

COORDINATION  
COMPOUNDSSynthesis and Crystal Structures of Two New Lanthanide  
Coordination Polymers with 2,3-Dichlorobenzoic Acid  
and 4,4'-BipyridineRen Ning<sup>a</sup>, Wu Jun-Chen<sup>b, c</sup>, Liu Wei-Jie<sup>a</sup>, Zheng Xin-Fang<sup>a</sup>, and Zhang Jian-Jun<sup>b, c, \*</sup><sup>a</sup>College of Chemical engineering and Material, Handan University, Handan, 056005 P. R. China<sup>b</sup>Testing and Analysis Center, Hebei Normal University, Shijiazhuang, 050024 P.R. China<sup>c</sup>College of Chemistry & Material Science, Hebei Normal University, Shijiazhuang, 050024 P.R. China

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**Abstract**—Two new lanthanide complexes  $[\text{Ln}(2,3\text{-DCIBA})_3(\text{CH}_3\text{CH}_2\text{O})(\text{H}_2\text{O})]_{2n} \cdot n(4,4'\text{-bipy})$  ( $\text{Ln} = \text{Eu}$  (1),  $\text{Tb}$  (2); 2,3-DCIBA = 2,3-dichlorobenzoate; 4,4'-bipy = 4,4'-bipyridine) have been synthesized by aqueous solution synthesis and characterized by elemental analysis and X-ray crystallography analysis. The results showed that complexes **1** and **2** are isostructural and are built of two-dimensional layered structures. Complex **1** belongs to triclinic system, space group  $P\bar{1}$ ,  $a = 9.7239(7) \text{ \AA}$ ,  $b = 12.0736(13) \text{ \AA}$ ,  $c = 14.6611(12) \text{ \AA}$ ,  $\alpha = 103.356(2)^\circ$ ,  $\beta = 93.0140(10)^\circ$ ,  $\gamma = 97.6200(10)^\circ$ ,  $V = 1653.7(3) \text{ \AA}^3$ ,  $Z = 1$ ,  $\rho = 1.735 \text{ g/cm}^3$ ,  $\mu = 18.453 \text{ mm}^{-1}$ ,  $F(000) = 850$ , the final  $R = 0.0591$  and  $wR = 0.0963$  for all data. Complex **2** belongs to triclinic system, space group  $P\bar{1}$ ,  $a = 9.6990(7) \text{ \AA}$ ,  $b = 12.0380(11) \text{ \AA}$ ,  $c = 14.6060(12) \text{ \AA}$ ,  $\alpha = 103.274(2)^\circ$ ,  $\beta = 93.0930(10)^\circ$ ,  $\gamma = 97.4250(10)^\circ$ ,  $V = 1639.7(2) \text{ \AA}^3$ ,  $Z = 1$ ,  $\rho = 1.764 \text{ g/cm}^3$ ,  $\mu = 2.694 \text{ mm}^{-1}$ ,  $F(000) = 854$ , the final  $R = 0.0545$  and  $wR = 0.0911$  for all data.

**Keywords:** lanthanide complexes, crystal structure, 2,3-dichlorobenzoic acid, 4,4'-bipyridine**DOI:** 10.1134/S0036023619040168

## INTRODUCTION

In recent years, much attention has been paid to the designs, synthesis, crystal structures and properties of lanthanide coordination polymers because these materials can be applied potentially in catalysis, sensors, ion exchange, gas storage and phase separation [1–7]. Aromatic carboxylic acids have also been used in the construction of coordination polymers due to their unique characteristics, especially aromatic carboxylic acid ligands with substituents have been widely used in the construction of lanthanide complexes due to the structural rigidity and stability. The carboxyl group can display a variety of interesting bonding geometries, for example, monodentate and bidentate chelating, bidentate bridging and tridentate chelating-bridging. Until now, many chain, layered and network lanthanide complexes are built owing to intermolecular weak interaction (including hydrogen bonds,  $\pi$ – $\pi$  interactions) [8–12]. In order to design complexes with novel structures, nitrogen heterocyclic ligands (1,10-phenanthroline, 2,2'-bipyridine, 4,4'-bipyridine, 2,2':6',2''-terpyridine) have been added into the synthesis of lanthanide complexes [13–17], which can not only increase the degree of conjugation for complexes, and improve the luminescent intensity of the

complexes, but also change the coordination mode of carboxylic acid, and properties of complexes. Therefore, the design and synthesis of novel structures is a very important research direction.

