

一维链状 3-碘苯甲酸铽配合物的合成、晶体结构和性质表征

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摘要: 溶液法合成了配合物 $\{[\text{Tb}(\text{3-IBA})_3(\text{H}_2\text{O})_2] \cdot 0.5(4,4'\text{-bipy})\}_n$ (3-IBA=3-碘苯甲酸根; 4,4'-bipy=4,4'-联吡啶), 并通过 X-射线衍射单晶结构分析、红外光谱、紫外光谱、荧光光谱以及热重分析对配合物进行了结构和性质表征。配合物晶体属三斜晶系, $P\bar{1}$ 空间群。该配合物具有一维链状结构。 Tb^{3+} 离子与 8 个 O 原子配位, 其中 6 个 O 原子来自 5 个 3-碘苯甲酸根, 2 个 O 原子来自水分子。相邻 Tb^{3+} 离子通过 2 个双齿桥联的 3-碘苯甲酸根联结成一维链状结构。未配位的 4,4'-联吡啶分子与配位水分子之间形成氢键, 并将相邻的一维链联结起来形成二维网状结构。沿 a 轴的分子堆积形成一维孔道, 是由于相邻一维链的苯环之间部分重叠而形成的。在紫外光照射下, 配合物发出很强的绿色荧光。配合物的荧光光谱中, 4 个峰位于 490、544、583 和 619 nm, 分别对应于 Tb^{3+} 离子的 $^5\text{D}_4 \rightarrow ^7\text{F}_6$ 、 $^5\text{D}_4 \rightarrow ^7\text{F}_5$ 、 $^5\text{D}_4 \rightarrow ^7\text{F}_4$ 和 $^5\text{D}_4 \rightarrow ^7\text{F}_3$ 跃迁。

关键词: 铽配合物; 3-碘苯甲酸; 一维链; 晶体结构; 荧光

中图分类号: O614.341 文献标识码: A 文章编号: 1001-4861(2008)11-1738-05

Synthesis, Crystal Structure and Characterization of 1D Chain-like Terbium 3-iodobenzoate Complex

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Abstract: The complex of $\{[\text{Tb}(\text{3-IBA})_3(\text{H}_2\text{O})_2] \cdot 0.5(4,4'\text{-bipy})\}_n$ (3-IBA=3-iodobenzoate; 4,4'-bipy=4,4'-bipyridine) was prepared by solvent method and further characterized by X-ray single crystal structural analysis, IR spectrum, UV spectrum, fluorescence spectrum, and thermogravimetric analysis. The complex crystallizes in triclinic crystal system and $P\bar{1}$ space group with the cell dimensions: $a=0.957\ 9(2)$ nm, $b=1.020\ 3(2)$ nm, $c=1.667\ 5(3)$ nm, $\alpha=95.4660(10)^\circ$, $\beta=105.0010(10)^\circ$, $\gamma=106.9940(10)^\circ$. The complex has 1D chain-like structure. Tb^{3+} ion is eight-coordinated by six oxygen atoms from five 3-IBA ligands and two oxygen atoms from water molecules. The adjacent Tb^{3+} ions are linked by two bidentate-bridging 3-IBA ligands forming 1D chain-like structure. The hydrogen bonds are formed between the free 4,4'-bipy molecules and the coordination water molecules, which connect the 1D chains into 2D network structure. Viewed along a -axis, there appear 1D channels caused by the partial overlapping between the benzene rings of the neighboring chains. The complex exhibits strong green fluorescence under ultraviolet light and the fluorescence spectrum has four main peaks at 490, 544, 583 and 619 nm, corresponding to $^5\text{D}_4 \rightarrow ^7\text{F}_6$, $^5\text{D}_4 \rightarrow ^7\text{F}_5$, $^5\text{D}_4 \rightarrow ^7\text{F}_4$ and $^5\text{D}_4 \rightarrow ^7\text{F}_3$ transition emissions of the Tb^{3+} ion, respectively. CCDC: 661739.

