

基于柔性配体的双核铽配位聚合物 $[\text{Tb}_2(\text{tda})_3(\text{H}_2\text{O})_2]$ 的合成、晶体结构和荧光性质

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摘要: 在水热条件下,利用硫代羟基二乙酸配体[thiodiglycolic acid= H_2tda]和 $\text{TbCl}_3 \cdot n\text{H}_2\text{O}$ 合成了新型稀土配合物 $[\text{Tb}_2(\text{tda})_3(\text{H}_2\text{O})_2]$ 。单晶结构表明,配合物是以共边多面体 $[\text{Tb}_2\text{O}_{16}]$ 为基本单元构筑的二维结构,并通过弱相互作用拓展为三维超分子体系。中心原子铽与氧原子的配位数是 8 和 9,分别形成了单帽反四棱柱和三帽三角棱柱构型的空间配位多面体。配体 H_2tda 在配合物中存在两种配位模式:(a) 双“顺-顺桥式双齿、螯合桥式三齿”模式和(b) 双“螯合双齿、顺-反桥式双齿”模式。荧光光谱研究表明:该配合物在室温下呈现较强的绿色荧光发射。配合物属三斜晶系,空间群 $P\bar{1}$ 。

关键词: 铽配合物;合成;晶体结构;荧光性质

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Dinuclear Terbium Coordination Polymer Based on Flexible Ligand: Synthesis, Crystal Structures and Luminescence Properties of $\text{Tb}_2(\text{tda})_3(\text{H}_2\text{O})_2$

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Abstract: The lanthanide coordination polymer, $\text{Tb}_2(\text{tda})_3(\text{H}_2\text{O})_2$, and its single crystals were self-assembled from thiodiglycolic acid (H_2tda) and corresponding terbium(III) chlorides under hydrothermal conditions. Single-crystal structure shows that the compound presents a 2D network, an edge-sharing dinuclear polyhedral $[\text{Tb}_2\text{O}_{16}]$ was found to be the building unit of the network, in which the eight-coordinated TbO_8 and nine-coordinated TbO_9 cores exhibit distinct coordination environments, that is, one is in a distorted monocapped square antiprism surrounding and the other is in a triply capped trigonal prism. The H_2tda ligand exhibits two different coordination modes in framework, including mode a: Bis “syn, syn-bridging bidentate, chelating-bridging tridentate”, mode b: Bis “chelating-bridging bidentate, syn, anti-bridging bidentate”. Eventually, through the weak interaction, the networks formed 3D supramolecular architectures. Photoluminescence measurements indicate that the terbium compound is a strong green emitter in the solid state at room temperature. Crystal data for the complex: triclinic, space group $P\bar{1}$, with $a=0.794\ 66(8)$ nm, $b=1.067\ 96(11)$ nm, $c=1.433\ 23(14)$ nm, $\alpha=70.517\ 00(10)^\circ$, $\beta=75.648\ 0(2)^\circ$, $\gamma=76.975\ 0(2)^\circ$, $V=1.097\ 26(19)$ nm³, and $Z=2$. CCDC: 667667.

Key words: terbium complex; synthesis; crystal structures; luminescence properties

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Rapidly, the research activities concerning metal-organic frameworks (MOFs) based on the lanthanide family are expanding, not only for their fascinating coordination geometry and versatile architecture, but also for their potential utilization as luminescent and sensory materials^[1-4]. Because of the high coordination nature, controlling the overall frameworks of lanthanide-based coordination polymers, undoubtedly, is a challenge. However, this provides an opportunity for the construction of various MOFs with different topologies and specific properties. To date, the majority of the reported work has been the lanthanide-based complexes with polydentate rigid ligands, these rigid ligands are well-known to form grids, rods, bricks, honeycombs, diamondoid and other noteworthy species^[5,6]. Nevertheless, the flexible carboxylic acid ligands have not been extensively exploited, except for some limited cases^[7], this is probably because the varied conformations and geometries of these ligands make it difficult to forecast and control the final structures^[8]. Therefore, much more work is required to enrich our knowledge of the lanthanide-based coordination chemistry of the flexible ligands.

