

## 以 2-氯苯甲酸、5,5'-二甲基-2,2'-联吡啶构筑的双核铽配合物的晶体结构和荧光性质

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**摘要:** 水热条件下采用  $\text{Tb}(\text{NO}_3)_3 \cdot 6\text{H}_2\text{O}$ 、2-氯苯甲酸和 5,5'-二甲基-2,2'-联吡啶作为反应物合成出一个双核铽金属配合物  $\text{Tb}_2(2\text{-cb})_4(\text{dmpy})_2(\text{NO}_3)_2$  (2-cb=2-氯苯甲酸, dmpy=5,5'-二甲基-2,2'-联吡啶)(1), 并分别用元素分析, 红外光谱图, 差热分析和 X-射线单晶衍射等表征了该结构。晶体结构分析结果表明: 化合物 1 为双核铽(III)配合物, 通过分子间的 C-H...O 氢键作用, 双核分子进一步被连接成二维平面结构。热稳定性表明化合物 1 能够稳定到 280 °C; 荧光分析表明常温固态下配合物 1 发射绿色荧光, 荧光寿命为 431.8  $\mu\text{s}$ 。

**关键词:** 铽(III)配合物; 晶体结构; 2-氯苯甲酸; 5,5'-二甲基-2,2'-联吡啶; 荧光性质

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## A Dinuclear Terbium(III) Complex Based on 2-Chlorobenzoate and 5, 5'-Dimethyl-2,2'-bipyridine Ligands: Crystal Structure and Luminescence

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**Abstract:** The reaction of 2-chlorobenzoic acid, 5, 5'-dimethyl-2,2'-bipyridine and  $\text{Tb}(\text{NO}_3)_3 \cdot 6\text{H}_2\text{O}$  under hydrothermal condition gave one new dinuclear terbium(III) complex,  $\text{Tb}_2(2\text{-cb})_4(\text{dmpy})_2(\text{NO}_3)_2$  (1) (2-cb=2-chlorobenzoate, dmpy=5, 5'-dimethyl-2, 2'-bipyridine), which has been characterized by elemental analysis, IR, TGA and single-crystal X-ray diffraction. Complex 1 is a dinuclear terbium(III) complex, which is further extended to a 2D layered network by C-H...O hydrogen bonding interactions. The results of thermal analysis indicate that complex 1 is quite stable up to 280 °C. 1 emits the intensely green characteristic luminescence of  $\text{Tb}^{3+}$  ion at room temperature, with lifetime of up to 431.8  $\mu\text{s}$ . CCDC: 865399.

**Key words:** terbium complex; crystal structure; 2-chlorobenzoate; 5, 5'-dimethyl-2, 2'-bipyridine; luminescent

## 0 Introduction

The study of luminescent lanthanide metal complexes has gained great recognition over the last decade due to their superior functional properties and variety of potential applications<sup>[1-7]</sup>. Lanthanide ions, especially Eu(III) and Tb(III), are excellent luminescent

centers and their luminescent properties depend on organic ligands. Compared to first-row transition metals, lanthanide ions have a larger coordination sphere and more flexible coordination geometry, which make it even more difficult to control the structures. Thus, to be able to rationally design and construct lanthanide coordination polymers with predicted

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geometries is still a great challenge, as many factors can affect the overall structural formation. A variety of fascinating lanthanide complexes have been constructed by carboxylate ligands and/or N-containing ligands as the auxiliary ligands<sup>[8-12]</sup> because of their ability to possess unusual structures and their sensitivity to molecular environments. 2-chlorobenzoate (2-cb) is interesting in the field of coordination complexes due to its strong and various coordination modes. For example, Li et al.<sup>[13-14]</sup> obtained two dinuclear lanthanide complexes based on 2-cb and 2, 2'-bipy ligands. Zhang also successfully synthesized one dinuclear lanthanum complex involving 2-cb and 1, 10-phenanthroline ligands<sup>[15]</sup>. As part of an on-going study related to lanthanide metal carboxylates, we report the preparation and structural characterization of a new dinuclear lanthanide complex, Tb<sub>2</sub>(2-cb)<sub>4</sub>(dmpy)<sub>2</sub>(NO<sub>3</sub>)<sub>2</sub> (**1**).

