

Synthesis, crystal structure and thermal stability property of a new terbium(III) coordination polymer based on 2,5-thiophenedicarboxylic acid

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Abstract: A new coordination polymer $[\text{Tb}_2\text{L}_2(\text{Ox})(\text{H}_2\text{O})_4]_n \cdot n\text{H}_2\text{O}$ ($\text{H}_2\text{L} = 2,5$ -thiophenedicarboxylic acid, $\text{H}_2\text{Ox} = \text{Oxalic acid}$) has been synthesized under hydrothermal reaction and characterized by single crystal X-ray diffraction analysis, IR spectra, and thermogravimetric analyses. The two Tb atoms are eight-coordinated in a distorted dodecahedron geometry for Tb1 and in a distorted bicapped trigonal prism geometry for Tb2. The structure possesses a 3D (3,8)-connected topology net with $\text{Tb}_2(\text{COO})_2\text{O}_{12}$ SBUs and L^{2-} , Ox^{2-} ligands. The thermogravimetric property of **1** has been investigated.

Supporting information: CIF file.

Keywords: 2,5-Thiophenedicarboxylic acid, Coordination polymer, Crystal structure, Topology.

1. INTRODUCTION

In recent years, coordination polymers have attracted considerable attentions in the fields of supramolecular chemistry due to the intriguing network topologies [1-5] and their potential applications such as catalysis, magnetism, luminescence and porosity, etc. [6-13]. The coordination polymer materials are normally realized by deliberate design of the ligands with adjustable connectivity and the judicious selection of metal ions with a specific coordination tendency, such as solvents used, reaction temperature, pH value and so on [14-15]. Therefore, the selection of special inorganic and organic building blocks is the key to the construction of a desired framework [16].

In this respect, 2,5-thiophenedicarboxylic acid has been picked since it may be important for providing potential supramolecular recognition sites for hydrogen-bonding interactions, preparing new materials with intriguing network topologies and excellent physical properties [17-30]. 2,5-Thiophenedicarboxylic acid can potentially be a monodentate, a bidentate and a tridentate ligand. It can also be a bridging or chelating ligand. Wang reported a series of coordination polymers based on 2,5-thiophenedicarboxylic acid with unusual magnetism and good photoluminescence properties, and proved the wonderful coordination flexibility of 2,5-thiophenedicarboxylic acid [22]. Zhang [20] reported a 3D iron coordination polymer based on 2,5-thiophenedicarboxylic acid and 2,2-bipyridine with diamag-

netism property. Marques reported that 2,5-thiophenedicarboxylic acid play a versatile role toward different lanthanide ions to form coordination polymers in which the lanthanides ions are heptacoordinated [21]. In special, some lanthanide polymers containing 2,5-thiophenedicarboxylate anion have been described in the literature and all of them present at least one of remarkable properties [23-25]. Herein, we report the synthesis, crystal structure and thermal stability property of a new terbium(III) coordination polymer based on 2,5-thiophenedicarboxylic acid.

2. EXPERIMENTAL

2.1. Materials and Measurements

All reagents were purchased commercially and used without further purification. The hydrothermal reaction was performed in the 25 mL Teflon-lined stainless steel Parr bomb. The diffraction data collection was performed with Mo- $K\alpha$ radiation ($\lambda = 0.71073 \text{ \AA}$) on a Bruker APEX II area-detector diffractometer. IR spectrum was measured in KBr pellets on a Nicolet 5DX FT-IR spectrometer. The thermogravimetric measurement was performed on preweighed samples in an oxygen stream using a Netzsch STA449C apparatus with a heating rate of $10 \text{ }^\circ\text{C}/\text{min}$. Elemental analyses were carried out using a Perkin-Elmer 2400 II elemental analyzer.

