



Research paper

Syntheses, structures, photoluminescence, and magnetism of a series of discrete heavy lanthanide complexes based on a tricarboxylic acid



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ABSTRACT

Seven heavy lanthanide tricarboxylate complexes, $[\text{Ln}_2(\text{TCT})_2(\text{H}_2\text{O})_6] \cdot 6\text{H}_2\text{O}$ [$\text{Ln} = \text{Tb}$ (**1**), Dy (**2**), Ho (**3**), Er (**4**), Tm (**5**), Yb (**6**), and Lu (**7**)], $\text{H}_3\text{TCT} = 2,4,6\text{-tri}(\text{carboxymethylmercapto})\text{-1,3,5-triazine}$ acid], were successfully synthesized and characterized by single-crystal X-ray diffraction, elemental analysis, IR, powder X-ray diffraction (PXRD), thermogravimetric analysis (TGA), and differential thermoanalysis (DTA). Complexes **1–7** possess a discrete dinuclear structure. The adjacent dinuclear molecules are extended into a three-dimensional (3D) supramolecular architecture by the hydrogen bonding and $\pi\text{-}\pi$ interactions. Complexes **1** and **2** show the characteristic fluorescent emissions of Tb^{III} and Dy^{III} , respectively, and complex **6** displays a near-infrared (NIR) emission of Yb^{III} . Complex **2** also exhibits a field-induced slow magnetic relaxation behavior.

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1. Introduction

Single-molecule magnets (SMMs) have attracted considerable attention over the past two decades. Such works were motivated by a discrete Mn_{12} cluster complex exhibiting a slow magnetic relaxation below the blocking temperature [1]. Following this first example, a large number of discrete transition metal cluster complexes have been prepared for investigation of their SMM behaviors [2]. It is well-known that SMMs generally possess a large spin ground state and a large uniaxial magnetic anisotropy. Due to their large magnetic anisotropy deriving from the unquenched orbital angular momentum, the lanthanide ions have been widely employed to construct discrete complexes with SMM behaviors. The SMM behaviors of such discrete lanthanide complexes are governed by the ligand field, coordination geometry, and magnetic interactions between the lanthanide ions [3,4]. Therefore, the organic ligands play an important role in constructing the lanthanide SMMs. Several types of multidentate ligands such as oxime-like, hydrazine-like, Schiff-base-like, and β -diketone-like compounds have been successfully utilized in the construction of lanthanide SMMs [5].

In contrast to the above-mentioned multidentate ligands, the carboxylic-acid-like compounds have rarely been used for the preparation of lanthanide SMMs [6,7], which may be attributed to the fact that only monocarboxylates with steric hindrance can

coordinate with the lanthanide ions to form discrete complexes, whereas most of multicarboxylates facilitate the formation of high-dimensional lanthanide complexes [8,9]. In this work, we selected a tricarboxylic acid H_3TCT [2,4,6-tri(carboxymethylmercapto)-1,3,5-triazine acid] as a bridging ligand, and constructed a series of discrete heavy lanthanide tricarboxylate complexes $[\text{Ln}_2(\text{TCT})_2(\text{H}_2\text{O})_6] \cdot 6\text{H}_2\text{O}$ [$\text{Ln} = \text{Tb}$ (**1**), Dy (**2**), Ho (**3**), Er (**4**), Tm (**5**), Yb (**6**), and Lu (**7**)]. This work provides an example of discrete lanthanide multicarboxylate complexes. The H_3TCT ligand has been used in the previous work. Bai and Xie and their co-workers reported a series of TCT-based lanthanide complexes with three structural types from zero-dimensional (0D) dimer unit to 3D framework [10,11]. It has been found that discrete complexes involving the highly anisotropic Dy^{III} ion generally exhibit SMM behaviors [12]. Therefore, the magnetic properties of **2** were investigated. In addition, lanthanide complexes have attracted extensive attention due to their fascinating luminescent properties [13,14]. Thus, the photoluminescent properties of **1–6** were also studied.

2. Experimental

2.1. Materials and methods

All reagents except $\text{LnCl}_3 \cdot n\text{H}_2\text{O}$ and H_3TCT were commercially available and were used without further purification. $\text{LnCl}_3 \cdot n\text{H}_2\text{O}$ were prepared by the reactions of Ln_2O_3 and hydrochloric acid in aqueous solution. H_3TCT was synthesized according to a literature procedure [10]. Elemental analyses (C, H, and N) were performed

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on a Perkin-Elmer 2400 CHN elemental analyzer. IR data were collected on a Magna FT-IR 560 spectrometer using KBr plate. Powder X-ray diffraction (PXRD) data were collected on a Bruker AXS D8-Advanced diffractometer with Cu K α ($\lambda = 1.5406 \text{ \AA}$) radiation. Thermogravimetric analyses (TGA) and differential thermoanalyses (DTA) were simultaneously performed on a Pyris-Diamond thermal analyzer in the temperature range of 30–800 °C at a heating rate of 10 °C min⁻¹ under a flowing N₂ atmosphere. Photoluminescence measurements were performed on an FLS 920 Combined Steady State Fluorescence and Phosphorescence Lifetime spectrometer. Magnetic measurements were performed on a Quantum Design MPMS XL-7 SQUID-VSM magnetometer. Pascal's constants were used to determine the diamagnetic corrections.

