
O(1)-Gd(1)-O(11)#1	85.48(9)	O(2)#2-Gd(1)-O(13)#4	72.20(8)	O(6)#3-Gd(2)-O(9)	118.97(8)
O(1)-Gd(1)-O(5)	77.28(8)	O(2)#2-Gd(1)-O(3)#3	134.10(8)	O(6)#3-Gd(2)-O(10)	78.26(8)
O(1)-Gd(1)-O(7)	151.46(8)	O(2)#2-Gd(1)-O(13)	69.25(8)	O(6)#3-Gd(2)-O(3)#3	74.55(8)
O(1)-Gd(1)-O(2)#2	85.61(9)	O(2)#2-Gd(1)-C(7)#3	141.13(9)	O(6)#3-Gd(2)-O(7)	74.50(8)
O(1)-Gd(1)-O(4)#3	81.21(8)	O(3)#3-Gd(2)-O(7)	66.67(8)	O(6)#3-Gd(2)-O(8)	95.31(9)
O(1)-Gd(1)-O(13)#4	74.43(8)	O(3)#3-Gd(2)-O(8)	116.78(8)	O(6)#3-Gd(2)-N(5)	134.48(9)
O(1)-Gd(1)-O(3)#3	131.48(8)	O(3)#3-Gd(2)-N(5)	142.96(9)	O(6)#3-Gd(2)-N(4)	76.54(9)
O(1)-Gd(1)-O(13)	136.73(8)	O(3)#3-Gd(2)-N(4)	151.09(9)	O(6)#3-Gd(2)-C(15)	98.65(9)
O(1)-Gd(1)-C(7)#3	106.37(9)	O(3)#3-Gd(2)-C(15)	81.31(9)	O(6)#3-Gd(2)-C(14)	84.09(9)
O(2)#2-Gd(1)-O(4)#3	138.64(8)	O(3)#3-Gd(2)-C(14)	92.24(9)		

Symmetry transformations used to generate equivalent atoms: #1:  $x-1, y, z$ ; #2:  $-x+1, -y+1, -z+2$ ; #3:  $x+1, y, z$ ; #4:  $-x+2, -y+1, -z+2$ .

## 2 Results and discussion

### 2.1 Crystal structure of 1

The title compound displays a one-dimensional chain structure along the  $a$  axis, in which the asymmetric unit includes two gadolinium atoms, three PDC ligands, one phen ligand, one coordination water molecule and one lattice water molecule. As shown in Fig.1, the two Gd centers exhibit different coordination environments. Gd1 is nine-coordinated by seven O atoms (O(1), O(2)#2, O(3)#3, O(4)#3, O(5), O(7), O(11)#1) from five different H<sub>2</sub>PDC ligands, and two O atoms (O(13), O(13)#4) from two coordinated water molecules. Whereas Gd2 center is coordinated by seven O atoms (O(3)#3, O(6)#3, O(7), O(8), O(9), O(10), O(12)#1) from five different PDC ligands, and two N atoms (N(4), N(5)) from a phen ligand. The Gd1 and Gd2 atoms are bridged by three PDC ligands to form a binuclear Gd<sub>2</sub>(PDC)<sub>3</sub>(phen)(H<sub>2</sub>O) subunits. The two binuclear subunits connect head to head via coordination water [O13 and O13A] and two PDC ligands to form tetranuclear Gd<sub>4</sub>(3,4-pyda)<sub>6</sub>(phen)<sub>2</sub>(H<sub>2</sub>O)<sub>2</sub> subunits which are interconnected by PDC ligands to form a 1D infinite belt-like chain. The distances of the Gd1...Gd2 and Gd1...Gd1 are 0.410 4 nm and 0.435 6 nm, respectively.