Key words: terbium complex; 3-iodobenzoic acid; 1D chain-like; crystal structure; fluorescence

收稿日期: 2008-01-14。收修改稿日期: 2008-04-04。

北京市自然科学基金项目资助(No.2073022)。

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0 Introduction

Considering the various coordination forms of carboxylate anions as well as the large radius, high coordination numbers, special fluorescence and magnetic properties of lanthanide ions, a large number of lanthanide complexes constructed by carboxylic acid have been obtained^[1-7]. These lanthanide carboxylate complexes have attracted much attentions also attributing to the structural diversity and potential applications in sensors, optical fiber lasers and amplifiers, luminescent label, magnetic molecular materials, and so on^[1-4]. It is reported that many of these complexes are dimers, 1D chain-like structure, 2D grid structure or 3D supermolecular structure^[7-9]. As rigid ligands, benzoic acid and its derivatives have been widely used because they can bridge the center ions and form the π - π stacking to increase the stability of the structure, and lanthanide complexes with benzoic acid and its derivatives often show higher thermal stability.

Our lab has synthesized a series of lanthanide complexes with the derivatives of benzoic acid^[9-14]. To our surprise, some of them have amusing structures^[11-13]. In order to further investigate the structural characteristics of lanthanide complexes with the derivatives of benzoic acid, we used 3-iodobenzoic acid and 4,4'-bipyridine as ligands and obtained a new complex, namely, $\{[\text{Tb}(\text{3-IBA})_3(\text{H}_2\text{O})_2] \cdot 0.5(4,4'\text{-bipy})\}_n$ (3-IBA=3-iodobenzoate; 4,4'-bipy=4,4'-bipyridine). The synthesis, crystal structure, luminescent properties and thermal stability of the complex are reported in this paper.

1 Experimental section

1.1 Reagents and instrumentation

All analytical grade reagents and solvents were purchased commercially and used without further purification, such as 3-iodobenzoic acid, 4,4'-bipy, ethanol, DMSO and so on. $\text{Tb}(\text{NO}_3)_3 \cdot 6\text{H}_2\text{O}$ was made by the reaction of terbium oxide (99.90%) and nitric acid.

IR spectra ($4\,000\sim 400\text{ cm}^{-1}$) were recorded on a

Bruker EQUINOX-55 using the KBr pellet technique. The UV spectra were measured in DMSO solvent ($c=1\times 10^{-3}\text{ mol}\cdot\text{L}^{-1}$) by TU-1810 Ultraviolet-Visible spectrophotometer. The excitation spectrum and emission spectrum of the complex in DMSO solvent ($c=1\times 10^{-3}\text{ mol}\cdot\text{L}^{-1}$) were recorded on an F-4500 Fluorescence Spectrophotometer. The thermogravimetric analysis was performed on a WCT-1A Thermal Analyzer.

1.2 Synthesis of $\{[\text{Tb}(\text{3-IBA})_3(\text{H}_2\text{O})_2] \cdot 0.5(4,4'\text{-bipy})\}_n$

1.2 mmol 3-iodobenzoic acid and 0.4 mmol 4,4'-bipy were dissolved in 25 mL ethanol, subsequently the mixture was heated under reflux with stirring and the pH value was adjusted to be about 5 by $1\text{ mol}\cdot\text{L}^{-1}$ NaOH aqueous solution. And then ethanol solution of $\text{Tb}(\text{NO}_3)_3 \cdot 6\text{H}_2\text{O}$ (0.4 mmol) was dropped into the mixture. The resulting solution was filtered and the colorless square single crystals suitable for X-ray structural analysis were obtained from the mother liquid after several weeks (Yield: 42.45%). Selected IR (KBr pellet, ν/cm^{-1}): 3 627s, 3 385s, 1 579s, 1 538s, 1 471m, 1 419s, 1 299m, 1 265m, 1 061m, 995m, 899w, 866w, 802w, 754s, 698m, 617m, 563w, 527w, 465w, 415w.

