

间氯苯甲酸构筑的双核铽(III)配合物的水热合成、晶体结构及荧光性质

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Hydrothermal Synthesis, Crystal Structure and Luminescent Property of Tb(III) Complex by *m*-Chlorobenzoic Acid Ligand

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Abstract: The complex $[\text{Tb}_2(\text{ClC}_6\text{H}_4\text{COO})_6(2,2'\text{-bipy})_2] \cdot (\text{ClC}_6\text{H}_4\text{COOH}) \cdot (\text{H}_2\text{O})$ with *m*-chlorobenzoic acid and 2,2'-bipyridine as ligands has been synthesized by means of hydrothermal way. Crystal data for this complex are as follows: monoclinic, space group $P\bar{1}$, $a=1.143\ 9(4)$ nm, $b=1.211\ 6(4)$ nm, $c=1.419\ 9(5)$ nm, $\alpha=103.600(6)^\circ$, $\beta=95.382(3)^\circ$, $\gamma=99.506(4)^\circ$, $V=1.868\ 4(10)$ nm³, $D_c=1.692$ g·cm⁻³, $Z=2$, $\mu(\text{Mo } K\alpha)=2.236$ mm⁻¹, $F(000)=943$, final discrepancy factors $R_1=0.052\ 0$, $wR_2=0.118\ 6$. In the crystal, two neighboring Tb(III) ions are bridged by four *m*-chlorobenzoic acid anions, and their end positions coordinate with one 2,2'-bipyridine molecule and one *m*-chlorobenzoic acid anions, respectively, giving a binuclear cage structure, of which the spacing between Tb(III)···Tb(III) is 0.408 1 nm. Each Tb(III) ion coordinates with two nitrogen atoms and six oxygen atoms, giving an eight-coordinated distorted square antiprism geometry. The luminescent property of the complex is also studied. CCDC: 761110.

Key words: terbium(III) complex; *m*-chlorobenzoic acid; hydrothermal synthesis; crystal structure; luminescent property

0 Introduction

The synthesis of rare earth complexes as electroluminescent materials with good monochromaticity and high luminescence intensity has recently become one of the hottest research subjects in the domain of rare earth chemistry^[1-4]. Through research, one fact is made clear that proper selection of organic ligands is a very critical

step toward successful synthesis of rare earth complexes. Now that aromatic carboxylic acid complexes can exhibit high thermal and photoluminescent stability in practical use, aromatic carboxylic acids are often used as ligands to construct rare earth complexes. As far as rare earth complexes with aromatic carboxylic acids are concerned, Tb(III) complexes are the focus of academic research^[5-11]. However, compared with the

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large number of literature reports about their properties, the number of reports about their determined structures is quite few^[12-19]. In order to obtain new aromatic carboxylic acid rare earth electroluminescent materials and study systematically the relationship between their structure and their luminescence property, we synthesized a novel terbium(III) complex $[\text{Tb}_2(\text{ClC}_6\text{H}_4\text{COO})_6(2,2'\text{-bipy})_2] \cdot (\text{ClC}_6\text{H}_4\text{COOH}) \cdot (\text{H}_2\text{O})$, using *m*-chlorobenzoic acid as the ligand. Herein, we report its synthesis method, crystal structure and luminescent property.

1 Experimental

1.1 Materials and instrumentation

All materials were of analytical grade and used without further purification. IR spectra were recorded on a Shimadzu FTIR-8700 instrument in the range of $400\sim 4\,000\text{ cm}^{-1}$ by using KBr discs. C, H, N analysis was performed on a PE-2400 (II) apparatus. Crystal structure determination was carried out on a Bruker SMART APEX CCD diffractometer. Excitation and luminescence spectra were performed at room temperature on a WGY-10 fluorescence spectrophotometer.

