

Short communication

# Synthesis, Crystal Structure and Fluorescence of an Unusual Terbium Carboxylate

Wen-Tong Chen,<sup>1,\*</sup> Zhi-Gang Luo<sup>1</sup> and Zhong-Liang Yao<sup>2</sup><sup>1</sup> Institute of Applied Chemistry, School of Chemistry and Chemical Engineering, Jinggangshan University, Ji'an, Jiangxi, 343009, China<sup>2</sup> Biology and Chemistry Engineering Department, Fuqing Branch of Fujian Normal University, Fuqing, Fujian 350300, P. R. China\* Corresponding author: E-mail: wtchen\_2000@yahoo.cn;  
Tel.: +86(796)8100490; fax +86(796)8100490

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## Abstract

A novel terbium-containing fluorescent material,  $[\text{Tb}(\text{CH}_3\text{COO})_2(\text{H}_2\text{O})_3]\text{Cl}$  (**1**), has been prepared by a facile approach, i.e. an ultrasonic synthesis. Compound **1** has been structurally characterized via single-crystal X-ray diffraction and it crystallizes in the space group  $P2_1/n$  of the monoclinic system with four formula units in a cell. Compound **1** features a novel one-dimensional (1-D) chain-like structure. The 1-D chains are interconnected by hydrogen bonds to yield a 3-D supramolecular framework. Photoluminescent investigation reveals that compound **1** displays strong emission bands identified as the characteristic emissions of  $^5D_4 \rightarrow ^7F_J$  ( $J = 3, 4, 5, 6$ ) of  $\text{Tb}^{3+}$ .

**Keywords:** Lanthanide, photoluminescence, terbium, ultrasonic synthesis, X-ray diffraction

## 1. Introduction

Lanthanide compounds have attracted increasing attention because they display ideal properties for applications in the areas of luminescent materials and probes.<sup>1–3</sup>

In particular, lanthanide carboxylates exhibit intriguing structural motifs due to the generally high coordination numbers of the lanthanide ions and to the different coordination modes of the carboxylate moieties.<sup>4</sup> Recently, a number of lanthanide carboxylates have been documented. Acetate, as the most common carboxylate, can be adopted for constructing different structures such as dimers,<sup>5</sup> polymeric chains<sup>6</sup> and layers.<sup>7</sup> We concluded that 4f-3d compounds with carboxylic acids as ligands might have diverse structures and properties, such as luminescence, magnetism, and catalysis, among others. Therefore, we recently became interested in the crystal engineering of 4f-3d compounds with carboxylic acids as ligands. Continuing our investigations of coordination chemistry of 4f-3d compounds with carboxylate ligands,<sup>8–10</sup> we obtained a lanthanide compound with both acetate and halide ligands. We now report the preparation, structural characterization and properties of a novel com-

pound  $[\text{Tb}(\text{CH}_3\text{COO})_2(\text{H}_2\text{O})_3]\text{Cl}$  (**1**) with a 1-D chain-like structure, prepared by an ultrasonic method. Several similar compounds with a formula  $[\text{M}(\text{CH}_3\text{COO})_2(\text{H}_2\text{O})_3]\text{Cl}$  ( $\text{M} = \text{Ce} - \text{Lu}, \text{Y}$ ) have previously been structurally characterized by X-ray powder diffraction<sup>11</sup> after the structures of the respective compounds with  $\text{M} = \text{Eu}$  and  $\text{Gd}$  had been determined by single-crystal X-ray diffraction.<sup>12,13</sup>

## 2. Experimental

### 2.1. Materials and Instrumentation

All reactants of analytical reagent grade were commercially obtained and used without further purification. Fluorescent measurements were conducted at room temperature on a computer-controlled JY FluoroMax-3 spectrometer. Elemental analyses of carbon and hydrogen were carried out with an Elementar Vario EL III microanalyser. Infrared spectral data were recorded on Nicolet 5DX FT-IR spectrophotometer over the frequency range of 4000–400  $\text{cm}^{-1}$  using a KBr pellet. The UV-vis absorption spectra were recorded at room temperature on a com-

puter-controlled Hewlett Packard 89090A UV-vis spectrometer with the wavelength range of 190–1100 nm.