2.2. Syntheses of 1–7

A methanol (10 mL) solution of H₃TCT (0.035 g, 0.1 mmol) and NaOH (0.012 g, 0.3 mmol) was slowly diffused into a water (10 mL) solution of LnCl₃·*n*H₂O (Ln = Tb, Dy, Ho, Er, Tm, Yb, or Lu, 0.1 mmol) in a test tube. Light pink block crystals of **4** and white block crystals of **1–3** and **5–7** were obtained in two weeks. The crystalline products were collected, washed with water, and dried in air. Yield: 75–85%. Elem. Anal. Calcd. for **1**: C, 17.57; H, 2.95; N, 6.83. Found: C, 17.32; H, 2.89; N, 6.79%. Calcd. for **2**: C, 17.46; H, 2.93; N, 6.79. Found: C, 17.62; H, 2.89; N, 6.80%. Calcd. for **3**: C, 17.40; H, 2.92; N, 6.76. Found: C, 17.26; H, 2.86; N, 6.79%. Calcd. for **4**: C, 17.33; H, 2.91; N, 6.74. Found: C, 17.04; H, 2.92; N, 6.79%. Calcd. for **5**: C, 17.28; H, 2.90; N, 6.72. Found: C, 17.04; H, 2.86; N, 6.81%. Calcd. for **6**: C, 17.17; H, 2.88; N, 6.68. Found: C, 16.98; H, 2.86; N, 6.79%. Calcd. for **7**: C, 17.12; H, 2.87; N, 6.65. Found: C, 17.18; H, 2.86; N, 6.69%. IR (KBr, cm⁻¹) for **1**: 3497 (m), 3354 (m), 3179 (m), 2970 (w), 2924 (w), 2360 (w), 1570 (s), 1479 (s), 1429 (s), 1371 (m), 1278 (m), 1234 (s), 941 (w), 900 (w), 845 (m), 785 (w), 700 (m), 582 (w). For **2**: 3497 (m), 3348 (m), 3179 (m), 2972 (w), 2924 (w), 2362 (w), 1570 (s), 1480 (s), 1428 (s), 1369 (m), 1278 (m), 1233 (s), 942 (w), 896 (w), 844 (m), 786 (w), 701 (m), 578 (w). For **3**: 3495 (m), 3356 (m), 3179 (m), 2972 (w), 2924 (w), 2366 (w), 1570 (s), 1479 (s), 1431 (s), 1373 (m), 1278 (m), 1234 (s), 943 (w), 900 (w), 847 (m), 785 (w), 702 (m), 580 (w). For **4**: 3495 (m), 3348 (m), 3179 (m), 2974 (w), 2924 (w), 2363 (w), 1571 (s), 1479 (s), 1431 (s), 1373 (m), 1278 (m), 1234 (s), 943 (w), 900 (w), 847 (m), 785 (w), 704 (m), 582 (w). For **5**: 3495 (m), 3348 (m), 3179 (m), 2974 (w), 2924 (w), 2361 (w), 1575 (s), 1479 (s), 1431 (s), 1372 (m), 1278 (m), 1234 (s), 943 (w), 898 (w), 847 (m), 785 (w), 704 (m), 582 (w). For **6**: 3497 (m), 3348 (m), 3179 (m), 2974 (w), 2926 (w), 2363 (m), 1575 (s), 1479 (s), 1433 (s), 1373 (m), 1278 (m), 1234 (s), 943 (w), 898 (w), 847 (m), 784 (w), 704 (m), 582 (w). For **7**: 3502 (m), 3349 (m), 3179 (m), 2974 (w), 2926 (w), 2361 (m), 1576 (s), 1477 (s), 1435 (s), 1373 (m), 1278 (m), 1234 (s), 943 (w), 896 (w), 847 (m), 783 (w), 705 (m), 581 (w).

2.3. X-ray crystallography

X-ray single-crystal diffraction data for **1**, **3**, **5**, and **7** were collected on a Bruker Smart APEX II diffractometer with Mo K α ($\lambda = 0.71073 \text{ \AA}$) radiation. The structures were solved by direct methods and refined by the full-matrix least-squares methods on F^2 using the SHELXTL package [15]. All non-hydrogen atoms were refined with anisotropic temperature parameters. Pertinent crystal data and refinement parameters for **1**, **3**, **5**, and **7** are summarized in Table 1. Selected bond lengths for **1**, **3**, **5**, and **7** are given in Table S1. CCDC 1448562, 1448564, 1448566, and 1448568 contain the supplementary crystallographic data for **1**, **3**, **5**, and **7**. These data can be obtained free of charge from The Cambridge Crystallographic Data Centre via www.ccdc.cam.ac.uk/data_request/cif.