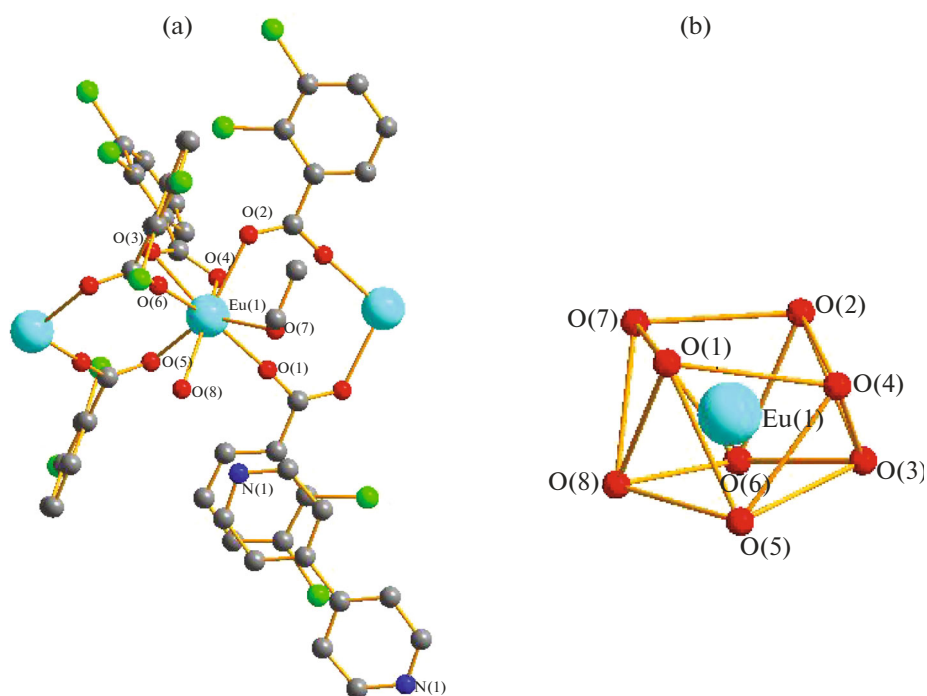
Herein, we report the synthesis and crystal structures of two new 2D polymers  $[\text{Ln}(2,3\text{-DCIBA})_3(\text{CH}_3\text{CH}_2\text{O})(\text{H}_2\text{O})]_{2n} \cdot n(4,4'\text{-bipy})$  ( $\text{Ln} = \text{Eu}$  (1),  $\text{Tb}$  (2)) with 2,3-dichlorobenzoic acid and 4,4'-bipyridine.