For flexible ligands containing two carboxylate groups, much investigations has focused on coordination polymers, containing iminodiacetate $[\text{HN}(\text{CH}_2\text{COO})_2]^{2-}$, oxydiacetate $[\text{O}(\text{CH}_2\text{COO})_2]^{2-}$, glutarate $[\text{H}_2\text{C}(\text{CH}_2\text{COO})_2]^{2-}$ ions, with various metal cations; as confirmed by the definitely abundance number of the crystal structure of the metal complexes contained in CCDC. Whereas coordination polymers containing thiodiacetate $[\text{S}(\text{CH}_2\text{COO})_2]^{2-}$ ions are rare, only a few transition metal complexes and coordination polymers containing rare-earth cations are reported^[9,10].

Taking account of these, we focused on the synthesis of coordination polymer using H_2tda ligand to coordinate with lanthanide metal ions under hydrothermal conditions. Our aim is to synthesize new rare earth complexes, to explore for the complex composition, structure and character, to establish experimental basis for the further synthesis of a new type of complex with novelty structure and special luminescence properties. Therefore, in this paper, we

report the synthesis, characterization of luminescence properties of the complex, $\text{Tb}_2(\text{tda})_3(\text{H}_2\text{O})_2$ and the crystal structure.

1 Experimental section

1.1 Materials and Instrumentation

All available solvents and starting materials of analytical grade except $\text{TbCl}_3 \cdot n\text{H}_2\text{O}$, in the experiments were obtained from commercial sources and available without further purification, the $\text{TbCl}_3 \cdot n\text{H}_2\text{O}$ were prepared according to the literature methods^[11]. Elemental analysis was determined on a Perkin-Elmer 2400 type elemental analyzer. Infrared spectra were recorded in a Bruker EQUINOX-55 spectrophotometer in the range $400 \sim 4\,000\text{ cm}^{-1}$ using KBr disks. Thermogravimetric analyses were recorded on a Shimadzu DTG-50 thermal analyzer. Photoluminescence analyses of the solid samples were performed on an Edinburgh Instrument F920 fluorescence spectrometer at ambient temperature.

1.2 Synthesis of the compound

A mixture of $\text{TbCl}_3 \cdot n\text{H}_2\text{O}$ (0.1 mmol), H_2tda (0.15 mmol), and NaOH (0.1 mmol) in a mixed solution of water (10 mL) and ethanol (5 mL) was sealed into a 25 mL poly (tetrafluoroethylene)-lined stainless steel container under autogenous pressure heated at $85\text{ }^\circ\text{C}$ for 10 days and cooled to $20\text{ }^\circ\text{C}$ at $5\text{ }^\circ\text{C} \cdot \text{h}^{-1}$, colorless Prismatic single crystals of the Lanthanide Coordination Polymer suitable for X-ray analyses were obtained by slow evaporation of the solvent after five weeks. The crystals were collected by filtration, washed with distilled water and ethanol, and dried at room temperature. Yield: 75% (based on Tb). Elemental analysis: calcd for $\text{Tb}_2(\text{tda})_3(\text{H}_2\text{O})_2$ (%): C 15.69, H 1.97, Found (%): C 15.78, H 2.01. FTIR: Spectra(KBr pellet, cm^{-1}): $\nu_{\text{as}}(\text{CH}_2)$ 3 024, $\nu_{\text{s}}(\text{CH}_2)$ 2 968, $\nu_{\text{as}}(\text{COO})$ 1 583, $\nu_{\text{s}}(\text{COO})$ 1 396, $\nu_{\text{as}}(\text{H}_2\text{O})$ 3 437 $\nu_{\text{s}}(\text{H}_2\text{O})$ 3 278, σ 1 634, $\nu(\text{C-S})$ 728 and 713.

1.3 Crystal structure determination

Crystal data for the compound was collected at 273(2) K using Bruker Smart-Apex 1000CCD diffractometer. Graphite monochromatized Mo $K\alpha$ ($\lambda=0.071\,073\text{ nm}$) radiation was used. The single crystal structure of

the compound was solved by direct methods using the SHELXS-97^[12] and refined on F^2 by the full-matrix least-squares methods using the SHELXL-97 program package^[13]. All non-hydrogen atoms were anisotropically refined. Hydrogen atoms were located from difference

Fourier maps. The crystal data and refinement details of the compound are summarized in Table 1. The selected interatomic distances and bond angles are given in Table 2.

CCDC: 667667.