## 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. Infrared spectra were recorded (4 000~400 cm<sup>-1</sup>) as KBr disks on Bruker 1600 FTIR spectrometer. Luminescence spectra and lifetime for crystal solid samples were recorded at room temperature on an Edinburgh FLS920 phosphorimeter. Thermogravimetry analyses (TGA) were performed on an automatic simultaneous thermal analyzer (DTG-60, Shimadzu) under a flow of N<sub>2</sub> at a heating rate of 10 °C·min<sup>-1</sup> between ambient temperature and 800 °C.

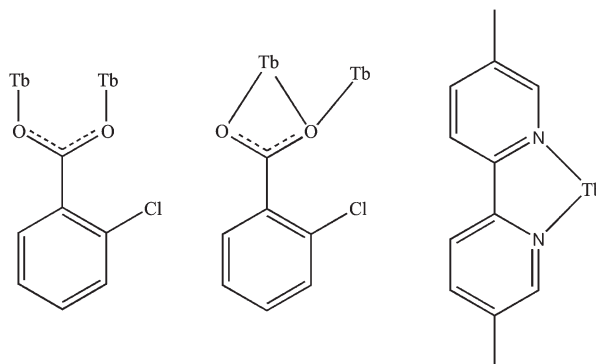
### 1.2 Synthesis of **1**

A mixture of Tb(NO<sub>3</sub>)<sub>3</sub>·6H<sub>2</sub>O (0.226 g, 0.5 mmol), 2-chlorobenzoic acid (0.08 g, 0.5 mmol), 5, 5'-dimethyl-2, 2'-bipyridine (0.092 g, 0.5 mmol) and H<sub>2</sub>O (15 mL) was stirred for 30 min in air and then sealed in a 23 mL Teflon reactor and kept under autogenous pressure at 150 °C for 72 h. The mixture was cooled to room temperature at a rate of 5 °C·h<sup>-1</sup>

and colorless block crystals were obtained in a yield of 42% based on the 2-cb. Anal. Calcd. for C<sub>52</sub>H<sub>40</sub>Cl<sub>4</sub>N<sub>6</sub>O<sub>14</sub>Tb<sub>2</sub> (%): C, 43.56; H, 2.80; N, 5.86. Found (%): C, 43.50; H, 2.82; N, 5.89. IR (KBr pellet) (cm<sup>-1</sup>): 3 470(s), 1 617(s), 1 475(m), 1 428(m), 1 499(s), 1 384(vs), 1 307(m), 1 215(w), 1 087(w), 1 024(w), 808(m), 761(m), 705(w), 616(s).

### 1.3 Crystal structure analysis

A single crystal with dimensions of 0.33 mm × 0.28 mm × 0.22 mm was mounted on a glass fiber for data collection which was performed on a Bruker Apex II CCD diffractometer operating at 50 kV and 30 mA using Mo K $\alpha$  radiation ( $\lambda$  = 0.071 073 nm) at room temperature. In the range of 2.00° <  $\theta$  < 25.2°, a total of 19923 reflections were collected, of which 4863 were unique ( $R_{\text{int}}$  = 0.0268) and 3 993 observed ones ( $I > 2\sigma(I)$ ) were used in the succeeding structure calculations. Data collection and reduction were performed using the APEX II software<sup>[16]</sup>. Multi-scan absorption corrections were applied for all the data sets using the SADABS<sup>[12]</sup>. The structure was solved by direct methods and refined by full matrix least squares on  $F^2$  using the SHELXTL program package<sup>[17]</sup>. All non-hydrogen atoms were refined with anisotropic displacement parameters. Hydrogen atoms attached to carbon were placed in geometrically idealized positions and refined using a riding model. The final  $R$  = 0.024 5 and  $wR$  = 0.090 6 ( $w = 1/[\sigma^2(F_o^2) + (0.046 7P)^2 + 3.411 8P]$ , where  $P = (F_o^2 + 2F_c^2)/3$ ) for 3993 observed reflections with  $I > 2\sigma(I)$ .  $S$  = 1.124, ( $\Delta/\sigma$ )<sub>max</sub> = 0.001, ( $\Delta\rho$ )<sub>max</sub> = 1 777 e·nm<sup>-3</sup> and ( $\Delta\rho$ )<sub>min</sub> = -617 e·nm<sup>-3</sup>. Crystal parameters and details of the data collection and refinement are given in Table 1.