## EXPERIMENTAL

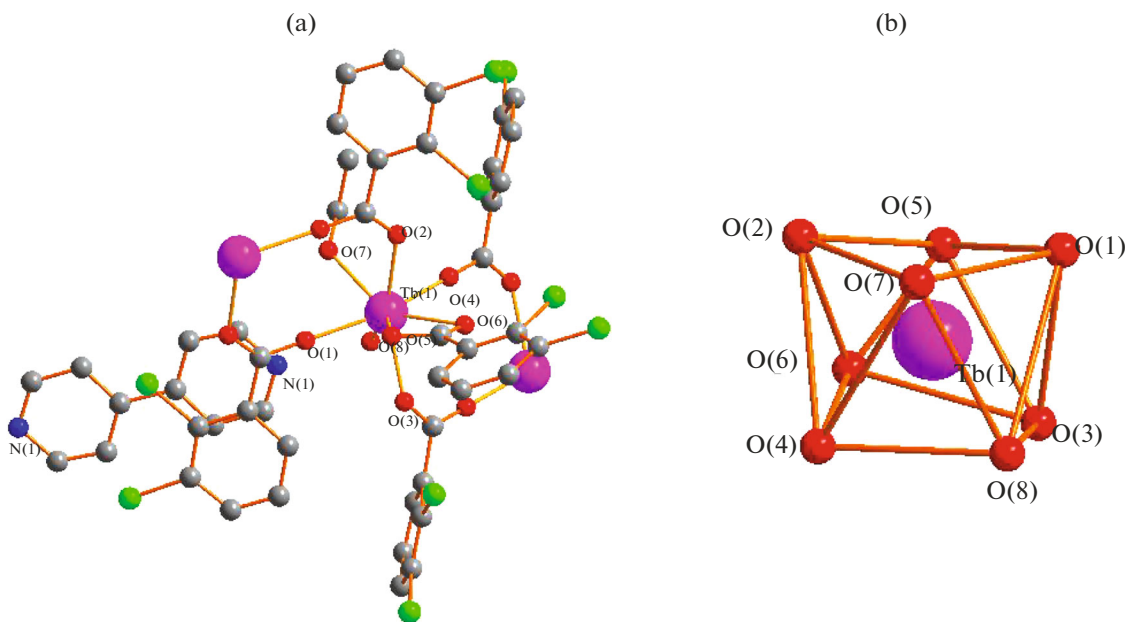
*Synthesis*

$\text{LnCl}_3 \cdot 6\text{H}_2\text{O}$  ( $\text{Ln} = \text{Eu}, \text{Tb}$ ) were prepared by dissolving europium and terbium oxide in hydrochloric acid followed by drying. All other materials were purchased and used without further purification. Elemental analysis (C, H, N) were determined using a Vario-EL II element analyzer.

**Synthesis of the complexes 1 and 2.** The title complexes were prepared by aqueous solution synthesis. 2,3-dichlorobenzoic acid (0.6 mmol) and 4,4'-bipyridine (0.2 mmol) were mixed in a 6 mL ethanol solution (95%). pH of the mixed solution was adjusted to 5–7 using a 1.0 mol L<sup>-1</sup> NaOH solution.  $\text{LnCl}_3 \cdot 6\text{H}_2\text{O}$



**Fig. 1.** (a) Molecular structure of complex **1** and (b) coordination geometry of Eu(III) ion.



**Fig. 2.** (a) Molecular structure of complex **2** and (b) coordination geometry of Tb(III) ion.

(Ln = Eu, Tb) (0.2 mmol) was dissolved in 3 mL of distilled water. Then the solution of the mixed ligand was dropped into the lanthanide chlorides solution under stirring for 6 h. The solution was filtered, and the product was washed with distilled water and dried.

The crystals suitable for X-ray structure analysis were obtained after two weeks by slow evaporation of the filtrate. For  $C_{56}H_{42}Cl_{12}Eu_2N_2O_{16}$  anal. calcd. (%): C, 38.88; H, 2.43; N, 1.62. Found (%): C, 38.00; H, 2.33; N, 1.60. For  $C_{56}H_{42}Cl_{12}N_2O_{16}Tb_2$  anal. calcd. (%): C,

38.57; H, 2.41; N, 1.60. Found (%): C, 38.50; H, 2.48; N, 1.70.

