

## 配合物 $[\text{Tb}(p\text{-ClBA})_3(\text{phen})]_2$ 的结构和性能

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### Crystal Structure and Properties of Complex $[\text{Tb}(p\text{-ClBA})_3(\text{phen})]_2$

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**Abstract:** Terbium *p*-chlorobenzoate complex with 1,10-phenanthroline,  $[\text{Tb}(p\text{-ClBA})_3\text{phen}]_2$  (**1**) has been obtained in the ethanol solution, where *p*-ClBA = *p*-chlorobenzoate and phen = 1,10-phenanthroline. It crystallizes in the triclinic system, space group  $P\bar{1}$ ,  $a=1.008\ 1(2)$  nm,  $b=1.185\ 7(2)$  nm,  $c=1.431\ 1(3)$  nm,  $\alpha=110.826(4)^\circ$ ,  $\beta=96.436(4)^\circ$ ,  $\gamma=101.737(4)^\circ$ ,  $Z=2$ . The two Tb(III) ions are linked by four carboxylate groups through their bidentate bridging modes, forming a dimeric unit with crystallographic inversion center. Each terbium ion has an eight-coordinate geometry with four of the coordination sites occupied by four oxygen atoms from the four bridging carboxylates, respectively, two oxygen atoms from bidentate carboxylate, and the remaining positions occupied by two nitrogen atoms from a 1,10-phenanthroline molecule. The Tb(III) ion adopt a distorted square antiprism coordination geometry. The excitation and luminescence data observed at room temperature show that the title complex emits very intensive green fluorescence under ultraviolet light. The result of thermal analysis indicates the complex  $[\text{Tb}(p\text{-ClBA})_3\text{phen}]_2$  is quite stable to heat. CCDC: 221921.

**Key words:** terbium complex; *p*-chlorobenzoic acid; 1,10-phenanthroline; crystal structure; luminescence

## 0 Introduction

Photoactive lanthanide organic complexes are of both fundamental and technological interest due to their diverse structure and potential applications in fluorescent materials, electroluminescent materials and luminescent probes, which based on their

emission peaks in the visible and near-infrared region under UV excitation<sup>[1~9]</sup>. In these complexes, rare-earth carboxylate complexes have attracted much interest because the various coordination modes of carboxylate groups (such as chelating bidentate, bridging bidentate and bridging tridentate). Most of them show interesting polymeric network or chain structure<sup>[10~16]</sup>.

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The luminescence of lanthanide ions has specific requirements regarding the coordination environment of the metal ions and the energy of the singlet and triplet states of the ligands, since the oscillator strengths of the forbidden f-f transitions are very faint. The luminescent intensity is strongly dependent on the efficiency of ligand absorption, the efficiency of ligand-to-metal energy transfer, and the efficiency of metal luminescence. In our work, we found that some neutral conjugated heterocyclic ligands (such as phen or bipy) can enhance the luminescent intensity of Eu(III) or Tb(III) in their aromatic carboxylate compounds. In this paper a ternary complexes of Tb(III) with *p*-chlorobenzoate and phen is reported. It exhibited strong green luminescence under UV excitation and good thermal stability.

## 1 Experimental

### 1.1 General

All the starting materials were of analytical grade. Excitation and luminescence spectra were performed at room temperature using a F-4500 fluorescence spectrophotometer. The TG and DTG experiment was performed using a Perkin-Elmer TGA7 thermogravimetric analyzer.

### 1.2 Preparation of [Tb(*p*-ClBA)<sub>3</sub>(phen)]<sub>2</sub> (1)

A stoichiometric amount of TbCl<sub>3</sub>·6H<sub>2</sub>O, *p*-chlorobenzoic acid and 1,10-phenanthroline were dissolved

in 95% C<sub>2</sub>H<sub>5</sub>OH respectively. The pH of the *p*-chlorobenzoic acid was adjusted to the range of 6~7 with 1 mol·L<sup>-1</sup> NaOH solution. The C<sub>2</sub>H<sub>5</sub>OH solutions of two ligands were mixed and the mixture was added dropwise to the ethanolic TbCl<sub>3</sub> solution, while a white precipitate formed. The colorless transparent crystals suitable for X-ray analysis were obtained by the slow evaporation of the filtrates. Anal. Calcd. (%) for C<sub>66</sub>H<sub>40</sub>N<sub>4</sub>O<sub>12</sub>Cl<sub>6</sub>Tb<sub>2</sub>: C 48.60 (49.19), H 2.73 (2.50), N 3.14 (3.48), Tb 19.40 (19.72).