## 2. 2. Synthesis of [Tb(CH<sub>3</sub>COO)<sub>2</sub>(H<sub>2</sub>O)<sub>3</sub>]Cl (**1**)

Tb(CH<sub>3</sub>COO)<sub>3</sub> · 4H<sub>2</sub>O (1 mmol, 408.1 mg) and CuCl<sub>2</sub> · 2H<sub>2</sub>O (1 mmol, 170.5 mg) were dissolved in 40 mL distilled water, ultrasonicated for 4 hours and filtered. The filtrate was allowed to stand at room temperature for 2 weeks and colorless crystals suitable for X-ray analysis were obtained. Yield: 22% (based on terbium). Anal. Calcd.: C, 13.10; H, 3.27. Found: C, 12.98; H, 3.34. IR peaks (KBr, cm<sup>-1</sup>): 3455(vs), 3379(vs), 3274(s), 1602(vs), 1446(s), 1386(s), 1356(w), 1054(w), 1033(w), 691(m), 630(m) and 516(m).

## 2. 3. X-ray Structure Determination

The intensity data set was collected on a Rigaku Mercury CCD X-ray diffractometer with graphite monochromated Mo-K $\alpha$  radiation ( $\lambda = 0.71073 \text{ \AA}$ ) by using an  $\omega$  scan technique. CrystalClear software was used for data reduction and empirical absorption corrections.<sup>14</sup> The structure was solved for terbium and chlorine atoms by the direct method using the Siemens SHELXTLTM Version 5 package of crystallographic software.<sup>15</sup> The remaining atoms apart from hydrogens were found in the subsequent difference electron density map. Hydrogen atoms were generated theoretically. Multi-scan3 correction has been applied to the absorption correction. The structures were refined using a full-matrix least-squares refinement on F<sup>2</sup>. All non-hydrogen atoms were refined anisotropically. Crystal data as well as details of data col-

**Table 2.** Summary of Crystallographic Data and Structure Analysis

Formula	C <sub>9</sub> H <sub>12</sub> ClO <sub>7</sub> Tb
<i>M<sub>r</sub></i>	366.51
Color	colorless
Crystal size/mm <sup>3</sup>	0.45 0.30 0.20
Crystal system	Monoclinic
Space group	<i>P</i> 2 <sub>1</sub> / <i>n</i>
<i>a</i> (Å)	7.801(2)
<i>b</i> (Å)	7.855(2)
<i>c</i> (Å)	17.413(4)
$\beta$ (°)	98.062(2)
<i>V</i> (Å <sup>3</sup> )	1056.5(4)
<i>Z</i>	4
$2\theta_{\text{max}}$	50
Reflections collected	6584
Independent, observed reflections ( <i>R</i> <sub>int</sub> )	1861, 1716 (0.0418)
<i>d</i> <sub>calcd.</sub> (g/cm <sup>3</sup> )	2.304
$\mu$ /mm <sup>-1</sup>	6.951
<i>T</i> /K	123
<i>F</i> (000)	696
<i>R</i> 1, <i>wR</i> 2	0.0232, 0.0552
<i>S</i>	1.077
Largest and mean $\Delta f/\sigma$	0.001, 0
$\Delta$ (max, min) (e/Å <sup>3</sup> )	1.049, -0.946

lection and refinement for **1** are summarized in Table 2. Selected bonded lengths and angles are shown in Table 1.

## 3. Results and Discussion

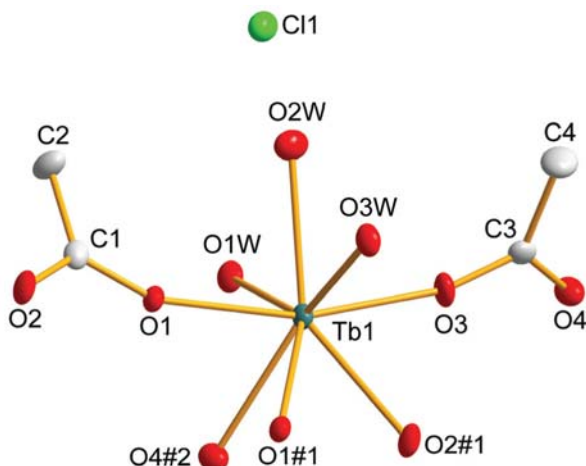
In contrast to traditional solution methods or hydro/solvothermal reactions, compound **1** was synthe-