2.2. Synthesis of $[\text{Tb}_2\text{L}_2(\text{Ox})(\text{H}_2\text{O})_4]_n \cdot n\text{H}_2\text{O}$ (**1**)

A mixture of H_2L (0.0861 g, 0.5 mmol), $\text{Tb}(\text{NO}_3)_3$ (0.1724 g 0.5 mmol) and Oxalic acid (0.0450 g, 0.5 mmol) were dissolved in purified water (15 ml) in a 25 ml stainless steel reactor with a teflon liner and heated at 433 K for 72 h, and then cooled to room temperature at a speed of 5 degrees per hour. Colorless single crystals of **1** were obtained by slow evaporation of the filtrate over a few days; 29.4 % yield (based on H_2L). Anal. Calcd (%) for $\text{C}_{14}\text{H}_{14}\text{O}_{17}\text{S}_2\text{Tb}_2$ (836.23): C, 20.11; H, 1.69; O, 32.53; S, 7.67. Found(%):C, 20.21; H, 1.62; O, 32.51; S, 7.69. IR (KBr, cm^{-1}): 2961, 2589, 1664, 1558, 1415, 1274, 1066, 688.

2.3 Single-crystal structure determination

The diffraction data for the polymer **1** were collected on a Bruker SMART APEX II CCD diffractometer at 296(2) K. Data intensity was corrected by Lorentz-polarization factors and em-

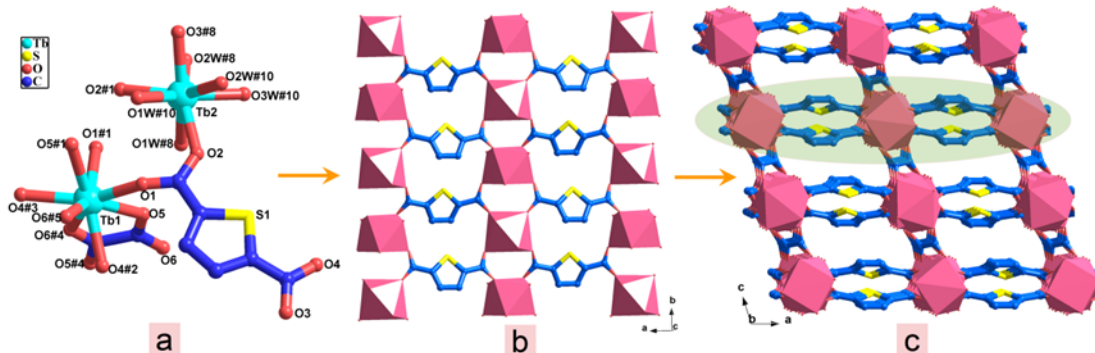


Figure 1: (a) Coordination environment of the Tb(III) ions in **1**. (b) View of 2D framework of **1**. (c) View of 3D framework of **1**. H atoms are omitted for clarity.

pirical absorption. The structure was solved with direct methods and expanded with difference Fourier techniques. All non-hydrogen atoms were refined anisotropically. Except the hydro-

gen atoms on oxygen atoms were located from the difference Fourier maps, the other hydrogen atoms were generated geometrically. All calculations were performed using SHELXS-97