1.3 Crystal structure determination of the complex

A light single crystal of the complex having dimensions of $0.22\text{ mm} \times 0.20\text{ mm} \times 0.18\text{ mm}$ was selected for the structural analysis. The data collection were performed at 293 (2) K on a Siemens SMART APEX CCD diffractometer equipped with a graphite monochromatized $\text{Mo K}\alpha$ radiation ($\lambda=0.071\,073\text{ nm}$). Semi-empirical absorption correction was applied to the intensity data using the SADABS program. The structure was solved by direct methods and refined by full matrix least squares method on F^2 using SHELXS-97 and SHELXL-97 programs, respectively. A summary of the crystallographic data and details of the structure refinements are listed in Table 1. The selected bond lengths and bond angles of the complex are listed in Table 2.

CCDC: 661739.

Table 1 Crystal data and structure refinement for the complex

Empirical formula	C ₂₆ H ₃₀ I ₃ NO ₈ Tb	Absorption coefficient / mm ⁻¹	5.567
Formula weight	1 014.05	<i>F</i> (000)	942
Crystal system	Triclinic	Crystal size / mm	0.22 × 0.20 × 0.18
Space group	<i>P</i> $\bar{1}$	θ range for data collection / (°)	3.63 to 28.30
<i>a</i> / nm	0.957 9(2)	Limiting indices	-12 ≤ <i>h</i> ≤ 12; -13 ≤ <i>k</i> ≤ 12; -22 ≤ <i>l</i> ≤ 22
<i>b</i> / nm	1.020 3(2)	Reflections collected / unique	23 452 / 7 273 (<i>R</i> _{int} =0.020 4)
<i>c</i> / nm	1.667 5(3)	Reflections observed [<i>I</i> >2σ(<i>I</i>)]	6 776
α / (°)	95.466 0(10)	Data / restraints / parameters	7 237 / 0 / 368
β / (°)	105.001 0(10)	Goodness-of-fit on <i>F</i> ²	1.017
γ / (°)	106.994 0(10)	Final <i>R</i> indices [<i>I</i> >2σ(<i>I</i>)]	<i>R</i> ₁ =0.023 3, <i>wR</i> ₂ =0.055 2
Volume / nm ³	1.479 5(5)	<i>R</i> indices (all data)	<i>R</i> ₁ =0.025 5, <i>wR</i> ₂ =0.056 3
<i>Z</i>	2	Largest diff. peak and hole / (e·nm ⁻³)	954 and -850
Calculated density / (Mg·m ⁻³)	2.276		

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

Tb(1)-O(1)	0.246 2(2)	Tb(1)-O(2)	0.250 7(2)	Tb(1)-O(3)	0.237 2(2)
Tb(1)-O(4)#2	0.228 4(2)	Tb(1)-O(5)	0.23 51(2)	Tb(1)-O(6)#1	0.230 8(2)
Tb(1)-O(7)	0.241 9(2)	Tb(1)-O(8)	0.246 7(2)		
O(1)-Tb(1)-O(2)	52.43(6)	O(3)-Tb(1)-O(1)	76.83(7)	O(4)#2-Tb(1)-O(1)	76.74(7)
O(5)-Tb(1)-O(1)	134.31(7)	O(6)#1-Tb(1)-O(1)	78.31(7)	O(7)-Tb(1)-O(1)	130.00(7)
O(1)-Tb(1)-O(8)	140.99(8)	O(3)-Tb(1)-O(2)	72.85(7)	O(4)#2-Tb(1)-O(2)	128.56(7)
O(5)-Tb(1)-O(2)	83.46(7)	O(6)#1-Tb(1)-O(2)	73.69(8)	O(7)-Tb(1)-O(2)	145.17(7)
O(8)-Tb(1)-O(2)	129.42(8)	O(4)#2-Tb(1)-O(3)	105.83(7)	O(5)-Tb(1)-O(3)	79.38(7)
O(6)#1-Tb(1)-O(3)	146.02(8)	O(3)-Tb(1)-O(7)	74.69(7)	O(3)-Tb(1)-O(8)	141.73(8)
O(4)#2-Tb(1)-O(5)	147.91(8)	O(4)#2-Tb(1)-O(6)#1	90.48(8)	O(4)#2-Tb(1)-O(7)	72.75(8)
O(4)#2-Tb(1)-O(8)	84.13(8)	O(6)#1-Tb(1)-O(5)	102.53(7)	O(5)-Tb(1)-O(7)	78.49(7)
O(5)-Tb(1)-O(8)	74.13(8)	O(6)#1-Tb(1)-O(7)	139.25(8)	O(6)#1-Tb(1)-O(8)	68.07(8)
O(7)-Tb(1)-O(8)	73.35(8)				

Symmetry transformations used to generate equivalent atoms: #1: *x*+2, -*y*, -*z*+1; #2: -*x*+1, -*y*, -*z*+1.