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

Bond Lengths (Å)			
Tb(1)-O(1)	2.318(3)	O(3)-Tb(1)-O(1)	164.3(1)
Tb(1)-O(3)	2.286(3)	O(3)-Tb(1)-O(1W)	85.15(9)
Tb(1)-O(1W)	2.380(3)	O(1)-Tb(1)-O(1W)	88.21(9)
Tb(1)-O(2W)	2.413(3)	O(3)-Tb(1)-O(3W)	89.24(9)
Tb(1)-O(3W)	2.410(3)	O(1)-Tb(1)-O(3W)	86.82(9)
Tb(1)-O(1)#2	2.616(3)	O(1W)-Tb(1)-O(3W)	140.3(1)
Tb(1)-O(2)#2	2.433(3)	O(3)-Tb(1)-O(4)#1	117.37(9)
Tb(1)-O(4)#1	2.412(3)	O(1)-Tb(1)-O(4)#1	74.38(9)
		O(1W)-Tb(1)-O(4)#1	75.47(9)
Bond Angles (°)		O(3W)-Tb(1)-O(4)#1	139.7(1)
O(1W)-Tb(1)-O(1)#2	141.21(9)	O(3)-Tb(1)-O(2W)	81.0(1)
O(3W)-Tb(1)-O(1)#2	70.63(9)	O(1)-Tb(1)-O(2W)	83.4(1)
O(2)#2-Tb(1)-O(1)#2	51.21(9)	O(4)#1-Tb(1)-O(2W)	138.4(1)
O(3)-Tb(1)-O(3)#1	68.7(1)	O(3)-Tb(1)-O(2)#2	75.5(1)
O(1W)-Tb(1)-O(3)#1	68.77(9)	O(1W)-Tb(1)-O(2)#2	136.59(9)
O(3W)-Tb(1)-O(3)#1	143.51(8)	O(3W)-Tb(1)-O(2)#2	78.69(9)
O(4)#1-Tb(1)-O(3)#1	48.67(8)	O(4)#1-Tb(1)-O(2)#2	79.6(1)
O(2W)-Tb(1)-O(3)#1	129.30(9)	O(2W)-Tb(1)-O(2)#2	141.9(1)
O(1)#2-Tb(1)-O(3)#1	98.03(9)	O(1)-Tb(1)-O(1)#2	67.4(1)

Symmetry codes: #1 -*x*, -*y*+2, -*z*; #2 -*x*+1, -*y*+2, -*z*.

sized via an ultrasonic reaction method.<sup>16–18</sup> Ultrasonic irradiation shows some advantages compared with conventional methods in the preparation of inorganic or organic compounds. These include mild reaction and easy operation, as well as enhanced reaction rates and shorter reaction times.

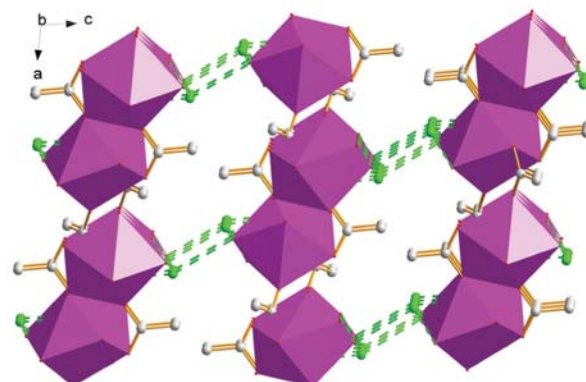


**Fig. 1:** An ORTEP drawing of **1** with 50% thermal ellipsoids. Hydrogen atoms were omitted for clarity. Symmetry codes: #1  $-x, -y+2, -z$ ; #2  $-x+1, -y+2, -z$ .