Scheme Coordination mode of 2,4-dcp and dmpy ligands in the structures of **1**

**Table 1** Crystal data and structure refinement information for compound **1**

Formula	C <sub>52</sub> H <sub>40</sub> Cl <sub>4</sub> N <sub>6</sub> O <sub>14</sub> Tb <sub>2</sub>	<i>Z</i>	2
Formula weight	1432.54	<i>D<sub>c</sub></i> / (g·cm <sup>-3</sup> )	1.754
Temperature / K	296(2)	Adsorption coefficient / mm	2.854
Crystal system	monoclinic	<i>F</i> (000)	1 408
Size / mm	0.33×0.28×0.22	$\theta$ range / (°)	2.00–25.20
Space group	<i>P</i> 2 <sub>1</sub> / <i>c</i>	Limiting indices	−13 ≤ <i>h</i> ≤ 12, −23 ≤ <i>h</i> ≤ 23, −17 ≤ <i>h</i> ≤ 16
<i>a</i> / nm	1.152 22(5)	Reflections collected/unique	19 923/4 863
<i>b</i> / nm	1.985 3(9)	Goodness-of-fit	1.124
<i>c</i> / nm	1.473 41(5)	Final <i>R</i> indices ( <i>I</i> > 2σ( <i>I</i> ))	<i>R</i> <sub>1</sub> =0.024 5, <i>wR</i> <sub>2</sub> =0.071 9
<i>V</i> / nm <sup>3</sup>	2.712 06(19)	<i>R</i> indices (all data)	<i>R</i> <sub>1</sub> =0.035 2, <i>wR</i> <sub>2</sub> =0.090 6

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

Tb1-N1	0.2567 (4)	Tb1-O2 <sup>i</sup>	0.2325(3)	Tb1-O4 <sup>i</sup>	0.2729(3)
Tb1-N2	0.2582(4)	Tb1-O3 <sup>i</sup>	0.2443(3)	Tb1-O5	0.2477(3)
Tb1-O1	0.2319(3)	Tb1-O4	0.2282(3)	Tb1-O6	0.2440(3)
O4-Tb1-O1	77.73(11)	O6-Tb1-N1	92.16(13)	O3 <sup>i</sup> -Tb1-O4 <sup>i</sup>	49.35(10)
O4-Tb1-O6	151.37(11)	O4-Tb1-N2	79.69(12)	N1-Tb1-N2	62.93(13)
O6-Tb1-O5	51.81(11)	O4 <sup>i</sup> -Tb1-O4	75.82(11)	N1-Tb1-O4 <sup>i</sup>	142.78(11)

Symmetry code: <sup>i</sup> 1−*x*, −*y*, 2−*z*.

Selected bond lengths and angles are given in Table 2. CCDC: 865399.

## 2 Results and discussion

### 2.1 Structure description

Single-crystal X-ray diffraction analysis reveals that compound **1** is a centrosymmetric dinuclear structure and crystallizes in triclinic *P*2<sub>1</sub>/*c* space group. Coordination environment of Tb (III) atom is shown in Fig.1a. Each Tb<sup>III</sup> ion is nine-coordinated by five oxygen atoms from four 2-cb ligands, two oxygen atoms from one nitrate ligand and two nitrogen atoms