### 1.3 Structure determination

Determination of the unit cell and data collection was performed on a Bruker Smart Apex CCD area detector diffractometer using graphite monochromatized Mo *K*α radiation (λ=0.071 073 nm) at 293(2) K. A total of 9 402 (*R*<sub>int</sub>=0.112 8) independent reflections were collected by  $\varphi$ - $\omega$  scan technique in the range 1.55° ≤  $\theta$  ≤ 28.31°, of which 6 806 [*I* > 2σ(*I*)] reflections were corrected by SADABS. The structure was solved using direct methods in SHELXS-97<sup>[17]</sup> and refined using a full-matrix least-square procedure on *F*<sup>2</sup> in SHELXL-97<sup>[18]</sup>. All non-hydrogen atoms were refined with anisotropic thermal parameters, hydrogen atoms were added theoretically and refined with riding model position parameters and fixed isotropic thermal parameters. Further details of the structure analysis are given in Table 1.

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Table 1 Data collection and processing parameters for complex 1

Empirical formula	C <sub>66</sub> H <sub>40</sub> Cl <sub>6</sub> N <sub>4</sub> O <sub>12</sub> Tb <sub>2</sub>	Absorption coefficient / mm <sup>-1</sup>	2.617
Formula weight	805.78	<i>F</i> (000)	792
Temperature / K	293(2)	$\theta$ range for data collection / (°)	1.55~28.31
Wavelength / nm	0.071 073	Limiting indices	-13 ≤ <i>h</i> ≤ 12, -10 ≤ <i>k</i> ≤ 15, -18 ≤ <i>l</i> ≤ 19
Crystal system	Triclinic	Reflections collected / unique	9 402 / 6 806 ( <i>R</i> <sub>int</sub> =0.112 8)
Space group	<i>P</i> $\bar{1}$	Completeness to $\theta$ =28.31°	89.3%
<i>a</i> / nm	1.0081(2)	Absorption correction	Sadabs
<i>b</i> / nm	1.185 7(2)	Max. and min. transmission	20.79 and 2.77
<i>c</i> / nm	1.431 1(3)	Refinement method	Full-matrix least-squares on <i>F</i> <sup>2</sup>
$\alpha$ / (°)	110.826(4)	Data / restraints / parameters	6 806/ 0 / 406
$\beta$ / (°)	96.436(4)	Goodness-of-fit on <i>F</i> <sup>2</sup>	0.849
$\gamma$ / (°)	101.737(4)	Final <i>R</i> indices [ <i>I</i> >2σ( <i>I</i> )]	<i>R</i> <sub>1</sub> =0.058 3, <i>wR</i> <sub>2</sub> =0.127 5
Volume / nm <sup>3</sup>	1.533 3(5)	<i>R</i> indices (all data)	<i>R</i> <sub>1</sub> =0.078 4, <i>wR</i> <sub>2</sub> =0.135 4
<i>Z</i>	2	Largest diff. peak and hole / (e·nm <sup>-3</sup> )	2 047 and -2 309
Calculated density / (Mg·m <sup>-3</sup> )	1.745		

## 2 Results and discussion

### 2.1 Crystal structure of $[\text{Tb}(p\text{-ClBA})_3(\text{phen})]_2$

The complex consists of binuclear molecules  $[\text{Tb}(p\text{-ClBA})_3(\text{phen})]_2$  (**1**). The perspective view of the complex is depicted in Fig.1. Selected bond lengths and angles are listed in Table 2. The two Tb(III) ions are linked by four carboxylate groups through their bidentate bridging modes, forming a dimeric unit with crystallographic inversion center, and the distance

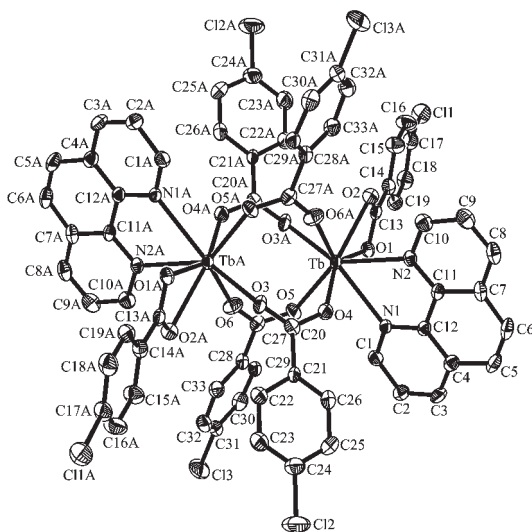


Fig.1 Dimeric structure for complex  $[\text{Tb}(p\text{-ClBA})_3(\text{phen})]_2$  (**1**) with 30% thermal ellipsoids

between two Tb(III) ions is 0.434 8 nm. Each Tb(III) ion has a eight-coordinate geometry with four of the coordination sites occupied by the oxygen atoms from the bridging carboxylate, two by the oxygen atoms from bidentate carboxylate and the remaining positions occupied by two nitrogen atoms from a 1,10-phenanthroline molecule. The analysis of the structural features of the coordination polyhedron indicates that the Tb(III) ion adopt a distorted square antiprism coordination geometry.