Table 1: Selected bond lengths (Å) and angles (°) for **1**

Bond	Dist	Bond	Dist
Tb(1)–O(1)	2.297(3)	Tb(2)–O(3)#6	2.305(3)
Tb(1)–O(1)#1	2.297(3)	Tb(2)–O(3) #7	2.305(3)
Tb(1)–O(4)#2	2.384(3)	Tb(2)–O(2)	2.336(3)
Tb(1)–O(4)#3	2.384(3)	Tb(2)–O(2)#1	2.336(3)
Tb(1)–O(6)#4	2.415(3)	Tb(2)–O(1W)	2.416(3)
Tb(1)–O(6)#5	2.415(3)	Tb(2)–O(1W)#1	2.416(3)
Tb(1)–O(5)#1	2.443(3)	Tb(2)–O(2W)#1	2.483(3)
Tb(1)–O(5)	2.443(3)	Tb(2)–O(2W)	2.483(3)
Angle	(°)	Angle	(°)
O(1)–Tb(1)–O(1)#1	90.83(16)	O(3)#6–Tb(2)–O(3)#7	97.28(15)
O(1)–Tb(1)–O(4)#2	90.47(11)	O(3)#6–Tb(2)–O(2)	87.49(10)
O(1)#1–Tb(1)–O(4)#2	146.11(11)	O(3)#7–Tb(2)–O(2)	137.79(11)
O(1)–Tb(1)–O(4)#3	146.11(11)	O(3)#6–Tb(2)–O(2)#1	137.79(11)
O(1)#1–Tb(1)–O(4)#3	90.47(11)	O(3)#7–Tb(2)–O(2)#1	87.49(10)
O(4)#2–Tb(1)–O(4)#3	106.67(15)	O(2)–Tb(2)–O(2)#1	116.36(16)
O(1)–Tb(1)–O(6)#4	140.12(10)	O(3)#6–Tb(2)–O(1W)	77.86(11)
O(1)#1–Tb(1)–O(6)#4	81.84(11)	O(3)#7–Tb(2)–O(1W)	150.17(11)
O(4)#2–Tb(1)–O(6)#4	75.67(10)	O(2)–Tb(2)–O(1W)	71.86(11)
O(4)#3–Tb(1)–O(6)#4	73.46(10)	O(2)#1–Tb(2)–O(1W)	77.69(11)
O(1)–Tb(1)–O(6)#5	81.84(11)	O(3)#6–Tb(2)–O(1W)#1	150.18(11)
O(1)#1–Tb(1)–O(6)#5	140.12(10)	O(3)#7–Tb(2)–O(1W)#1	77.86(11)
O(4)#2–Tb(1)–O(6)#5	73.46(10)	O(2)–Tb(2)–O(1W)#1	77.69(11)
O(4)#3–Tb(1)–O(6)#5	75.67(10)	O(2)#1–Tb(2)–O(1W)#1	71.86(12)
O(6)#4–Tb(1)–O(6)#5	127.09(13)	O(1W)–Tb(2)–O(1W)#1	120.36(15)
O(1)–Tb(1)–O(5)	74.10(10)	O(3)#6–Tb(2)–O(2W)#1	75.87(11)
O(1)#1–Tb(1)–O(5)#1	73.11(10)	O(3)#7–Tb(2)–O(2W)#1	69.59(11)
O(4)#2–Tb(1)–O(5)#1	139.19(10)	O(2)–Tb(2)–O(2W)#1	71.10(11)

Table 1: Selected bond lengths (Å) and angles (°) for **1** (cont..)

Angle	(°)	Angle	(°)
O(4)#3–Tb(1)–O(5)#1	73.94(10)	O(2)#1–Tb(2)–O(2W)#1	142.85(11)
O(6)#4–Tb(1)–O(5)#1	138.28(10)	O(1W)–Tb(2)–O(2W)#1	134.99(12)
O(6)#5–Tb(1)–O(5)#1	67.16(9)	O(1W)#1–Tb(2)–O(2W)#1	74.88(11)
O(1)–Tb(1)–O(5)	73.11(10)	O(3)#6–Tb(2)–O(2W)	69.58(11)
O(1)#1–Tb(1)–O(5)	74.10(10)	O(3)#7–Tb(2)–O(2W)	75.85(11)
O(4)#2–Tb(1)–O(5)	73.94(10)	O(2)#1–Tb(2)–O(2W)	71.10(11)
O(4)#3–Tb(1)–O(5)	139.19(10)	O(2)–Tb(2)–O(2W)	142.87(11)
O(6)#4–Tb(1)–O(5)	67.16(9)	O(1W)–Tb(2)–O(2W)	74.90(11)
O(6)#5–Tb(1)–O(5)	138.28(10)	O(1W)#1–Tb(2)–O(2W)	134.99(12)
O(5)#1–Tb(1)–O(5)	132.59(13)	O(2W)#1–Tb(2)–O(2W)	126.65(16)

Symmetry transformations used to generate equivalent atoms:

#1 $-x, y, -z+3/2$; #2 $-x+1/2, y-1/2, -z+3/2$; #3 $x-1/2, y-1/2, z$; #4 $-x, -y, -z+1$; #5 $x, -y, z+1/2$;

#6 $-x+1/2, y+1/2, -z+3/2$; #7 $x+1/2, y-1/2, z$; #8 $x+1/2, y-1/2, z$; #9 $x+1/2, y+1/2, z$

[31], and SHELXL-97 [32] program packages. Selected bond lengths and angles are listed in Table 1, further details for structural analyses are summarized in Table S1.

