

Luminescent Lanthanide-titanium-organic Compound Constructed by Tetra-nuclear Ln-Ti Building Units and Diphenylglycolic Acid^①

CHEN Zi-Bin CHEN Bing-Ben CHENG Jian-Wen^②

(Key Laboratory of the Ministry of Education for Advanced Catalysis Materials, Institute of Physical Chemistry, Zhejiang Normal University, Jinhua, Zhejiang 321004, China)

ABSTRACT Under solvothermal conditions with the mixed solvents of C₂H₅OH and H₂O, a new heterometallic lanthanide-titanium-organic compound, [TbTi(μ₃-O)(L₃)(H₂O)₄] H₃O (**1**, H₂L = diphenylglycolic acid), has been synthesized. Compound **1** exhibits a 3D supramolecular framework by incorporating the tetra-nuclear [Tb₂Ti₂(μ₃-O)₂] unit and L²⁻ ligand. Compound **1** shows intense green luminescence. Furthermore, the PXRD, TGA and IR spectra were also studied.

Keywords: lanthanide, titanium, cluster, luminescence; DOI: 10.14102/j.cnki.0254-5861.2011-2805

1 INTRODUCTION

The synthesis and characterization of heterometallic lanthanide-transition-metal (Ln-TM) clusters attract intense interest not only for the architectural beauty of their structures, but also for their applications as functional materials, including magnetism, and luminescence^[1-6]. To generate target heterometallic coordination metal cluster, a judicious choice of ligands provides a way of self-assembly of polynuclear Ln-TM-oxo/hydroxo complexes. To date, a great variety of nanosized Ln-Co, Ln-Mn, Ln-Cd, Ln-Fe, Ln-Cu and Ln-Ni clusters of various nuclearities and topologies have been reported^[7-9].

For example, the Wu group reported a series of high-nuclearity Ln-Cu clusters by using flexible amino acids as ligands^[10-12], polynuclear fan-shaped [Gd₆Cu₁₂] amino acid cluster shows a “hollow” [Gd₆(μ₃-OH)₈] octahedral core encapsulated by six [Cu₂] glycinato blade fragments, and exhibits unique molecular ferromagnetism^[12]. By using induced aggregation and synergistic coordination strategy, Yang and coworkers reported a series of Ln-Cu cluster organic architectures by using rigid ligands^[13-15]. The linkages between the high-nuclearity hydroxo lanthanide cluster [Ln₁₄(μ₆-O)(μ₃-OH)₂₀(H₂O)₈]²⁰⁺ cores and two different types of copper centers through isonicotinic acid give rise to an unprecedented 3D cluster organic framework^[13]. In addition,

Long and coworkers prepared a family of fullerene-like molecular Ln-Ni clusters, and these high-nuclearity Ln-TM clusters may act as potential molecular magnetic coolers^[16-18].

Polyoxo-titanium clusters are one of the most prosperous classes of cluster-based materials. Zhang and coworkers systematically investigated this system and prepared a large number of crystalline polyoxo-titanium clusters materials with various nuclearities and diverse structural types^[19]. The incorporation of lanthanide ions and polyoxo-titanium clusters into the same framework leads to new types of heterometallic Ln-Ti clusters^[20-23]. For example, Kong and Long groups obtained three heterometallic Ln-Ti oxo clusters (Eu₂Ti₄, Eu₅Ti₄ and Eu₈Ti₁₀) using 4-tert-butylbenzoate ligand. These compounds can act as luminescent molecular thermometers with high quantum yields^[20a]. In addition, they reported three 18-metal-ion Ln₈Ti₁₀ clusters that exhibit efficient photo-electrochemical water oxidation^[20b]. To date, the highest nuclearity Ln-Ti oxo cluster is [Eu₂₄Ti₈], which exhibits a wheel-like structure with diameter of 4.1 nm^[20c].

Diphenylglycolic acid is a multidentate ligand containing -OH and -COOH donor groups, which can provide flexible, multifunctional coordination sites and generate various interesting metal clusters. For example, Zheng and coworkers reported a giant [Ni₂₁Gd₂₀] cage by using diphenylglycolic acid as ligand in 2018^[24]. In this work, we report the systematic syntheses, structure and luminescent properties of

Received 16 March 2020; accepted 18 May 20 (CCDC 1990433)

① Supported by the NNSF of China (21975224)

② Corresponding author. E-mail: jwcheng@zjnu.cn

a new heterometallic lanthanide-titanium-organic compound, namely, $[\text{TbTi}(\mu_3\text{-O})(\text{L}_3)(\text{H}_2\text{O})_4] \text{H}_3\text{O}$ (**1**, H_2L = diphenylglycolic acid) under solvothermal conditions. Compound **1** contains tetra-nuclear Ln–Ti building units and diphenylglycolic acid.