The Tb-O distances are in a range of 0.228 0(6)~0.248 7(5) nm, in which the Tb-O bonds formed by the bidentate carboxylate group are the longest. The Tb-O bond distances formed by the bridging carboxylates are slightly shorter than that formed by the bidentate carboxylate groups. The average bond distance of Tb-O is 0.235 7 nm, slightly shorter than that found in the complex  $[\text{Tb}(m\text{-MBA})_3(\text{phen})]_2 \cdot 2\text{H}_2\text{O}$  (0.238 0 nm) ( $m\text{-MBA}=m\text{-methylbenzoate}$ )<sup>[19]</sup>. The average Tb-N distance is 0.259 8 nm, slightly longer than corresponding average distance 0.259 5 nm found in  $[\text{Tb}(m\text{-MBA})_3(\text{phen})]_2 \cdot 2\text{H}_2\text{O}$ . The fact indicates that the strength of Tb-O bond is stronger while the strength of Tb-N bond is weaker in  $[\text{Tb}(p\text{-ClBA})_3(\text{phen})]_2$ , compared with  $[\text{Tb}(m\text{-MBA})_3(\text{phen})]_2 \cdot 2\text{H}_2\text{O}$ . This is possibly caused

Table 2 Selected bond lengths (nm) and bond angles (°) for complex **1**

Tb-O(6)#1	0.228 0(6)	Tb-O(3)#1	0.232 2(6)	Tb-O(4)	0.233 0(5)
Tb-O(5)	0.234 1(5)	Tb-O(1)	0.237 9(5)	Tb-O(2)	0.248 7(5)
Tb-N(2)	0.256 6(6)	Tb-N(1)	0.262 9(6)	C(13)-O(1)	0.128 9(10)
C(13)-O(2)	0.127 7(9)	C(20)-O(3)	0.123 9(9)	C(20)-O(4)	0.131 8(9)
C(27)-O(5)	0.126 5(9)	C(27)-O(6)	0.126 8(9)		
O(6)#1-Tb-O(3)#1	76.4(2)	O(6)#1-Tb-O(4)	79.3(2)	O(6)#1-Tb-O(1)	132.1(2)
O(6)#1-Tb-O(5)	124.4(2)	O(6)#1-Tb-O(2)	78.9(2)	O(6)#1-Tb-N(2)	85.7(2)
O(6)#1-Tb-N(1)	139.5(2)	O(3)#1-Tb-O(2)	74.78(19)	O(3)#1-Tb-O(4)	125.70(18)
O(3)#1-Tb-O(1)	81.04(19)	O(3)#1-Tb-O(5)	76.9(2)	O(3)#1-Tb-N(2)	143.6(2)
O(3)#1-Tb-N(1)	143.8(2)	O(4)-Tb-O(1)	145.9(2)	O(4)-Tb-O(2)	144.70(19)
O(4)-Tb-O(5)	78.3(2)	O(4)-Tb-N(2)	80.25(19)	O(4)-Tb-N(1)	70.84(18)
O(5)-Tb-N(2)	138.2(2)	O(5)-Tb-O(1)	89.7(2)	O(5)-Tb-N(1)	76.00(19)
O(5)-Tb-O(2)	136.9(2)	O(1)-Tb-O(2)	54.43(18)	O(1)-Tb-N(2)	88.31(18)
O(1)-Tb-N(1)	75.32(18)	O(2)-Tb-N(2)	70.76(19)	O(2)-Tb-N(1)	111.02(18)
N(2)-Tb-N(1)	63.13(19)	O(2)-C(13)-O(1)	120.5(7)	O(5)-C(27)-O(6)	124.5(7)
O(3)-C(20)-O(4)	124.5(7)				

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

by the electronic effect of different substituent on the benzene ring and the steric effect.