2 Results and discussion

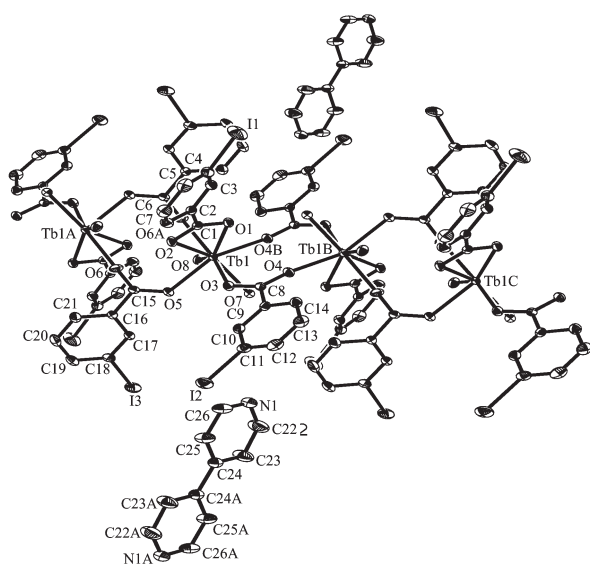
2.1 Crystal structure of {[Tb(3-IBA)₃(H₂O)₂]·0.5(4,4'-bipy)}_n

The structure of the complex is shown in Fig.1. The prominent characteristic is the 1D chain, in which the center Tb³⁺ ions act as nodes and are connected through 3-IBA ligands. Carboxyl (O3-C8-O4) adopts bidentate-bridging coordination mode, namely, the two oxygen atoms coordinate to two different Tb³⁺ ions. While the carboxyl (O1-C1-O2) adopts the bidentate-chelating fashion, namely, the two oxygen atoms coordinate to the same Tb³⁺ ion.

Each Tb³⁺ ion is coordinated with eight oxygen

atoms, in which four oxygen atoms from four bidentate-bridging 3-IBA ligands, two oxygen atoms from one bidentate-chelating 3-IBA ligand and two from water molecules. So each Tb³⁺ ion lies in a distorted square-antiprism coordination environment. Atoms O2, O5, O6A, O8 construct the upper plane of the square-antiprism and atoms O1, O3, O4B, O7 form the below one, with the dihedral angle of 11.1° between them. And the mean deviation from the upper and lower plane is 0.020 1 nm and 0.0185 nm, respectively.

The distance between two adjacent Tb³⁺ ions is 0.487 7(5) nm for Tb1A···Tb1 and 0.483 7(5) nm for Tb1···Tb1B. And the angle of Tb1A···Tb1···Tb1B is 160.9°. The bond lengths of Tb1-O (carboxyl) range



Symmetry transformations used to generate equivalent atoms:

A: $-x+2, -y, -z+1$; B: $-x+1, -y, -z+1$; C: $-x+1, -y+2, -z$

Fig.1 Molecular structure of the complex

from 0.228 4(2) to 0.250 7(2) nm, with a mean value of 0.238 0 nm. While the bond lengths of Tb1-O(water) are 0.241 9(2) and 0.246 7(2) nm, with a mean value of 0.244 3 nm. The average bond length of Tb1-O(water) is larger than that of Tb1-O(carboxyl), which is agree with the fact that the watery oxygen is less affinitive to the center ions than carboxyl oxygen. And the bond angles of O-Tb1-O(carboxyl) range from 52.43(6)° to 147.91(8)°.