3. RESULTS AND DISCUSSION

3.1. Crystal Structure of $\{[\text{Tb}_2\text{L}_2\text{Ox}(\text{H}_2\text{O})_4]\cdot\text{H}_2\text{O}\}_n$ (**1**)

1 crystallizes in the monoclinic space group $C2/c$ with an asymmetric unit consisting of one Tb(III) ion, one L^{2-} ligand, half a Ox^{2-} ligand, two coordinated water, and half a lattice water, as shown in Fig. 1a. The Tb1 is eight-coordinated by four O atoms from four L^{2-} ligands (Tb–O 2.297(3) ~ 2.384(3) Å), and four O atoms from two Ox^{2-} ligands (Tb–O 2.415(3) ~ 2.443(3) Å) in a slightly distorted dodecahedron geometry. The Tb2 is also eight-coordinated by eight oxygen atoms, four O atoms are from four L^{2-} ligands (Tb–O 2.305(3) ~ 2.336(3) Å), and four water (Tb–O 2.416(3) ~ 2.483(3) Å) in a distorted bicapped trigonal prism geometry. The Tb–O bond lengths are all in the normal ranges.

The carboxylate groups of the L^{2-} ligands are deprotonated, coordinate to Tb1 and Tb2 ions in bidentate mode, and connect

Tb1 and Tb2 ions to generate the 2D layers (Fig. 1b). The Ox^{2-} ligands between the layers connect the 2D network to give a 3D framework (Fig. 1c).

It is well-known that hydrogen bonds interactions are necessary in the formation and stability of supermolecular structures. As shown in Table 2, the O–H...O hydrogen bonds between lattice water molecules, coordinated water molecules, coordinated carboxylate oxygen atoms of L^{2-} ligands stabilized the 3D net.

In the structure, the metal center Tb1 and Tb2 are associated together by two carboxylate groups of two L^{2-} ligands to form a Tb_2 -based SBUs $[\text{Tb}_2(\text{CO}_2)_2\text{O}_{12}]$. Each L^{2-} ligand connects three Tb_2 -based SBUs, which can be considered as a 3-connected node; each Ox^{2-} ligand can be seen as a linear linker between two Tb_2 -based SBUs; while each Tb_2 -based SBU is surrounded by six L^{2-} ligands and two Ox^{2-} ligands to afford an 8-connected node. So the resulting structure is extended to a 3D (3,8)-connected net, as shown in Fig. 3. The topology analysis by the OLEX program suggests the (3,8)-connected net with the $(4^6.6^{18}.8^4)(4^3)$ topology.

Table 2. The O–H...O hydrogen bonds lengths (Å) and angles (°) for **1**.

D–H...A	d(D–H)	d(H...A)	d(D...A)	<(DHA)
O(1W)–H(1WA)...O(3)#10	0.825(18)	2.27(3)	2.994(4)	146(4)
O(1W)–H(1WA)...O(1W)#11	0.825(18)	2.44(4)	2.878(6)	114(4)
O(2W)–H(2WB)...O(6)#11	0.805(19)	2.13(2)	2.920(4)	169(6)
O(2W)–H(2WA)...O(3W)#7	0.838(19)	2.06(2)	2.889(9)	172(5)
O(3W)–H(3WB)...O(3W)#12	0.80(2)	1.90(3)	2.696(16)	171(14)

Symmetry transformations used to generate equivalent atoms:

#7 $x-1/2, y+1/2, z$; #10 $x-1/2, -y+1/2, z-1/2$; #11 $-x, -y+1, -z+1$; #12 $-x+1/2, -y+1/2, -z+1$

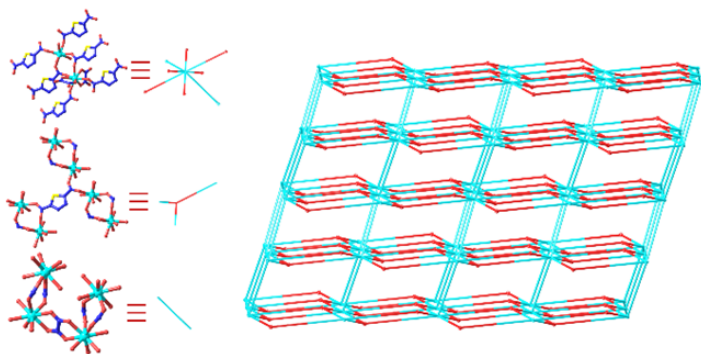


Figure 2. Schematic representation of the (3,8)-connected framework.