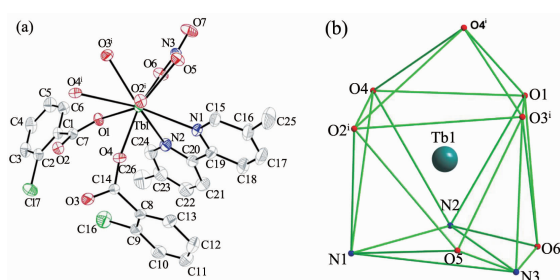


Fig.1 (a) View of the asymmetric unit of **1**. Non-H atoms are shown as 30 % probability displacement ellipsoids; (b) Monocapped square antiprism (MSAP) geometry surrounding a Tb(III) atom of **1**

from one dmpy ligand, adopting a distorted monocapped square antiprism (MSAP) geometry (Fig. 1b) with Tb-O, Tb-N bond lengths and O-Tb-O, O-Tb-N bond angles ranging from 0.2282 (3) to 0.2729(3) nm and 49.35(10) to 151.37(11)°, respectively, all of which are within the range of those reported in other nine-coordinated Tb (III) compounds with oxygen and nitrogen donating ligand<sup>[14,18-19]</sup>. Differing from [Tb(2-cb)<sub>2</sub>·2, 2-bipy]<sub>2</sub> (**a**)<sup>[14]</sup> and La<sub>2</sub>(phen)<sub>2</sub>(2-cb)<sub>6</sub> (**b**)<sup>[15]</sup>, whose 2-cb ligands exhibited three coordination modes, 2-cb coordinates to Tb(III) in two modes (scheme): bridging bidentate in the *syn-syn* configuration (Tb1-O1-C7 137.90(2)° and Tb1<sup>i</sup>-O2-C7 137.00(3)°) and chelating-bridging tridentate. The Tb···Tb separation of 0.396 3(2) nm is shorter than that of **a** (La···La 0.419 nm) and **b** (Tb···Tb 0.3991 nm), indicative of no metal-metal interaction. The centrosymmetric dinuclear molecules are further connected into a layer through intermolecular C-H···O hydrogen bonding interactions (Fig.2). Moreover, intramolecular C-H···O hydrogen bonds are also observed.

### 2.2 IR spectra and TGA

The IR spectra of compound **1** shows broad

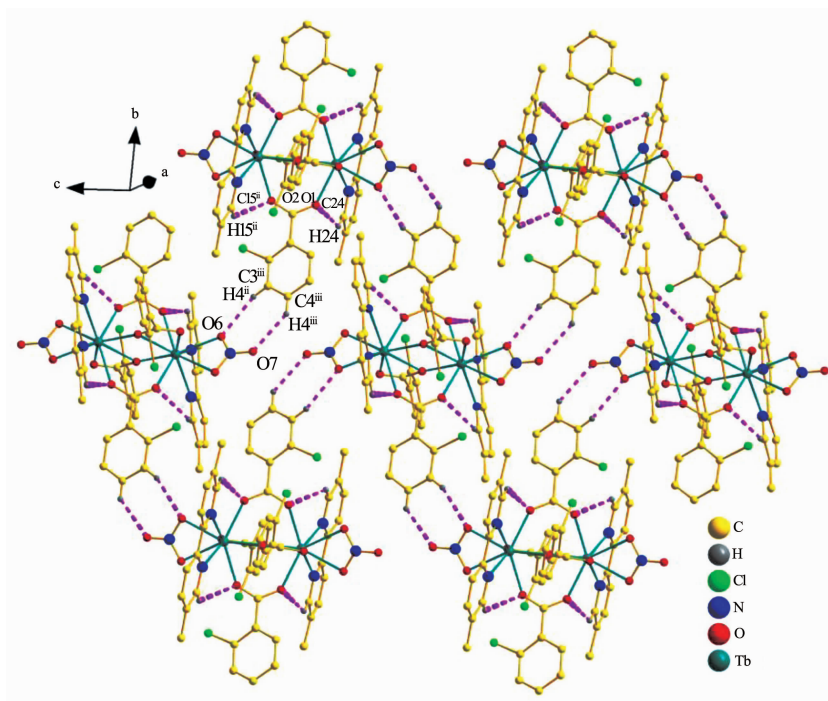


Fig.2 View of the 2D layer structure of **1** formed by C-H...O hydrogen bonds interactions