In the title complex, the C-O distances of carboxylate groups differ significantly. Coordination causes lengthening of C-O distance [average value 0.128 3 nm] for the bidentate carboxylate groups in comparison with the bidentate-bridging carboxylate groups [average distance 0.127 3 nm]. This is the same as in the ternary complex [Tb(*m*-MBA)<sub>3</sub>(phen)]<sub>2</sub> · 2H<sub>2</sub>O<sup>[19]</sup>. The O(1)-C(13)-O(2) angle in the bidentate carboxylate group is 120.5(7)°. The O(3)-C(20)-O(4) [O(5)-C(27)-O(6)] angle in the bidentate bridging carboxylate group is 124.5(7)°. The five atoms of the chelated ring containing two nitrogen atoms and terbium ion are coplanar in the dimer since the molecule of 1,10-phenanthroline is rigid.

## 2.2 Thermal decomposition

The TG and DTG curves of complex [Tb(*p*-ClBA)<sub>3</sub>(phen)]<sub>2</sub> (**1**) are shown in the Fig.2. The Tb(III) complex decomposed via intermediates to give the terbium oxide as an end product. The complex begins to decompose at 240 °C and ends at 870 °C. The TG degradation of [Tb(*p*-ClBA)<sub>3</sub>(phen)]<sub>2</sub> reveals two decomposition stages, as predicted by the DTG curve, and there are weight losses with maximum rate at 290 °C and 520 °C in the DTG curve. The first stage start from 240 °C to 385 °C, corresponding to the loss of 2 mol C<sub>12</sub>H<sub>8</sub>N<sub>2</sub>. This degradation can be explained based on the bond distances of the structure (Table 2): Tb-N distance is longer than any other bond distance, so the bond is less stable and easy to be broken down theoretically. The second stage degradation temperature

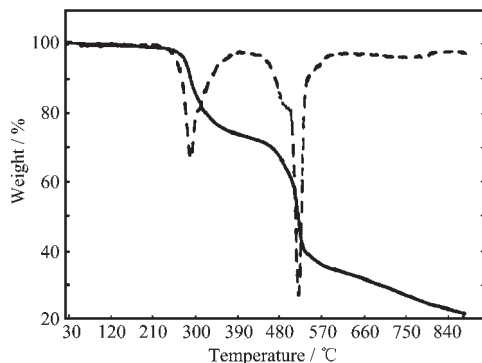


Fig.2 Thermogravimetric curves (DTG and TG) for complex [Tb(*p*-ClBA)<sub>3</sub>(phen)]<sub>2</sub> (**1**)

is in the range of 385~870 °C, which corresponds to the loss of *p*-chlorobenzoate and the forming of terbium oxide. In the end, 1,10-phenanthroline-tris(*p*-chlorobenzoate) terbium(III) was completely degraded into Tb<sub>4</sub>O<sub>7</sub> with a total loss of 76.69wt% (theoretical loss is 76.81wt%). The thermal decomposition of [Tb(*p*-ClBA)<sub>3</sub>(phen)]<sub>2</sub> can be described as follow:



## 2.3 Luminescence properties

The excitation and luminescence spectra of the title complex were recorded at room temperature and are shown in Fig.3. The excitation of complex [Tb(*p*-ClBA)<sub>3</sub>(phen)]<sub>2</sub> was effected in a range of 200~400 nm. The fluorescence was observed in a range of 400~700 nm by selective excitation at 300 nm. The emission spectrum composed of the characteristic emission peaks arising from the transition of Tb<sup>3+</sup>: <sup>5</sup>D<sub>4</sub> → <sup>7</sup>F<sub>6</sub> (490 nm), <sup>5</sup>D<sub>4</sub> → <sup>7</sup>F<sub>5</sub> (549 nm), <sup>5</sup>D<sub>4</sub> → <sup>7</sup>F<sub>4</sub> (585 nm), <sup>5</sup>D<sub>4</sub> → <sup>7</sup>F<sub>3</sub> (619 nm). The intensity of the emission band arising from the <sup>5</sup>D<sub>4</sub> → <sup>7</sup>F<sub>5</sub> transition is most intense. This is very similar to that of the complex [Tb(*m*-MBA)<sub>3</sub>(phen)]<sub>2</sub> · 2H<sub>2</sub>O<sup>[19]</sup>.

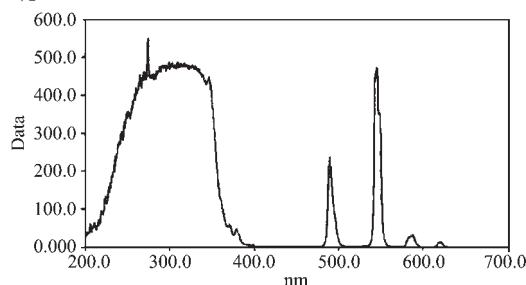


Fig.3 Excitation spectra (λ<sub>em</sub>=544 nm) and luminescence spectra (λ<sub>ex</sub>=300 nm) of complex **1**

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