Table 1
Crystal data and refinement parameters for **1**, **3**, **5**, and **7**.

	1	3	5	7
Formula	C ₁₈ H ₃₆ N ₆ O ₂₄ S ₆ Tb ₂	C ₁₈ H ₃₆ N ₆ O ₂₄ S ₆ Ho ₂	C ₁₈ H ₃₆ N ₆ O ₂₄ S ₆ Tm ₂	C ₁₈ H ₃₆ N ₆ O ₂₄ S ₆ Lu ₂
Formula weight	1230.73	1242.75	1250.75	1262.83
Crystal system	Triclinic	Triclinic	Triclinic	Triclinic
Space group	<i>P</i> $\bar{1}$	<i>P</i> $\bar{1}$	<i>P</i> $\bar{1}$	<i>P</i> $\bar{1}$
<i>a</i> (Å)	8.5865(5)	8.5745(6)	8.5522(5)	8.5375(7)
<i>b</i> (Å)	10.9281(6)	10.8916(8)	10.8668(6)	10.8452(8)
<i>c</i> (Å)	11.0008(6)	10.9738(8)	10.9483(6)	10.9202(8)
α (°)	70.1510(10)	70.2850(10)	70.3350(10)	70.3870(10)
β (°)	86.0820(10)	86.1130(10)	86.1360(10)	86.1700(10)
γ (°)	79.8920(10)	79.7870(10)	79.6990(10)	79.6470(10)
<i>V</i> (Å ³)	955.81(9)	949.45(12)	942.67(9)	936.92(12)
<i>Z</i>	1	1	1	1
<i>D</i> _{calcd.} 2.238	(g cm ⁻³)	2.138	2.174	2.203
μ (mm ⁻¹)	4.093	4.563	5.105	5.670
<i>F</i> (0 0 0)	604	608	612	616
<i>R</i> _{int}	0.0108	0.0145	0.0168	0.0148
<i>R</i> ₁ ^a [<i>I</i> > 2 σ (<i>I</i>)]	0.0178	0.0224	0.0223	0.0190
<i>wR</i> ₂ ^b (all data)	0.0468	0.0550	0.0526	0.0511
GOF	1.055	1.033	1.047	1.070

^a $R_1 = \sum ||F_o| - |F_c|| / \sum |F_o|$.

^b $wR_2 = [\sum w(F_o^2 - F_c^2)^2 / \sum w(F_o^2)]^{1/2}$.

3. Results and discussion

3.1. Syntheses

In this work, the solution diffusion reactions of Na₃TCT and LnCl₃·*n*H₂O (Ln = Tb, Dy, Ho, Er, Tm, Yb, or Lu) yielded a series of dinuclear heavy lanthanide carboxylate complexes **1–7**. It is worth mentioning that such discrete lanthanide tricarboxylate complexes have rarely been observed, because the multicarboxylate ligand facilitates usually the formation of high-dimensional lanthanide complex. Furthermore, no crystalline products were obtained in the corresponding light lanthanide reaction system, although some efforts have been made by modulating reaction solvents and molar ratios of reactants. It should be noted that complexes **2**, **4**, and **6** have been reported previously by Bai and co-workers, although their synthetic method was different from that employed in this work [10]. Their crystal data were reproduced in this work, but are not listed in Table 1.

3.2. Structural description

Single-crystal X-ray diffraction studies reveal that complexes **1–7** are isostructural and crystallize in the triclinic space group *P* $\bar{1}$. Thus, only the crystal structure of **1** is described here as a representative example. As shown in Fig. 1, complex **1** comprises two Tb^{III} ions, two TCT anions, six coordinated water molecules, and six interstitial water molecules. The Tb1 ion is coordinated by nine oxygen atoms from two TCT anions and three coordinated water molecules. These nine oxygen atoms surround Tb1 to form a distorted monocapped square-antiprismatic coordination geometry (Fig. S1). The Tb–O bond lengths vary in the range of 2.3268 (17)–2.5855(18) Å (Table S1). Interestingly, the Tb–O bond lengths [2.3268(17)–2.3885(19) Å] based on three coordinated water molecules are slightly shorter than those [2.4211(17)–2.5855 (18) Å] derived from two TCT anions.

In **1**, two TCT anions bridge two Tb^{III} ions to form a discrete dinuclear molecule (Fig. 1). The adjacent dinuclear molecules are

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