Table 1 Crystal data and structure refinement for the title complex 1

Empirical formula	C ₁₂ H ₁₆ O ₁₄ S ₃ Tb ₂	$D_c / (\text{Mg} \cdot \text{m}^{-3})$	2.416
Formula weight	798.27	θ range for data collection / (°)	2.68–28.17
Crystal system	Triclinic	Indices range (h, k, l)	$-9 \leq h \leq 9, -12 \leq k \leq 12, -17 \leq l \leq 17$
Space group	$P\bar{1}$	λ (Mo $K\alpha$) / nm	0.071 073
a / nm	0.794 66(8)	Reflections collected	8 337
b / nm	1.067 96(11)	Independent reflections	7 924
c / nm	1.433 23(14)	Data / restraints / parameters	4 039
α / (°)	70.517 0(10)	$F(000)$	756
β / (°)	75.648 0(10)	Z	2
γ / (°)	76.975 0(10)	Final R	$R_1=0.018\ 4, wR_2=0.048\ 7$
V / nm ³	1.097 26(19)	R indices (all data)	$R_1=0.019\ 3, wR_2=0.049\ 4$

Table 2 Selected bond lengths (nm), bond angles (°) for the title complex 1

Tb1-O5	0.230 1(3)	Tb1-O11B	0.240 6(2)	Tb1-O10	0.251 0(2)
Tb1-O1	0.233 2(2)	Tb1-O10C	0.241 9(2)	Tb1-O9	0.258 2(3)
Tb1-O12A	0.234 2(2)	Tb1-O3	0.242 6(2)		
O5-Tb1-O1	79.72(12)	O5-Tb1-O12A	137.10(10)	O1-Tb1-O3	84.60(9)
O5-Tb1-O11B	74.19(10)	O1-Tb1-O11B	70.44(9)	O3-Tb1-S1	64.20(6)
O1-Tb1-S1	63.41(7)	O1-Tb1-O10C	90.07(9)	O5-Tb1-O3	74.31(9)
Tb2-O7D	0.235 8(2)	Tb2-O6	0.237 8(2)	Tb2-O13	0.239 5(2)
Tb2-O4	0.241 0(3)	Tb2-O14	0.241 0(2)	Tb2-O2D	0.242 7(2)
Tb2-O7F	0.260 7(2)	Tb2-O3	0.256 1(2)	Tb2-O8F	0.248 3(3)
O7D-Tb2-O6	78.75(9)	O6-Tb2-O13	74.56(9)	O6-Tb2-O4	133.86(8)
O6-Tb2-O3	82.65(8)	O13-Tb2-O3	74.30(8)	O4-Tb2-O3	52.33(8)
O13-Tb2-O4	98.93(10)	O6-Tb2-O14	138.58(8)	O6-Tb2-O2D	141.74(9)

Symmetry code: A: $-x+1, -y+1, -z+1$; B: $x+1, y, z$; C: $-x+2, -y+1, -z+1$; D: $x-1, y, z$; F: $-x+2, -y, -z+2$

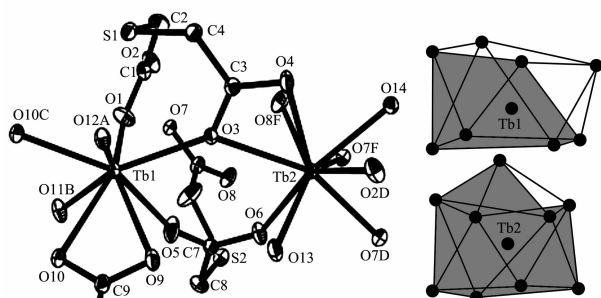
2 Results and discussion

2.1 Crystal structure of the Tb₂(tda)₃(H₂O)₂

Single-crystal structure shows that the compound presents a 2D network. The coordination environments around Tb ions and the numbering scheme of the compound are illustrated in Fig.1. There are two distinct terbium ions with different coordination spheres in the structure. The Tb1 ions are surrounded by eight oxygen atoms from six tda ligands, resulting a distorted

monocapped square antiprism surrounding^[14,15], the Tb2 ions are nine-coordinated in a triply capped trigonal prism^[16] by seven O atoms from five tda molecules, and two oxygen atom from two coordinated water molecules. Therefore, the ligands around each Tb1 ion are six tda ligands; around each Tb2 ion are five tda ligands, and two coordinated water molecules. The Tb-O distances range from 0.230 1(3) to 0.260 7(2) nm, the average distance of Tb1-O is 0.241 48 nm, which is little shorter than that of Tb2-O 0.244 77 nm. The bond

angles around the central Tb atom fall in the region $25.04^\circ \sim 156.82^\circ$. Which are similar to that found in other Tb complex^[17] and within the range of the normal Tb-O distance and bond angles around the central Tb atoms. The Selected bond distances and bond angles of the compounds are shown in Table 2.