The phen molecules located at both sides of the chain as wings. The two centroids of the adjacent  $\pi$  plane are referred to Ce1 and Ce1i ( $i: 2-x, 2-y, 1-z$ ), respectively, with the distance of Ce1...Ce1i is ca. 0.356 6 nm. The 1D structure connected with adjacent chains via  $\pi$ - $\pi$  stacking interaction of phen groups to form 2D layers as shown in Fig.2, which are further

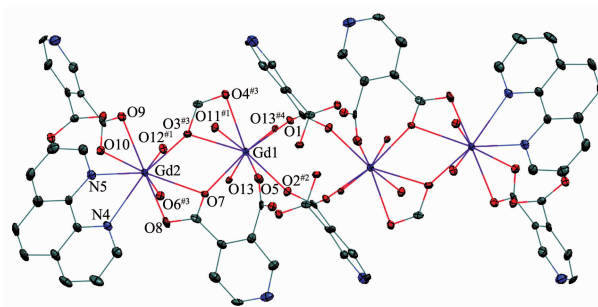


Fig.1 Coordinated conditions of Gd1 and Gd2

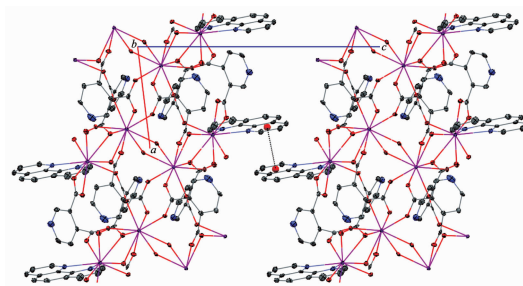


Fig.2 1D chain and  $\pi$ - $\pi$  stacking interaction of the title compound

extended to 3D network through H-bonds with the free water molecules and O atom of the PDC ligand carboxylate or N atom of the PDC ligand as the hydrogen-bonding donor and acceptor respectively, as shown in Table 3.

It is noteworthy that the PDC ligand exhibits two coordinated modes. First, one carboxylic group of PDC ligand coordinates with Gd2 by adopting a bidentate-

chelating modes and bridges Gd1, while the other carboxylic group of the same PDC ligand bridges Gd2 and Gd1, respectively. Second, one carboxylic group of PDC ligand coordinates with Gd1 by adopting a chelating and bridges Gd2, and the other carboxylic group of the same PDC ligand bridges two Gd1, respectively. It is interesting that pyridine nitrogen atom does not participate in coordination.

Table 3 Hydrogen bond lengths and bond angles

D-H...A	$d(\text{D-H}) / \text{nm}$	$d(\text{H...A}) / \text{nm}$	$d(\text{D...A}) / \text{nm}$	$\angle \text{DHA} / (^\circ)$
O(13)-H(13A)...O(14)#1	0.084 9	0.202 5	0.284 2	161.25
O(13)-H(13B)...O(6)#2	0.085 1	0.207 3	0.280 8	144.24
O(13)-H(13B)...O(3)#2	0.085 1	0.229 7	0.279 6	117.63
O(14)-H(14A)...O(4)#3	0.085 7	0.189 3	0.269 1	154.43
O(14)-H(14B)...N(2)#4	0.085 7	0.211 7	0.290 1	151.69

Symmetry modes: #1:  $x, y, z+1$ ; #2:  $x+1, y, z$ ; #3:  $-x+1, -y+1, -z+1$ ; #4:  $-x+1, -y+2, -z+1$ .

## 2.2 IR spectra

IR analysis shows that peaks appearing at 1 602 and 1 542  $\text{cm}^{-1}$  are attributed to the asymmetric vibrations of carboxylate groups, The bands of 1 425 and 1 395  $\text{cm}^{-1}$  should be assigned to the symmetric vibrations of carboxylate groups. The absorption peak of 1 646  $\text{cm}^{-1}$  correspond to the ring vibration, and 729, 845  $\text{cm}^{-1}$  are due to  $\delta(\text{C-H})$  of phen ligand respectively. The broad band at 3 435  $\text{cm}^{-1}$  belongs to the typical band of hydroxyl group, confirming the presence of water molecule in the compounds.

## 2.3 Thermal analysis

Thermogravimetric analyses of the title compound was carried out at a heating rate of 15  $^\circ\text{C} \cdot \text{min}^{-1}$ . TG analysis shows that the compound first lost corresponding two water molecules (observed 3.80%, calculated 3.51%) from 150 to 290  $^\circ\text{C}$ . Further weight loss, responsible for all organic components (observed 59.95%, calculated 61.16%), was observed between 250 and 600  $^\circ\text{C}$ . The remaining weight of 36.00% corresponds to the percentage (35.33%) of Gd and O components, indicating that the final product is  $\text{Gd}_2\text{O}_3$ .