The 4,4'-bipy molecule in the crystal lattice does not coordinate to Tb³⁺ ion and its two pyridine rings are exactly coplanar. The distance between N1 atom of 4,4'-bipy molecule and Tb³⁺ ion is 0.453 8(4) nm. The free 4,4'-bipy molecules form hydrogen bonds with the coordination water molecules, O(7)-H(7B)⋯N(1) ($x, y-$

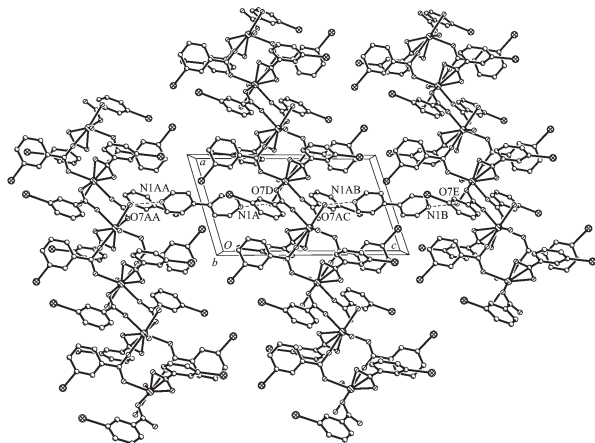


Fig.2 Packing diagram of the complex showing 2D networks structure constructed by hydrogen bonds

1, z) (0.278 4(4) nm, 177(5)°). Thus, the 1D chains are connected to 2D networks structure though 4,4'-bipy molecules as hydrogen bond bridges (Fig.2).

The structure of the title complex is similar to that of complex $\{[\text{Eu}(m\text{-MOBA})_3 \cdot 2\text{H}_2\text{O}]1/2(4,4'\text{-bpy})\}$ ($m\text{-MOBA} = m\text{-methoxybenzoate}$, 4,4'-bpy = 4,4'-bipyridine)^[14]. The latter complex is also 1D polymer chain structure, in which Eu³⁺ ions are connected through two carboxyl groups of two $m\text{-MOBA}$ ligands via bidentate-bridging coordination mode. The 4,4'-bipy molecule also does not coordinate to Eu³⁺ ion. Unlike the title complex, in the 1D polymer chain of complex $[\text{Eu}(2\text{-IBA})_3 \cdot \text{H}_2\text{O}]_n$ (2-IBA = 2-iodobenzoate)^[11], Eu³⁺ ions are connected through two carboxyl groups of two 2-IBA ligands via the bridging-chelating-bridging tetradentate coordination mode. This distinct difference may be caused by the different steric effect, for that the iodine atom lies in the different position of the benzene ring.

In addition, the Tb³⁺ ions and the benzene rings of 3-IBA ligands arrange regularly along a -axis, in which bidentate-chelating benzene rings parallel each other with the distance between them of 0.850 5 nm, and so do the bidentate-bridging benzene rings with the distance of 0.498 0 nm. Furthermore, the adjacent two 1D chains penetrate each other and the benzene rings overlap partially to form a 1D channel along a -axis, in which the distance between the opposite Tb³⁺ ions is 1.020 3 nm and the distance between the crossing benzene rings is 0.673 4 nm (Fig.3).

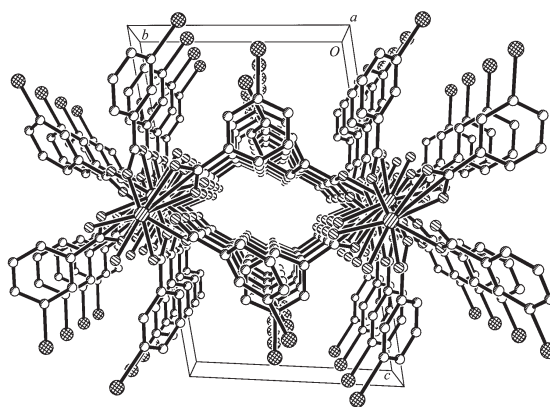


Fig.3 Packing diagram of the complex showing 1D channel

2.2 UV spectrum

The UV spectra of the ligands and the complex were recorded in DMSO solvent with the concentration