2 EXPERIMENTAL

2.1 Materials and measurements

All chemicals were purchased commercially and used without further purification. Powder X-ray diffraction (PXRD) data were obtained by placing the picked crystals onto the flat sample holders using a Philips PW3040/60 diffractometer with $\text{CuK}\alpha$ radiation ($\lambda = 1.54056 \text{ \AA}$). The Fourier transform infrared (FT-IR) spectra (KBr pellets) were recorded on a Nicolet NEXUS670 spectrometer. Thermogravimetric analyses (TGA) were performed on a Netzsch STA 449C analyzer at a heating rate of $10 \text{ }^\circ\text{C}/\text{min}$ under an air atmosphere. Photoluminescence analyses were performed on an Edinburgh Instrument FLS920 fluorescence spectrometer.

2.2 Synthesis

Synthesis of $[\text{TbTi}(\mu_3\text{-O})(\text{L}_3)(\text{H}_2\text{O})_4] \text{H}_3\text{O}$ (**1**) A mixture of $\text{Tb}(\text{NO}_3)_3 \cdot 5\text{H}_2\text{O}$ (1 mmol, 0.44 g), TiOSO_4 (0.5 mmol, 0.08 g), diphenylglycolic acid (1 mmol, 0.23 g), and NaBr (1 mmol, 0.10 g) was added to the mixed solvents of

$\text{C}_2\text{H}_5\text{OH}$ (6 mL) and H_2O (3 mL). The resulting mixture was stirred and slowly added with NaOH (pHs = 4~5), and sealed in a 30 mL Teflon-lined stainless-steel autoclave, heated at $100 \text{ }^\circ\text{C}$ for 6 days, and then cooled to room temperature, obtaining colorless block crystals of **1** (30% yield based on Ti). IR bands (cm^{-1}) for **1**: 3173 (vs), 2976 (w), 2920 (w), 2779(w), 2660 (w), 2554 (w), 1596 (vs), 1476 (m), 1434 (m), 1399 (m), 1357 (w), 1322 (m), 1266 (s), 1061 (s), 927 (m), 653 (m) (Fig. S1). The experimental powder X-ray diffraction (PXRD) patterns of compound **1** match well with the simulated PXRD pattern, and the difference in reflection intensities between the simulated and experimental patterns was due to the variation in the preferred orientation of the powder sample during collecting the experimental PXRD data (Fig. S2).

2.3 Crystal structure determination

The intensity data were collected on a Bruker APEX II with graphite-monochromatic $\text{Mo-K}\alpha$ radiation ($\lambda = 0.71073 \text{ \AA}$) at room temperature. All absorption corrections were performed using the multi-scan program. The structure was solved by direct methods and refined by full-matrix least-squares on F^2 with SHELXS-97 and SHELXL-97 programs^[25]. All atoms except H were refined anisotropically. Selected bond lengths of compound **1** are listed in Table 1.

Table 1. Selected Bond Lengths (\AA) for **1**

Bond	Dist.	Bond	Dist.
Tb–O(6)	2.433(4)	Tb–O(9)	2.605(3)
Tb–O(10)#1	2.447(3)	Ti–O(1)	1.884(3)
Tb–O(4W)	2.464(4)	Ti–O(2)	2.089(3)
Tb–O(4)	2.474(3)	Ti–O(7)	1.884(3)
Tb–O(2W)	2.480(4)	Ti–O(9)	2.104(3)
Tb–O(5W)	2.482(4)	Ti–O(10)	1.827(3)
Tb–O(3W)	2.561(5)	Ti–O(10)#1	2.001(3)
Tb–O(2)	2.603(3)		

Symmetry code for **1**: (#1) $-x-1/2, -y+1/2, -z+1$

3 RESULTS AND DISCUSSION

3.1 Crystal structure of the title complex

Structure of $[\text{TbTi}(\mu_3\text{-O})(\text{L}_3)(\text{H}_2\text{O})_4] \text{H}_3\text{O}$ (**1**) Single-crystal X-ray analysis reveals that compound **1** crystallizes in the monoclinic space group $C2/c$ ^[26]. The asymmetric unit of **1** contains one Tb^{3+} ion, one Ti^{4+} , three L^{2-} ligands, one $\mu_3\text{-O}$, and five water molecules. The Tb^{3+} ion is nine-coordinated with a tri-capped trigonal-prism coordination environment: one $\mu_3\text{-O}$, four water molecules, and four oxygen atoms (O)

from three L^{2-} ligands. The Ti^{4+} ion is six-coordinated with a distorted octahedral coordination environment: two $\mu_3\text{-O}$ and four O atoms from two L^{2-} ligands. The L^{2-} ligands show two types of coordination modes (Fig. S3). The Tb–O distances range from 2.433(4) to 2.605(3) \AA , and the Ti–O distances vary from 1.827(3) to 2.104(3) \AA (Table 1), which are similar to the reported results^[17, 20]. Two Tb^{3+} and two Ti^{4+} ions are linked by two $\mu_3\text{-O}$ ions to form a tetra-nuclear $[\text{Tb}_2\text{Ti}_2(\mu_3\text{-O})_2]$ cluster core (Fig. 1a) surrounded by six L^{2-} ligands (Fig. 1b).