1.2 Synthesis

$\text{Tb}(\text{NO}_3)_3$ (1.0 mmol) and 2,2'-bipyridine (1.5 mmol) were dissolved in the mixed solvent of water (5 mL) and methanol (15 mL). The reaction mixture was refluxed for nearly four hours under stirring. Then *m*-chlorobenzoic acid (3.0 mmol) was added into the former solution. The resultant solution was carefully adjusted to $\text{pH}=5.5\sim 6.0$ with dilute aqueous solution of NaOH. After that, the

resultant solution was transferred to a 25 mL hydrothermal auto-clave and reacted for 48 h at $155\text{ }^\circ\text{C}$. Afterwards the system was cooled to room temperature. The resultant solution was filtered and the filtrate was kept untouched and evaporated slowly at room temperature. Colorless crystals were obtained about one week later. Yield: 45%. Anal. Calcd. for $\text{C}_{38}\text{H}_{26.50}\text{Cl}_4\text{N}_2\text{O}_{8.75}\text{Tb}$ (%): C 47.95; H 2.81; N 2.94. Found (%): C 47.90; H 2.80; N 2.93. IR (ν/cm^{-1}): 3 419.6(w), 1 635.5(vs), 1 539.1(vs), 1 506.3(s), 1 473.5(s), 1 396.3(s), 1 014.5(w), 753.8(s), 748.3(m), 736.8(m), 493.7(w), 418.5(w).

1.3 Crystal structure determination

A crystal with dimensions of $0.32\text{ mm}\times 0.20\text{ mm}\times 0.18\text{ mm}$ was put on Bruker SMART APEX CCD diffractometer equipped with a graphite-monochromatic Mo $K\alpha$ radiation ($\lambda=0.071\,070\text{ nm}$) by using $\varphi\sim\omega$ scan mode at $113(2)\text{ K}$. Of the total 23 169 reflections collected in the range of $1.76^\circ\leq\theta\leq 27.84^\circ$, 8 798 were independent with $R_{\text{int}}=0.0410$, of which 7 756 were considered to be observed ($I>2\sigma(I)$) and used in the succeeding refinement. The crystal structure was solved with direct method using SHELXS-97 program^[20]. Corrections for Lp factors and empirical adsorption adjustment were applied and all non-hydrogen atoms were refined with anisotropic thermal parameters. The final refinement including hydrogen atoms converged to $R_1=0.052\,0$, $wR_2=0.118\,6$; $w=1/[S^2(F_0^2)+(0.060\,5P)^2+1.999\,0P]$, where $P=(F_0^2+2F_c^2)/3$, $(\Delta/\sigma)_{\text{max}}=0.002$, $S=1.129$. Crystallographic data of the complex are shown in table 1.

CCDC: 761110.

Table 1 Crystallographic data of the title complex

Empirical formula	$\text{C}_{38}\text{H}_{26.50}\text{Cl}_4\text{N}_2\text{O}_{8.75}\text{Tb}$	$\gamma / (^\circ)$	99.506(4)
Formula weight	951.83	V / nm^3	1.8684(10)
Color	Colorless	$D_c / (\text{g}\cdot\text{cm}^{-3})$	1.692
Size / mm	$0.32\times 0.20\times 0.18$	Z	2
θ range for data collection / $(^\circ)$	1.76 to 27.84	$F(000)$	943
Crystal system	Triclinic	$\mu (\text{Mo } K\alpha) / \text{mm}^{-1}$	2.236
Space group	$P\bar{1}$	Reflections collected	23 169
a / nm	1.143 9(4)	Independent reflections (R_{int})	8 798 (0.041 0)
b / nm	1.211 6(4)	Final Goof	1.131
c / nm	1.419 9(5)	$R_1, wR_2 [I>2\sigma(I)]$	0.052 0, 0.118 6
$\alpha / (^\circ)$	103.600(6)	$R_1, wR_2 (\text{all data})$	0.061 1, 0.125 6
$\beta / (^\circ)$	95.382(3)	Largest difference peak and hole / $(\text{e}\cdot\text{nm}^{-3})$	1 972, -2 009

2 Results and discussion

2.1 Crystal structure analysis

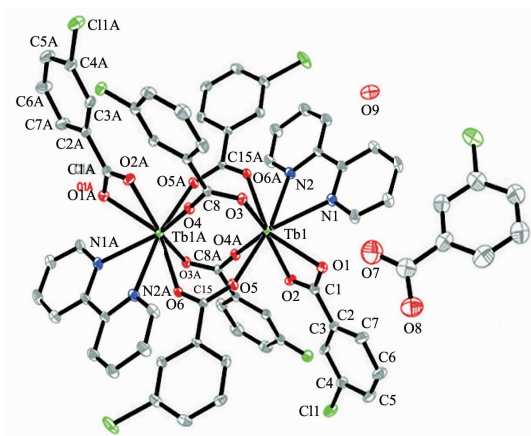
Selected bond lengths and bond angles are shown

in table 2. The crystal structure of the title complex is revealed in Fig.1 and its coordination polyhedron is shown in Fig.2.