Symmetry code: A: $-x+1, -y+1, -z+1$; B: $x+1, y, z$; C: $-x+2, -y+1, -z+1$; D: $x-1, y, z$; E: $-x+2, -y, -z+2$

Fig.1 Left: Coordination environment and numbering scheme around the two independent Tb centers in the compound **1**, hydrogen atoms are omitted for clarity; Right: Coordination polyhedra for the two independent Tb ions

Two types of crystallographically independent tda ligands with different carboxylate coordination modes are present in the framework of the title compound, Bis(syn, syn-bridging bidentate, chelating-bridging bidentate), Bis(chelating-bridging bidentate, syn, anti-bridging bidentate) modes as shown in Chart 1. The tda ligands provides μ_2 -O atom in a chelating-bridging bidentate mode and carboxyl in syn, syn-bridging bidentate mode to bridge terbium atoms, leading to the formation of 1D infinite metallic chains as illustrated in Fig.2. The terbium atoms are arrayed the basic unit in the order Tb1c...Tb2c...Tb2...Tb1, with four consecutive Tb...Tb distances of 0.465 35 (3), 0.418 15 (4), 0.465 35(3) and 0.391 58 (4) nm, respectively. Three kinds of macrocyclic rings, one is four-member ring, one is eight-member ring, and the other is six-member ring, are observed in this 1D chains. Interestingly, each tda ligand in mode a and b is connected with three or four Tb(III) ions, while each Tb1(III) is connected with six tda ligands and, Tb2(III) is connected with five tda ligands in different directions. Hence, through tda ligand in mode a and b, the 1D metallic chains are further cross-linked

to generate a 2D network structure (Fig.2), in which the 2D network containing a interval group with four consecutive Tb...Tb distances of 0.803 49 (7), 0.623 47(5), 0.885 06(8), and 0.803 49(7) nm, respectively. Eventually, these 2D networks, via $S \cdots S$ ^[18] and $C-H \cdots O$ hydrogen bonding^[15] weak interaction, formed a 3D supramolecular architectures (Fig.3). The S2...S3 atoms adopt face-to-face weak interaction. S...S distance is 0.383 nm slightly longer than the radius of the S...S covalent (0.370 nm). The $C-H \cdots O$ hydrogen bonds originate from the coordinated water molecule O14 atom and the tda ligand C-H (C4) from neighboring

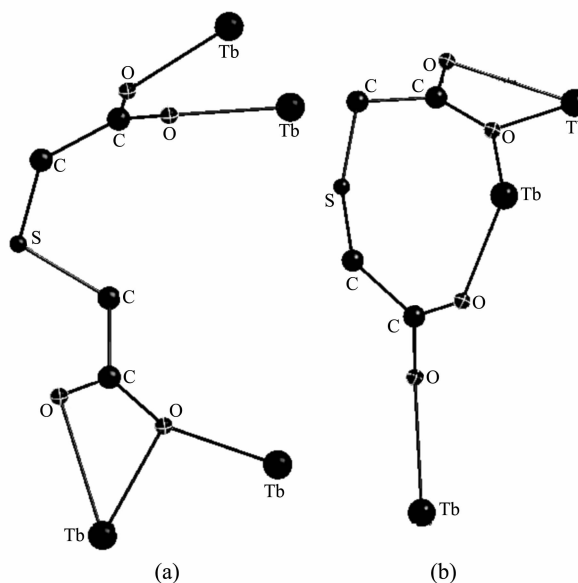
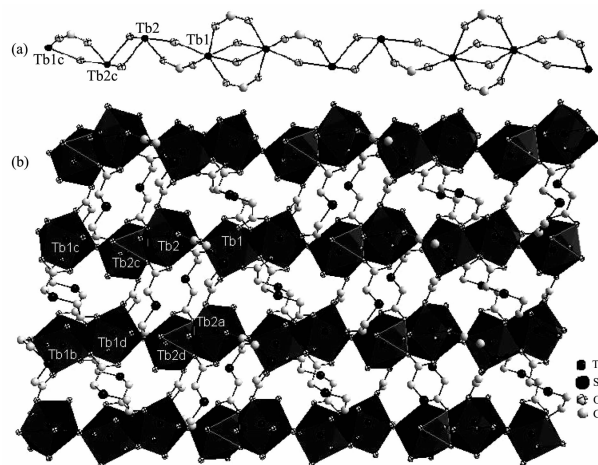


Chart 1 Two coordination modes in the complex **1**



Symmetry code: a: $1+x, y, z$; b: $x, 1-y, 1+z$; c: $1-x, -y, 2-z$; d: $2-x, -y, 2-z$

Fig.2 (a) 1D infinite metallic chains in the compound; (b) two-dimensional network of the compound

two-dimensional network structure, C—H, H···O, C···O distance is 0.097, 0.253, 0.3251 nm respectively. The bond angle C—H···O is 131.75°.