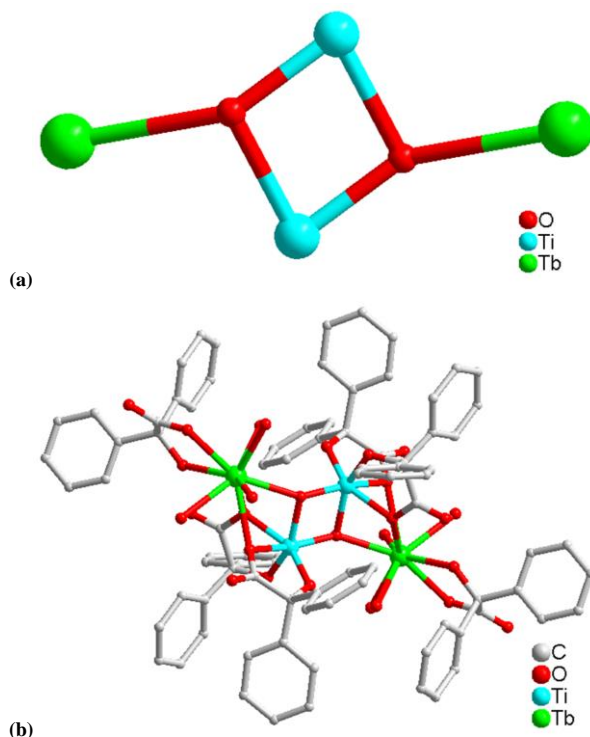


Fig. 1. (a) Tetra-nuclear $[\text{Tb}_2\text{Ti}_2(\mu_3\text{-O})_2]$ cluster core in **1**. (b) Coordination environment of $[\text{Tb}_2\text{Ti}_2(\mu_3\text{-O})_2]$ cluster core in **1**

3.2 Physical characterization

The thermal behavior of **1** was examined by thermogravimetric analyses (TGA) analysis in a dry air atmosphere from 25 to 800 °C. The TGA study of **1** showed that the first weight loss below 190 °C corresponds to removal of lattice-water and coordinated water molecules (Calcd./found: 9.1/8.4%) and the second weight loss between 190 and 800 °C is attributable to the loss of all organic ligands (Fig. S4). Compound **1** yields

intense green luminescence when excited at 270 nm. Four emission bands at 491, 547, 587 and 620 nm correspond to the characteristic $^5\text{D}_4 \rightarrow ^7\text{F}_J$ ($J = 6, 5, 4$, and 3) transition of the Tb^{3+} ion (Fig. 2). The absence of any ligand fluorescence in the emission spectra of **1** indicates that the intramolecular energy transfer from the coordinated ligand to the Tb^{3+} ions is efficient. The decay lifetime of compound **1** is 0.74 ms.

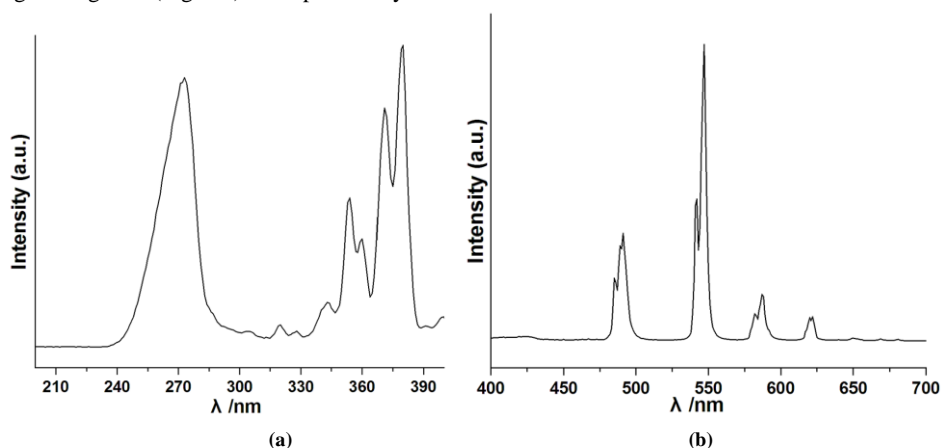


Fig. 2. Excitation (a) and emission (b) spectra of **1** in the solid state at room temperature

4 CONCLUSION

In summary, we have successfully obtained a heterometallic lanthanide-titanium-organic compound consisting of tetra-nuclear unit and the L^{2-} ligand under solvothermal conditions.

Compound **1** displays intense green luminescence. Our studies indicate that heterometallic lanthanide-titanium clusters can be obtained by using multidentate ligand containing both -OH and -COOH donor groups. Further work on this subject is still in progress.

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