Table 2 Selected bond lengths (nm) and bond angles (°) of the complex

Tb(1)-O(4) ⁱ	0.229 9(3)	Tb(1)-O(1)	0.245 1(4)	O(1)-C(1)	0.126 4(6)
Tb(1)-O(6) ⁱ	0.232 1(3)	Tb(1)-N(1)	0.257 1(4)	O(2)-C(1)	0.126 5(6)
Tb(1)-O(5)	0.234 9(3)	Tb(1)-N(2)	0.257 8(4)	O(3)-C(8)	0.125 8(6)
Tb(1)-O(3)	0.236 1(3)	O(4)-Tb(1) ⁱ	0.229 9(3)	O(4)-C(8)	0.127 2(6)
Tb(1)-O(2)	0.242 6(3)	O(6)-Tb(1) ⁱ	0.232 1(3)	O(5)-C(15)	0.125 7(5)
O(4) ⁱ -Tb(1)-O(6) ⁱ	80.43(12)	O(4) ⁱ -Tb(1)-O(1)	132.51(12)	O(1)-Tb(1)-N(1)	72.57(12)
O(4) ⁱ -Tb(1)-O(5)	76.51(12)	O(6) ⁱ -Tb(1)-O(1)	146.82(12)	O(4) ⁱ -Tb(1)-N(2)	82.95(13)
O(6) ⁱ -Tb(1)-O(5)	130.25(11)	O(5)-Tb(1)-O(1)	71.80(12)	O(6) ⁱ -Tb(1)-N(2)	70.33(12)
O(4) ⁱ -Tb(1)-O(3)	126.99(11)	O(3)-Tb(1)-O(1)	80.85(12)	O(5)-Tb(1)-N(2)	146.44(13)
O(6) ⁱ -Tb(1)-O(3)	80.06(12)	O(2)-Tb(1)-O(1)	53.93(12)	O(3)-Tb(1)-N(2)	133.55(12)
O(5)-Tb(1)-O(3)	79.77(12)	O(4) ⁱ -Tb(1)-N(1)	143.40(13)	O(2)-Tb(1)-N(2)	75.99(12)
O(4) ⁱ -Tb(1)-O(2)	84.83(12)	O(6) ⁱ -Tb(1)-N(1)	76.71(12)	N(1)-Tb(1)-N(2)	62.62(14)
O(6) ⁱ -Tb(1)-O(2)	144.54(12)	O(5)-Tb(1)-N(1)	139.67(13)	O(1)-C(1)-O(2)	122.0(5)
O(5)-Tb(1)-O(2)	75.97(12)	O(3)-Tb(1)-N(1)	76.49(12)	O(3)-C(8)-O(4)	122.3(4)
O(3)-Tb(1)-O(2)	133.34(12)	O(2)-Tb(1)-N(1)	97.61(12)	O(5)-C(15)-O(6)	125.5(4)

Symmetry transformation used to generate equivalent atoms: i: $-x, -y, -z+1$.



between the top plane and the bottom plane is 1.5° , which indicates that the two planes are nearly parallel to each other.

In the title complex, the Tb-O bonds formed by the oxygen atoms from the bidentate-chelating *m*-chlorobenzoic acid anions include Tb(1)-O(1)= $0.245\ 1(4)$ nm and Tb(1)-O(2)= $0.242\ 6(3)$ nm, and their average length is $0.243\ 85$ nm. Nevertheless, The Tb-O bonds formed by the bridging *m*-chlorobenzoic acid anions cover Tb(1)-O(3)= $0.236\ 1(3)$ nm and Tb(1)-O(5)= $0.234\ 9(3)$ nm, Tb(1)-O(4A)= $0.229\ 9(3)$ nm, Tb(1)-O(6A)= $0.233\ 1(3)$ nm, and their average length is $0.233\ 5(3)$ nm. It is clear that the average length of the former type of Tb-O bonds is longer than that of the latter type, suggesting the coordination ability of bridging carboxylic oxygen is stronger than that of bidentate-chelating oxygen. The bond length of Tb(1)-N(1) and Tb(1)-N(2) are $0.257\ 1(4)$ nm and $0.257\ 8(4)$ nm, respectively. The average bond length of Tb-N is $0.257\ 5$ nm. The O(1)-C(1)-O(2) angle in the bidentate-chelating *m*-chlorobenzoic acid anion is $122.0(5)^\circ$. Both O(3)-C(8)-O(4) and O(5)-C(15)-O(6) angles in the bridging *p*-methylbenzoic groups are $122.3(4)^\circ$, $125.5(4)^\circ$, respectively. The latter two are bigger than the former, which are characteristic of chelating carboxylic groups and bridging carboxylic groups. All in all, a conclusion could be drawn that the central metal is in a distorted square antiprism coordination environment.