3.2. Properties

Thermogravimetric analyses (TGA) were carried out under N_2 atmosphere to examine the thermal stability of **1**, as shown in Fig. 3. The weight loss of 10.12% between 70 and 130°C is attributed to the release of the lattice water molecules (calcd 10.77%); the second weight loss of 11.03% between 240 and 290° is attributed to the release of the Ox^{2-} ligands (calcd 10.53%); the framework collapsed in the tem-

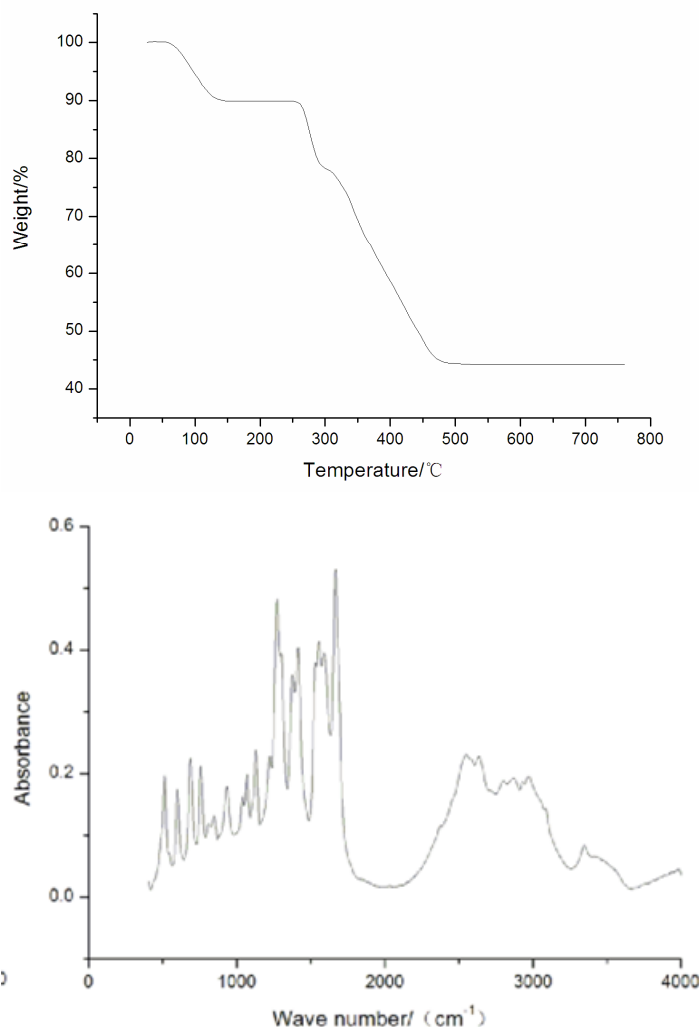


Figure 3: TG curves and IR spectra of polymer **1**.

perature 470° with weight loss of 35.23% and the final residuals may be Tb_2O_3 (calcd 34.95%). The IR spectra, two bonds of the modes $\nu_{as}(\text{COO})$ are at 1664 and 1558 cm^{-1} , two bonds of the modes $\nu_s(\text{COO})$ at 1415 and 1274 cm^{-1} and a sharp band of the mode $\nu(\text{O-Tb})$ is at 688 cm^{-1} .

4. CONCLUSION

In summary, we have successfully synthesized a new terbium (III) polymer based on 2,5-thiophenedicarboxylic acid and Oxalic acid under hydrothermal conditions and characterized by single crystal X-ray diffraction analysis, IR spectra, and thermogravimetric analyses. It is a 3D (3,8)-connected topology net with the Schläfli symbol of $(4^6.6^{18}.8^4)(4^3)$.

Acknowledgments

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