In summary, a 1D chain coordinated polymer  $[\text{Gd}_2(\text{PDC})_3(\text{phen})(\text{H}_2\text{O})\cdot\text{H}_2\text{O}]_n$  has been synthesized under hydrothermal condition. The 1D structure is connected with adjacent chains via  $\pi$ - $\pi$  stacking of phen groups to form 2D layers, which are further

extended to 3D network. The PDC ligands play a key role in extending the chains.

## References:

- [1] Zaworotko M. J. *Chem. Rev.*, **2001**, *101*:1629~1658
- [2] Zheng S L, Tong M L, Chen X M. *Coord. Chem. Rev.*, **2003**, *246*:185~202
- [3] Batten S R, Robson R. *Angew. Chem. Int. Ed.*, **1998**, *37*:1460~1494
- [4] Blake A J, Champness N R, Hubberstey P, et al. *Coord. Chem. Rev.*, **1999**, *183*:117~138
- [5] Rao C N R, Natarajan S, Vaidhyanathan R. *Angew. Chem., Int. Ed.*, **2004**, *43*(12):1466~1454
- [6] Kitagawa S, Kitaura R, Noro S I. *Angew. Chem., Int. Ed.*, **2004**, *43*(18):2334~2375
- [7] Tong M L, Kitagawa S, Chang H C, et al. *Chem. Comm.*, **2004**, (4):418~419
- [8] Ouchi A, Ohki Y, Koizumi Y. *Coord. Chem. Rev.*, **1988**, *92*:29~43
- [9] Ghosh S K, Savitha G, Parimal K. *Inorg. Chem.*, **2004**, *43*(18):5495~5497
- [10] Zhang Q Z, Lu C Z, Xia C K. *Inorg. Chem. Commun.*, **2005**, *8*(3):304~306
- [11] Yaghi O M, O'Keeffe M, Ockwig N W, et al. *Nature*, **2003**, *423*(6941):705~714
- [12] Zaman M B, Smith M D, Loye H Z. *Chem. Commun.*, **2001**, *21*:2256~2257
- [13] Bu X H, Chen W, Lu S L, et al. *Angew. Chem., Int. Ed.*,

- 2001,40**(17):3201~3203
- [14]Wang X Q, Liu L M, Jacobson A J. *Angew. Chem. Int. Ed.*, **2003,42**(18):2044~2047
- [15]Lo S M, Chui S S, Shek L, et al. *J. Am. Chem. Soc.*, **2000,122**(26):6293~6294
- [16]Ma B Q, Sun H L, Gao S. *Chem. Commun.*, **2003**:2164~2165
- [17]Barthelet K, Marrot J, Riou D, et al. *Chem. Int. Ed.*, **2002,41**(2):281~284
- [18]Dybtsev D, Chun H, Yoon S H, et al. *J. Am. Chem. Soc.*, **2004,126**(1):32~33
- [19]Wang L, Shi Z, Li G H, et al. *Solid State Sci.*, **2004,6**(1):85~90
- [20]Chen X M, Liu G F. *Chem. Eur. J.*, **2002,8**(20): 4811~4817
- [21]Zhou Y F, Yuan D Q, Wu B L, et al. *New. J. Chem.*, **2004,28**(12):1590~1594
- [22]Song Y S, Yan B, Chen Z X. *Inorganica Chimica Acta*, **2007,360**(10):3431~3435
- [23]Qin C, Wang X L, Wang E B, et al. *Inorganica Chimica Acta*, **2006,359**(2):417~423
- [24]Song Y S, Yan B, Chen Z X. *Journal of Molecular Structure*, **2005,750**(1~3):101~108
- [25]Pan L, Huang X Y, Li J, et al. *Angew. Chem. Int. Ed.*, **2000,39**(3):527~530
- [26]Sun Y Q, Zhang J, Chen Y M, et al. *Angew. Chem., Int. Ed.*, **2005,44**(36):5814~5817
- [27]Gu X J, Xue D F. *Cryst. Growth Des.*, **2006,6**(11):2551~2557
- [28]Gu X J, Xue D F. *Inorg. Chem.*, **2006,45**(23):9257~9261
- [29]Sheldrick G M. *SHELXS-97, Program for X-ray Crystal Structure Solution, and SHELXL-97, Program for X-ray Structure Refinement*, University of Göttingen, Germany, **1997**.