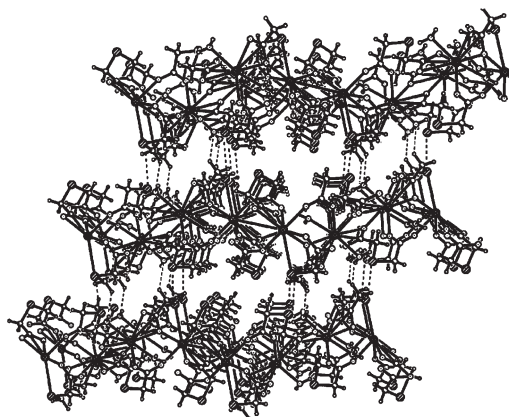


Fig.3 Three-dimensional network of tda in the complex 1

2.2 Thermal analyses

Thermogravimetric analyses for the compound were performed from 30 to 900 °C at a heating rate of 10 °C · min⁻¹ under a static air atmosphere (Fig.4). According to the thermogravimetric analyses curve. For the title compound: The first step loss of the coordinated water molecules, the total weight loss for two coordinated water molecules is 5.56% (calcd 5.77%) starts at 161.09 °C, ends at 243.8 °C. The final residual mass corresponds to the formation Tb₂O₃, supported by the expected value of 57.53% (calcd 58.61%), starts at 293.19 °C, ends at 721.66 °C. That is corresponds to the decomposition of the title compound.

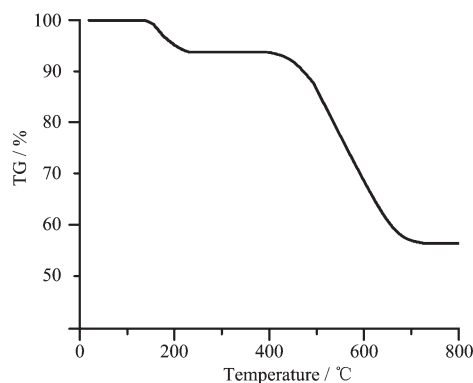


Fig.4 TG curves of the complex 1

2.3 Luminescent properties

Lanthanide luminescence is demonstrated to be very sensitive to local environments around the lanthanide center^[19]. The terbium complex show green

light emission upon excitation at 350 nm at room temperature. The characteristic luminescent bands of the terbium compound were recorded at 488, 545, 585, and 620 nm via the ligand to metal energy transfer mechanism, which can be attributed to $^5D_4 \rightarrow ^7F_J$ ($J=6, 5, 4$, and 3) transitions, respectively^[20,21]. The spectrum is dominated by the $^5D_4 \rightarrow ^7F_5$ transition, at 545 nm, which gives an intense green luminescence output for the solid sample, and which is induced by electric dipole moment and is hypersensitive to the environment of the Tb(III) (Fig.5). The additional peaks at 690 nm in the complex is concluded to be overtones of excited wavelengths. These characteristic emission bands indicate that the ligand-to-metal energy transfer is moderately efficient under the experimental conditions used^[22].

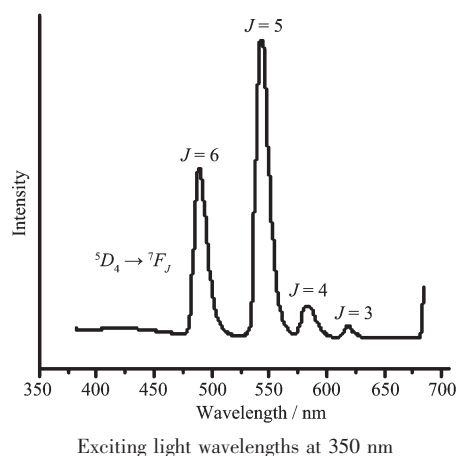


Fig.5 Luminescence spectrum of the title complex at the room

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