

## 三维混核 Cu(I)-Tb(III)配位化合物的溶剂热合成、 晶体结构和荧光性质

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**摘要:** 由溶剂热法合成了一种新型混核化合物 $[\text{CuTb}_2(\text{INAIP})_3(\text{HCOO})(\text{H}_2\text{O})_3] \cdot 3\text{H}_2\text{O}$  (**1**) (INAIP=异烟酰胺吡啶基异酞酸根), 并对其进行了元素分析、IR 及 X-射线衍射法表征。晶体结构研究表明: 配合物 **1** 属于三斜晶系,  $P\bar{1}$  空间群。配合物 **1** 是由配体异烟酰胺吡啶基异酞酸连接而成的三维二重贯穿结构。荧光测试研究表明配合物 **1** 具有典型的稀土铽离子绿色荧光。

**关键词:** 3d-4f 配合物; 晶体结构; 荧光性质

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## Solvothermal Synthesis, Crystal Structure and Luminescence of a Three-Dimensional Heteronuclear Cu-Tb Complex

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**Abstract:** A new 3d-4f coordination polymer  $[\text{CuTb}_2(\text{INAIP})_3(\text{HCOO})(\text{H}_2\text{O})_3] \cdot 3\text{H}_2\text{O}$  (**1**) was obtained by solvothermal assembly of  $\text{CuCl}_2 \cdot 2\text{H}_2\text{O}$  and  $\text{Tb}(\text{NO}_3)_3 \cdot 6\text{H}_2\text{O}$  with the  $\text{H}_2\text{INAIP}$  (5-(isonicotinamido)isophthalic acid) ligand. Complex **1** crystallizes in triclinic, space group  $P\bar{1}$  with  $a=1.088\ 79(16)$  nm,  $b=1.518\ 5(2)$  nm,  $c=1.565\ 3(2)$  nm,  $V=2.338\ 1(6)$  nm<sup>3</sup>,  $Z=2$ ,  $\text{C}_{43}\text{H}_{37}\text{CuTb}_2\text{N}_6\text{O}_{23}$ ,  $M_r=1387.17$ ,  $D_c=1.970\ \text{g} \cdot \text{cm}^{-3}$ ,  $\mu=3.538\ \text{mm}^{-1}$ ,  $F(000)=1360$ ,  $R_{\text{int}}=0.021\ 2$ ,  $R=0.058\ 9$ ,  $wR=0.129\ 2$ . Single-crystal X-ray diffraction analysis revealed that each  $\text{INAIP}^{2-}$  ligand uses its two carboxyl groups to connect two or three  $\text{Tb}(\text{III})$  ions into 2D lanthanide bi-layer structure. Then the 2D layers are further connected by pyridyl groups to give a three-dimensional (3D) pillared-layer structure. In addition, the luminescent property of complex **1** has been investigated at room temperature, and showed the obviously green photoluminescence in it. CCDC: 881422.

**Key words:** 3d-4f complex; crystal structure; luminescent property

## 0 Introduction

In recent years, the rational design and synthesis of higher-dimensional transition-lanthanide metal (*d-f*) heterometallic networks have attracted increasing

attention due to the fascinating structural diversity of the architectures and potential applications of these complexes as important functional solid materials<sup>[1-9]</sup>. As we know, the useful way to synthesize of the heterometallic coordination polymers is the assembly

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from the mixed metal ions and logic multidentate organic ligands. Furthermore, the lanthanide ions usually prefer O- to N-donors, while transition metal ions have a strong tendency to coordinate to both N- and O-donors<sup>[10-12]</sup>. Thus, ligands containing O- and N-donors can elaborately be selected and bond relatively easily to both Ln ions and d-block metal ions to form heterometallic MOFs. 5-(isonicotinamido)isophthalic acid ( $\text{H}_2\text{INAIP}$ ) can also show richer coordination modes due to its two carboxylate groups and one pyridyl group, accordingly, it is an excellent candidate for the construction of heterometallic frameworks<sup>[13-16]</sup>. Herein we report the solvothermal synthesis, crystal structure and photoluminescence property of a new 3d-4f coordination polymers, namely  $\{[\text{CuTb}_2(\text{INAIP})_3(\text{HCOO})(\text{H}_2\text{O})_3] \cdot 3\text{H}_2\text{O}\}_n$  (**1**).

## 1 Experimental

### 1.1 Materials and instruments

The reagents were used as commercial sources without further purification. Elemental analyses were performed on a Perkin-Elmer 240C elemental analyzer. The IR spectra were recorded on Bruker Vector22 FT-IR spectrophotometer using KBr discs. Thermogravimetric analyses were performed on a simultaneous SDT 2960 thermal analyzer under nitrogen with a heating rate of  $10\text{ }^\circ\text{C} \cdot \text{min}^{-1}$ . The luminescent spectra for the solid powdered samples were recorded at room temperature on an Aminco Bowman Series 2 spectrophotometer with xenon arc lamp as the light source. In the measurements of the emission and excitation spectra, the pass width was 4.0 nm. All the measure-

ments were carried out under the same conditions.