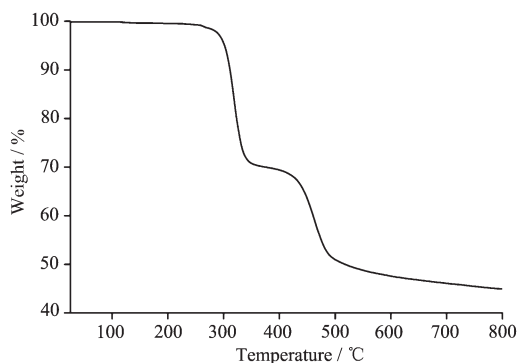


Fig.3 TGA trace of compound **1**

bands in the  $3470\text{ cm}^{-1}$ , which may be assigned to the  $\nu(\text{O-H})$  stretching vibrations of the free water molecules (impurity). The features at  $1\,617$  and  $1\,475$ ,  $1\,428\text{ cm}^{-1}$  are associated with the asymmetric ( $\text{COO}$ ) and symmetric ( $\text{COO}$ ) stretching vibrations. The  $\Delta\nu(\nu_{\text{as}}(\text{COO}^-)-\nu_{\text{s}}(\text{COO}^-))$  values are  $142$  and  $189\text{ cm}^{-1}$  (between  $105$  and  $200\text{ cm}^{-1}$ ), indicating the coordination of 2-cb with Tb(III) in bridging bidentate mode<sup>[20]</sup>, which is well consistent with X-ray diffraction structural analysis.

Thermal gravimetric analyses (TGA) were carried out to examine the thermal stability of **1**. The samples were heated up in flowing  $\text{N}_2$  with a heating rate of  $10$

$^{\circ}\text{C}\cdot\text{min}^{-1}$ . The TGA curve is depicted in Fig.3, which shows that **1** has thermal stability as no strictly clean weight loss step occurs below  $280\text{ }^{\circ}\text{C}$ . The weight-loss step occurred above  $280\text{ }^{\circ}\text{C}$  which corresponds to the decomposition of framework structure.

### 2.3 Luminescent properties

Solid-state excitation and emission luminescence spectra of **1** at room temperature is shown in Fig.4. The excitation spectrum for **1** showed a wide excitation band centered at  $339\text{ nm}$ . The emission spectrum of **1** revealed the characteristic emission of Tb(III) with intense green-emission, attributed to  $^5\text{D}_4 \rightarrow ^7\text{F}_J$  ( $J=6, 5, 4$ , and  $3$ ) centered at  $490$ ,  $543$ ,  $584$ , and

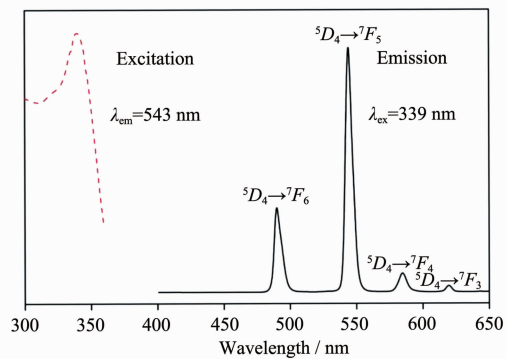


Fig.4 Excitation and emission spectra for **1** at room temperature

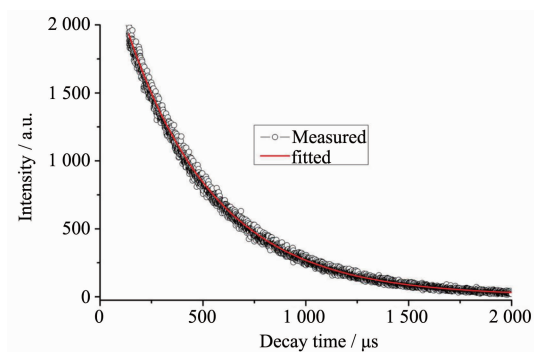


Fig.5 Luminescent lifetime of **1** in solid state

620 nm, respectively.  $^5D_0 \rightarrow ^7F_5$  is the strongest emission, indicating efficient ligand-to-metal energy transfer (LMCT)<sup>[21-22]</sup>. The luminescent lifetimes of solid **1** using an Edinburgh FLS920 phosphorimeter with 450 W xenon lamp as excitation source show lifetimes for **1** of 431.8  $\mu\text{s}$  (Fig.5), which could be used for light-emitting luminescent materials.

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