### Structure Determination

The colorless single crystals of complexes **1** ( $0.37 \times 0.13 \times 0.08$ ) and **2** ( $0.42 \times 0.13 \times 0.11$ ) were selected for X-ray diffraction analysis. The crystal data of complex **1** was collected on a Smart-1000 diffractometer with graphite-monochromatic  $\text{CuK}\alpha$  ( $\lambda = 1.54178 \text{ \AA}$ ) at the temperature of 293(2) K using an  $\omega$  scan mode in the ranges of  $3.11^\circ < \theta < 66.18^\circ$ . A total of 9762 reflections were recorded and 5800 were unique ( $R_{\text{int}} = 0.0696$ ), in which 3694 ( $-11 \leq h \leq 8$ ,  $-14 \leq k \leq 14$ ,  $-17 \leq l \leq 17$ ) were observed ( $I > 2\sigma(I)$ ). The final refinement  $R = 0.0591$ ,  $wR = 0.0963$ ,  $S = 1.018$ ,  $(\Delta/\sigma)_{\text{max}} = 0.001$ ,  $(\Delta\rho)_{\text{max}} = 0.759$ ,  $(\Delta\rho)_{\text{min}} = -0.946 \text{ e \AA}^{-3}$ . The crystal data of complex **2** was collected on a Smart-1000 diffractometer with graphite-monochromatic  $\text{MoK}\alpha$  ( $\lambda = 0.71073 \text{ \AA}$ ) at the temperature of 293(2) K using an  $\omega$  scan mode in the ranges of  $2.46^\circ < \theta < 25.02^\circ$ . A total of 8368 reflections were recorded and 5691 were unique ( $R_{\text{int}} = 0.0696$ ), in which 3450 ( $-11 \leq h \leq 8$ ,  $-14 \leq k \leq 14$ ,  $-17 \leq l \leq 17$ ) were observed ( $I > 2\sigma(I)$ ). The final refinement  $R = 0.0545$ ,  $wR = 0.0911$ ,  $S = 1.054$ ,  $(\Delta/\sigma)_{\text{max}} = 0.001$ ,  $(\Delta\rho)_{\text{max}} = 1.311$ ,  $(\Delta\rho)_{\text{min}} = -1.071 \text{ e \AA}^{-3}$ . The structures of title complexes were solved using the SHELXS-97 program (direct methods) [18] and refined by the full-matrix least-squares on  $F^2$  using the SHELXL-97 program [18]. Hydrogen atoms were generated geometrically. Molecular illustrations and crystal structures were made using diamond program. CCDC nos. 1409255 (**1**); 1409259 (**2**).

## RESULTS AND DISCUSSION

The molecular structures and coordination polyhedron of complexes **1** and **2** are depicted in Figs. 1 and 2, respectively. The selected bond length and bond

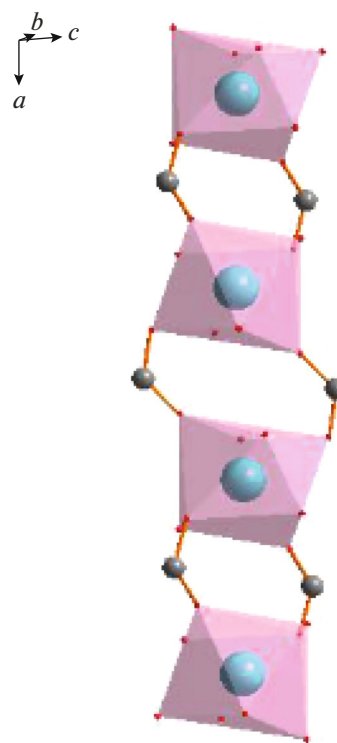


Fig. 3. One dimensional chain structure of complex **1** along  $a$  axis.

angles of complexes **1** and **2** are shown in Tables 1 and 2, respectively. The crystal structures of two complexes are isomorphic, therefore the crystal structure of complex **1** is discussed below as a representative.

As shown in Fig. 1a, Eu(III) ion is coordinated with eight oxygen atoms, six of which belong to one bidentate chelating 2,3-dichlorobenzate ligand and two bidentate bridging 2,3-dichlorobenzate ligands, two from one monodentate coordinate water molecule

Table 1. Selected bond lengths ( $\text{\AA}$ ) and bond angles ( $^\circ$ ) of complex **1**