of $10^{-3} \text{ mol} \cdot \text{L}^{-1}$. Any of the three spectra has one absorption peak at 298 nm attributing to $\pi \rightarrow \pi^*$ transition, however, the intensities are different. The absorption intensity of the complex is the strongest ($\varepsilon = 8.98 \times 10^2$), that of the 3-IBA ($\varepsilon = 7.04 \times 10^2$) is the second and the 4,4'-bipy is the least ($\varepsilon = 5.60 \times 10^2$) (Fig.4). When compared with the single ligand, the absorption intensity of the complex is strengthened obviously attributing to the synergistic effect between the ligands and the center Tb^{3+} ions. This indicates that the ligands can effectively transfer the absorption energy to the center Tb^{3+} ions.

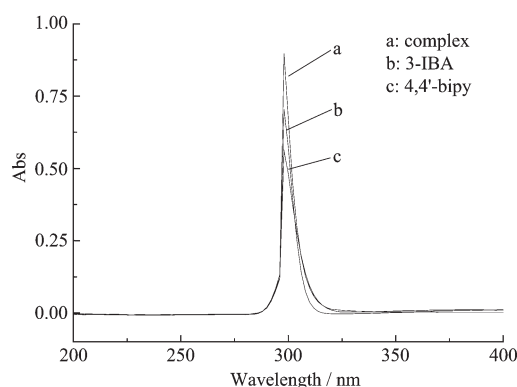


Fig.4 UV spectra of the ligands and the complex

2.3 Fluorescence spectrum

The solid sample of the complex emits green fluorescence under ultraviolet light. The excitation and emission spectra of DMSO solvent ($c = 1 \times 10^{-3} \text{ mol} \cdot \text{L}^{-1}$) for the complex were obtained at room temperature (Fig. 5). The excitation spectrum was recorded in the range of 200~400 nm, setting 545 nm as the emission wavelength, in which there is a strong peak at 302 nm. Then the emission spectrum of the complex was observed

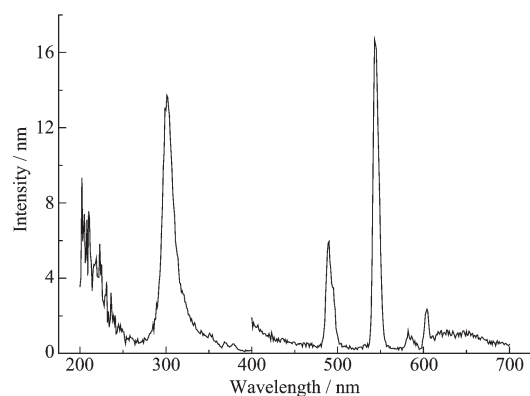


Fig.5 Excitation and emission spectra of the complex in DMSO solvent ($c = 1 \times 10^{-3} \text{ mol} \cdot \text{L}^{-1}$)

from 400 to 700 nm under the excitation wavelength of 302 nm. There are four main peaks at 490, 544, 583 and 619 nm, corresponding to $^5\text{D}_4 \rightarrow ^7\text{F}_6$, $^5\text{D}_4 \rightarrow ^7\text{F}_5$, $^5\text{D}_4 \rightarrow ^7\text{F}_4$ and $^5\text{D}_4 \rightarrow ^7\text{F}_3$ transition emissions of Tb^{3+} ion, respectively. The most intense emission peak appears at 545 nm attributing to $^5\text{D}_4 \rightarrow ^7\text{F}_5$ transition.

2.4 Thermogravimetric analysis

The TG-DTA analysis was performed in air atmosphere with a heating rate of $10 \text{ }^\circ\text{C} \cdot \text{min}^{-1}$ in the temperature range from 20 to 1 000 $^\circ\text{C}$.

The TG-DTA curve exhibits that the complex decomposes by three steps. The first weight loss is 4.24%, the second one is 6.83% and the third one is 67.87%. The complex begins to decompose at 159 $^\circ\text{C}$ with a small endothermic peak. And then there appears a big exothermic peak at 548 $^\circ\text{C}$ ascribing to the complete collapse of the complex. Tb_4O_7 was the last residue, corresponding to the total loss of 78.94% (calculated: 81.57%).

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