Offset face-to-face π - π stacking interaction is found in the complex. As shown in Fig. 3, the two planes defined by adjacent intermolecular aromatic phen rings from C9 to C14 and from C9B to C14B are parallel to each other. The distance between the two planes is $0.350\ 0$ nm^[21] and the distance between the

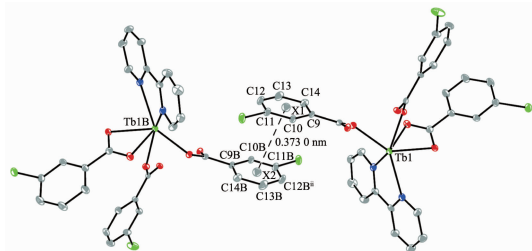


Fig.3 π - π stacking interaction of the title complex
X1 is the center of the plane defined by C9 to C14 and X2 by C9B to C14B, ⁱⁱ $1-x, -y, 1-z$

Fig.3 π - π stacking interaction of the title complex

plane centers X1 and X2 is $0.373\ 0$ nm (longer than $0.340\ 0$ nm but shorter than $0.380\ 0$ nm)^[22]. The whole structure is somewhat stabilized as a result of π - π stacking interaction.

2.2 Infrared spectrum analysis

The IR spectrum of the title complex exhibits the strong and broad band at $3\ 419.6\ \text{cm}^{-1}$, which can be assigned to the stretching vibration of uncoordinated water molecule. The strong band at $1\ 635.5\ \text{cm}^{-1}$, $1\ 539.1\ \text{cm}^{-1}$ may be assigned to coordinated carboxylic anions $\nu_{\text{as}}(\text{coo}^-)$ and the bands at $1\ 506.3\ \text{cm}^{-1}$ and $1\ 473.5\ \text{cm}^{-1}$ to coordinated carboxylic anions $\nu_{\text{s}}(\text{coo}^-)$, respectively. The $\Delta\nu [\nu_{\text{as}}(\text{coo}^-) - \nu_{\text{s}}(\text{coo}^-) = 129.2\ \text{cm}^{-1}$, $65.6\ \text{cm}^{-1}]$ is less than $200\ \text{cm}^{-1}$, which shows that there are two types of coordinated carboxylic anions: bidentate-chelating carboxylic group and bridging carboxylic group^[23]. All this is consistent with the results of the above crystal structural analysis. In addition, another absorption band at $753.8\ \text{cm}^{-1}$ can be assigned to the stretching vibration of the ligand 2,2'-bipyridine.

2.3 Luminescence property analysis

Fig.4 shows the emission spectrum of the title complex at ambient temperature recorded in the range of $480\ \text{nm}$ ~ $650\ \text{nm}$ with the best excitation wavelength of $311\ \text{nm}$. The complex displays the characteristic emission peaks at $501\ \text{nm}$, $556\ \text{nm}$, $596\ \text{nm}$ and $632\ \text{nm}$, resulted respectively from the $^5D_4 \rightarrow ^7F_6$, $^5D_4 \rightarrow ^7F_5$, $^5D_4 \rightarrow ^7F_4$ and $^5D_4 \rightarrow ^7F_3$ transition of terbium (III) ion^[24]. The intensity of the emission band arising from the $^5D_4 \rightarrow ^7F_5$ ($556\ \text{nm}$) transition is most intense.

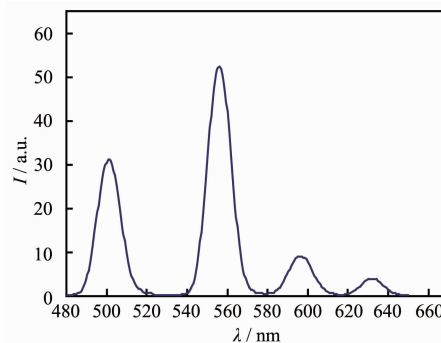


Fig.4 Emission spectra of the title complex in solid state at ambient temperature

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