Bond	Length, $\text{\AA}$	Bond	Length, $\text{\AA}$	Bond	Length, $\text{\AA}$
Eu(1)–O(6)#1	2.299(6)	Eu(1)–O(2)#2	2.417(5)	Eu(1)–O(1)	2.311(5)
Eu(1)–O(3)	2.519(6)	Eu(1)–O(5)	2.402(6)	Eu(1)–O(4)	2.522(6)
Eu(1)–O(8)	2.403(5)				
Angle	deg	Angle	deg	Angle	deg
O(6)#1–Eu(1)–O(1)	154.3(2)	O(1)–Eu(1)–O(3)	128.9(2)	O(1)–Eu(1)–O(2)#2	107.18(18)
O(6)#1–Eu(1)–O(5)	105.8(2)	O(5)–Eu(1)–O(3)	72.6(2)	O(8)–Eu(1)–O(4)	146.5(2)
O(1)–Eu(1)–O(5)	82.6(2)	O(8)–Eu(1)–O(3)	127.49(19)	O(5)–Eu(1)–O(2)#2	143.2(2)
O(6)#1–Eu(1)–O(8)	73.7(2)	O(2)#2–Eu(1)–O(3)	74.1(2)	O(8)–Eu(1)–O(2)#2	139.5(2)
O(1)–Eu(1)–O(8)	85.48(19)	O(6)#1–Eu(1)–O(4)	127.0(2)	O(6)#1–Eu(1)–O(3)	76.6(2)
O(5)–Eu(1)–O(8)	75.2(2)	O(1)–Eu(1)–O(4)	78.6(2)	O(2)#2–Eu(1)–O(4)	73.8(2)
O(6)#1–Eu(1)–O(2)#2	80.9(2)	O(5)–Eu(1)–O(4)	73.7(2)	O(3)–Eu(1)–O(4)	52.13(18)

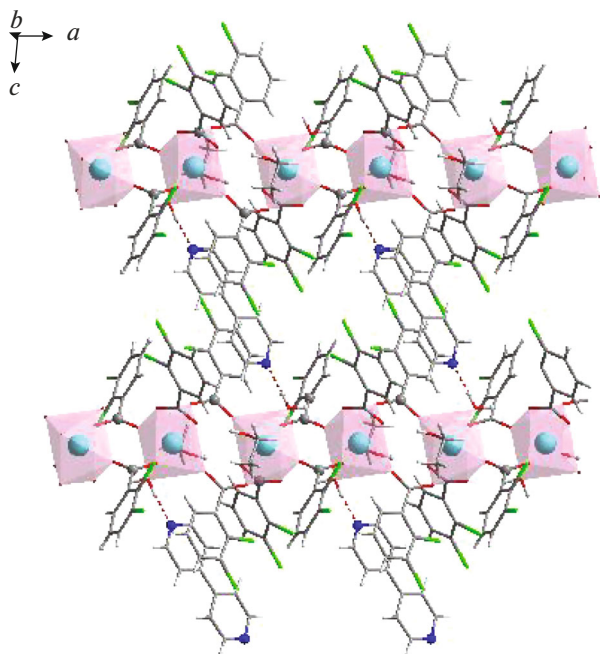
**Table 2.** Selected bond lengths (Å) and bond angles (deg) of complex **2**

Bond	Length, Å	Bond	Length, Å	Bond	Length, Å
Tb(1)–O(4)#1	2.262(6)	Tb(1)–O(8)	2.382(5)	Tb(1)–O(3)	2.364(5)
Tb(1)–O(1)	2.265(5)	Tb(1)–O(7)	2.442(5)	Tb(1)–O(2)#2	2.368(5)
Tb(1)–O(6)	2.475(5)	Tb(1)–O(5)	2.484(6)		
Angle	deg	Angle	deg	Angle	deg
O(4)#1–Tb(1)–O(1)	154.99(18)	O(8)–Tb(1)–O(7)	72.98(18)	O(1)–Tb(1)–O(8)	85.06(18)
O(4)#1–Tb(1)–O(3)	105.56(19)	O(4)#1–Tb(1)–O(6)	76.4(2)	O(3)–Tb(1)–O(8)	75.05(19)
O(1)–Tb(1)–O(3)	82.38(18)	O(1)–Tb(1)–O(6)	128.4(2)	O(2)#2–Tb(1)–O(8)	139.6(2)
O(4)#1–Tb(1)–O(2)#2	81.1(2)	O(3)–Tb(1)–O(6)	72.44(18)	O(4)#1–Tb(1)–O(7)	86.40(19)
O(1)–Tb(1)–O(2)#2	106.79(18)	O(2)#2–Tb(1)–O(6)	74.64(18)	O(1)–Tb(1)–O(7)	73.68(18)
O(3)–Tb(1)–O(2)#2	143.56(19)	O(8)–Tb(1)–O(6)	127.94(18)	O(3)–Tb(1)–O(7)	141.28(18)
O(4)#1–Tb(1)–O(8)	74.56(19)	O(7)–Tb(1)–O(6)	145.94(18)	O(2)#2–Tb(1)–O(7)	73.79(18)
O(4)#1–Tb(1)–O(5)	126.79(19)	O(3)–Tb(1)–O(5)	74.21(19)	O(8)–Tb(1)–O(5)	146.52(19)
O(1)–Tb(1)–O(5)	78.05(19)	O(2)#2–Tb(1)–O(5)	73.50(19)	O(7)–Tb(1)–O(5)	127.59(18)
O(6)–Tb(1)–O(5)	52.23(18)				