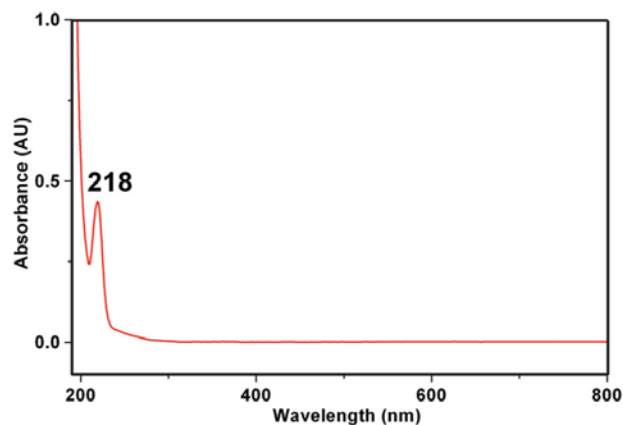
X-ray diffraction analysis shows that the structure of **1** is comprised of 1-D  $[\text{Tb}(\text{CH}_3\text{COO})_2(\text{H}_2\text{O})_3]_n^{n+}$  cationic chains and chloride anions. All the crystallographically independent atoms are in conventional locations. There are two crystallographically unique acetate anions; both are bidentate ligands. As shown in Fig. 1, the terbium ion is bound by eight oxygen atoms, among which three are from coordinating water molecules and five are from acetate ligands, yielding a distorted square anti-prism of  $\text{TbO}_8$  with the top and bottom planes defined by O(2W), O(3W), O(1)( $-x, -y+2, -z$ ), O(1) and O(1W), O(4)( $-x+1, -y+2, -z$ ), O(2)( $-x, -y+2, -z$ ), O(3) atoms, respectively. The bond lengths of  $\text{Tb}-\text{O}_{\text{acetate}}$  range from 2.286(3) Å to 2.616(3) Å with a mean value 2.413(3) Å, which is normal and comparable with that reported.<sup>19</sup> The bond lengths of  $\text{Tb}-\text{O}_{\text{water}}$  are from 2.380(3) Å to 2.413(3) Å. For the carboxyl groups, the bond lengths of O(1)-C(1), O(2)-C(1), O(3)-C(3), O(4)-C(3) are similar, with the values being of 1.282(5), 1.257(5), 1.269(5), 1.265(5) Å, respectively, suggesting that delocalization of the  $\text{COO}^-$  groups. Every two  $\text{TbO}_8$  moieties are connected to each other, yielding a edge-shared dimer with the  $\text{Tb}\cdots\text{Tb}$  distance of *ca.* 4.107 Å. The dimers are further bridged via acetate groups to give a 1-D infinite chain running along the *a*-axis, with the  $\text{Tb}\cdots\text{Tb}$  distance being of *ca.* 4.234 Å, as shown in Fig. 2. The chains are interlinked by hydrogen bonds between chloride ions and water molecules to form a 3-D supramolecular framework, as shown in Fig. 3. It is noteworthy that compound **1** is the first example of ter-



**Fig. 2:** 1-D chain-like structure of **1** with the polyhedra representing  $\text{TbO}_8$  moieties



**Fig. 3:** Packing diagram of **1** with the dashed lines representing hydrogen bonds (Å): O1W $\cdots$ Cl1 3.063(3), O2W $\cdots$ Cl1( $x, -1+y, z$ ) 3.052(3), O2W $\cdots$ Cl1( $1/2-x, -1/2+y, 1/2-z$ ) 3.190(3), and O3W $\cdots$ Cl1( $x, -1+y, z$ ) 3.116(3). Polyhedra:  $\text{TbO}_8$  moieties.



**Fig. 4:** UV-vis absorption spectrum measured in distilled water at room temperature.

bium-acetate-halide compounds with an extended structure, although several terbium-acetate-halide compounds with an isolated structure have been reported.<sup>20–23</sup>

Fig. 4 displays the UV-vis absorption spectrum for compound **1**. It is clear that compound **1** has one absorption band locating at 218 nm.

Taking into account the excellent luminescent property of  $\text{Tb}^{3+}$  ions, the luminescent spectra of **1** were studied under room temperature (Fig. 5). As shown in Fig. 5, the emission spectrum of **1** shows sharp, narrow and well-separated emission bands. The excitation

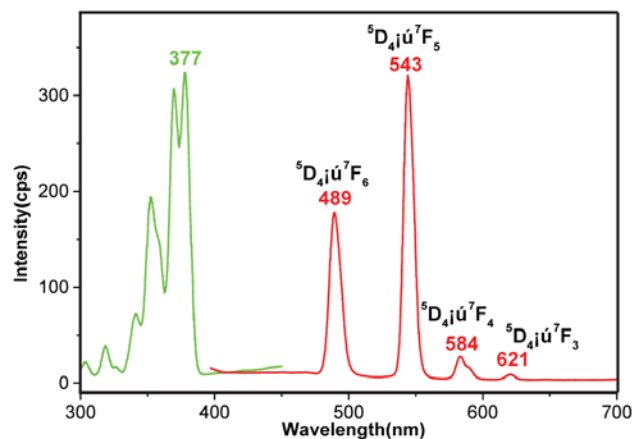


Fig. 5: Fluorescence spectra with green and red lines representing excitation and emission spectra respectively.

spectrum of **1** confirms that the effective energy absorption is mainly found in the ultraviolet region of 350–380 nm. The excitation bands under 543 nm have several peaks, 318, 340, 352, 369 and 377 nm, respectively. The emission spectrum exhibits four emission bands upon excitation at 377 nm: 489, 543, 584 and 621 nm, corresponding to the characteristic emission  ${}^5D_4 \rightarrow {}^7F_J$  transitions ( $J = 6, 5, 4$  and  $3$ , respectively) of  $Tb^{3+}$  ions.<sup>24,25</sup> This suggests that efficient energy transfer takes place and that a conjugated system is formed between the acetate ligand and the chelated terbium ion in **1**. The intensity of the green luminescence of  ${}^5D_4 \rightarrow {}^7F_5$  transition is the strongest among the emission  ${}^5D_4 \rightarrow {}^7F_J$  transitions ( $J = 6, 5, 4$  and  $3$ ).

## 4. Conclusions

In conclusion, we have prepared a terbium compound via an ultrasonic synthetic method. The crystal structure of the title compound is characterized by a 1-D chain-like structure constructed from edge-shared dimers bridged by acetate groups. The title compound displays intense emissions that are ascribed to the characteristic emissions of  ${}^5D_4 \rightarrow {}^7F_J$  ( $J = 3, 4, 5, 6$ ) of terbium ions. We anticipate that the title compound can be used as a green-light luminescent material in display and other imaging applications.

## 5. Acknowledgements

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## 6. Supplementary Material

Crystallographic data for the structure reported in this paper have been deposited with the Cambridge Crystallographic Data Centre as supplementary publication no. CCDC 840269. Copies of the data can be obtained free of charge on application to CCDC, 12 Union Road, Cambridge CB2 1EZ, UK (fax: (44) 1223 336-033; e-mail: deposit@ccdc.cam.ac.uk).

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## Povzetek

Z ultrasonično sintezo smo pripravili nov terbij vsebujoč fluorescentni material,  $[\text{Tb}(\text{CH}_3\text{COO})_2(\text{H}_2\text{O})_3]\text{Cl}$  (**1**). Koordinacijski spojini **1** smo z rentgensko strukturno analizo določili kristalno strukturo. Spojina kristalizira v monoklinski prostorski skupini  $P21/n$  s štirimi formulskimi enotami v osnovni celici. Ima karakteristično enodimenzionalno (1-D) strukturo. 1-D verige so z vodikovimi vezmi povezane v 3-D supramolekularno ogrodje. V emisijskem spektru spojine **1** so prisotni štiri močni trakovi, ki so posledica značilnih emisijskih  ${}^5\text{D}_4 \rightarrow {}^7\text{F}_j$  prehodov ( $J = 6, 5, 4$  in  $3$ ) terbijevih(3+) ionov.