#1  $-x + 2, -y + 1, -z + 1$ ; #2  $-x + 1, -y + 1, -z + 1$ .

**Table 3.** Hydrogen bond lengths (Å) and bond angles (deg) of complex **1**

D–H...A	$d(\text{D–H})$	$d(\text{H...A})$	$d(\text{D...A})$	$\angle \text{DHA}$
$\text{O}_7\text{–H}_7\text{...O}_4$	0.820	1.931	2.750	178.75
$\text{O}_8\text{–H}_{8\text{C}}\text{...N}_1$	0.850	1.838	2.686	175.89
$\text{O}_7\text{–H}_{8\text{D}}\text{...O}_3$	0.850	1.978	2.827	176.14

**Fig. 4.** Two dimensional layers structure of complex **1** (red dotted lines represent hydrogen bonds).

and monodentate ethanol molecule. The coordination polyhedron of Eu(III) ion is a distorted tetragonal prism (Fig. 1b). The Eu–O bond length is in the range of 2.299(6)–2.522(6) Å. The Eu–O (bidentate chelating) distance is longer than the Eu–O (bidentate bridging) distance, indicating that one – dimensional chain structure is steady. The adjacent Eu(III) ions are linked by bridged 2,3-dichlorobenzate ligands, and one dimensional chain are formed along a axis, as shown in Fig. 3. Two dimensional layers (Fig. 4) is stabilized by hydrogen bonds between the free 4,4'-bipyridine and coordinated water molecule. Hydrogen bonds parameters of complexes **1** and **2** are listed in Tables 3 and 4, respectively.

Compared with the reported dinuclear molecule with the formula of  $[\text{Eu}(2,3\text{-DCIBA})_3(\text{terpy})(\text{H}_2\text{O})_2]$  (terpy = 2,2':6'2''-terpyridine) [19], which includes two Eu(III) ions, six 2,3-DCIBA ligands, two terpy ligands and two coordinated water molecules, it is clear that the nitrogen atoms of 4,4'-bipyridine are not coordinated with Eu(III) ions in the title complex. In order to compensate for the high number of properties of lanthanide ions, the solvent molecule ethanol was coordinated with lanthanide ions. So, the terpy ligands has a stronger affinity with  $\text{Ln}^{3+}$  ions than 4,4'-bipyridine, and the introduction of the auxiliary ligand plays a key role in the structure of the complex.

#### ACKNOWLEDGMENTS

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**Table 4.** Hydrogen bond lengths (Å) and bond angles (deg) of complex **2**

D–H···A	<i>d</i> (D–H)	<i>d</i> (H···A)	<i>d</i> (D···A)	∠DHA
O <sub>7</sub> –H <sub>7</sub> ···O <sub>5</sub>	0.820	1.962	2.782	179.85
O <sub>8</sub> –H <sub>8C</sub> ···N <sub>1</sub>	0.850	1.806	2.654	175.60
O <sub>7</sub> –H <sub>8D</sub> ···O <sub>6</sub>	0.850	2.000	2.849	175.61

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