### 1.2 Synthesis of the compound 1

Complex **1** was synthesized by solvothermal method in a 16 mL Teflon-lined autoclave by heating a mixture of  $\text{Tb}(\text{NO}_3)_3 \cdot 6\text{H}_2\text{O}$  (0.05 mmol, 23.5 mg),  $\text{CuCl}_2 \cdot 2\text{H}_2\text{O}$  (0.05 mmol, 8.5 mg),  $\text{H}_2\text{INAIP}$  (0.1 mmol, 28.7 mg),  $\text{NaOH}$  (0.15 mmol, 6.0 mg), DMF (5 mL) and ethanol (5 mL) at  $140\text{ }^\circ\text{C}$  for 4 d under autogenous pressure. Cooling the reactor subsequently to room temperature at a rate of  $10\text{ }^\circ\text{C} \cdot \text{h}^{-1}$ , yellow crystals of **1** were obtained. IR ( $\text{cm}^{-1}$ ): 3 424(s), 2 938 (w), 1 662 (m), 1 554(s), 1 526(s), 1 447(s), 1 373(s), 1 240 (m), 1 109 (m), 835 (s), 771 (s), 601 (w). Anal. Calcd. For  $\text{C}_{43}\text{H}_{37}\text{CuTb}_2\text{N}_6\text{O}_{23}$ (%): C, 37.20, H, 2.67, N, 6.06. Found(%): C, 37.28, H, 2.59, N, 6.01. Although the starting materials are copper(II) salts, the Cu center has an oxidation state of +1, attributed to a reduction reaction involving the hydrolyzed DMF molecules, which is consistent with a linear geometry for the  $\text{Cu}^+$  ion.

### 1.3 X-ray crystallography

The X-ray diffraction measurement for **1** was performed on the Bruker Apex-II CCD diffractometer with graphite-monochromated  $\text{Mo K}\alpha$  radiation ( $\lambda = 0.071\ 073\text{ nm}$ ) at room temperature. The data were integrated by using the SAINT program<sup>[17]</sup>, which also did the intensity corrections for Lorentz and polarization effect. An empirical absorption correction was applied using the SADABS program<sup>[18]</sup>. The structures were solved by direct methods using the program SHELXS-97 and all the non-hydrogen atoms were refined anisotropically on  $F^2$  by the full-matrix least-

Table 1 Crystal data and structure parameters for complex 1

Empirical formula	$\text{C}_{43}\text{H}_{37}\text{CuTb}_2\text{N}_6\text{O}_{23}$	$Z$	4
Formula weight	1387.17	Absorption coefficient / $\text{mm}^{-1}$	3.538
Temperature / K	291(2)	$F(000)$	1 360
Crystal system	Triclinic	Crystal size / mm	0.28×0.24×0.22
Space group	$P\bar{1}$	$\theta / (^\circ)$	1.67 to 26.00
$a / \text{nm}$	1.088 79(16)	Reflections collected / unique	12 607 / 8 922 ( $R_{\text{int}}=0.021\ 2$ )
$b / \text{nm}$	1.518 5(2)	Data / restraints / parameters	8 922 / 0 / 676
$c / \text{nm}$	1.565 3(2)	Goodness of fit on $F^2$	1.072
$V / \text{nm}^3$	2.338 1(6)	final $R$ indices ( $I > 2\sigma(I)$ )	$R_1=0.058\ 9$ , $wR_2=0.129\ 2$
$D_c / (\text{g} \cdot \text{cm}^{-3})$	1.970	Largest diff. peak and hole / ( $\text{e} \cdot \text{nm}^{-3}$ )	1 396 and -1 347

Table 2 Selected bond lengths (nm) for complex 1

Cu(1)-N(5)	0.186 5(7)	Cu(1)-N(1E)	0.188 2(7)	Tb(1)-O(9)	0.241 8(5)
Tb(1)-O(10)	0.247 6(5)	Tb(1)-O(2W)	0.240 4(6)	Tb(1)-O(3W)	0.239 7(5)
Tb(1)-O(12)	0.242 7(6)	Tb(1)-O(13)	0.241 4(6)	Tb(1)-O(14A)	0.220 6(6)
Tb(1)-O(15B)	0.228 4(5)	Tb(2)-O(2)	0.227 3(6)	Tb(2)-O(7)	0.256 4(6)
Tb(2)-O(8)	0.244 6(6)	Tb(2)-O(16)	0.226 6(5)	Tb(2)-O(3C)	0.232 7(5)
Tb(2)-O(1W)	0.242 3(5)	Tb(2)-O(4D)	0.257 7(5)	Tb(2)-O(5D)	0.236 6(6)

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

squares technique using the SHELXL-97 crystallographic software package<sup>[19-20]</sup>. Crystal data and structure refinement parameters are listed in Table 1. The selected bond lengths and bond angles are given in Table 2.

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## 2 Results and discussion

### 2.1 Structure description

X-ray diffraction analysis reveals that it is a two-fold interpenetrated 3D heterometallic coordination compound. As illustrated in Fig.1a, there is one Cu(I) atom, two Tb(III) atoms, three INAIP<sup>2-</sup> ligands, one formate anion, three coordinated and three lattice water molecules in the asymmetric unit of **1**. In **1**, both Tb(III) atoms are eight-coordinated in distorted square antiprismatic arrangement with different coordinated environment. Namely, Tb (1) is eight coordinated with six carboxylate groups O atoms (O9, O10, O12, O13, O14A and O15B) from four different INAIP<sup>2-</sup> ligands and two O atoms (O2W, O3W) from two water molecules, while Tb(2) is eight coordinated with seven carboxylate groups O atoms (O2, O7, O8,

O3C, O4D, O5D and O16) from the other four different INAIP<sup>2-</sup> ligands and one formate, the other O atom is (O1W) from one water molecule. When the coordination interactions between the carboxylate group and Cu(I) are omitted, the Cu center has a little distorted linear coordination environment of two N atoms from two INAIP<sup>2-</sup> ligands with the Cu-N bond lengths of 0.186 5(7) and 0.188 2(7) nm, which is similar to that in such reported complex as [Ln<sub>2</sub>(bdc)<sub>2</sub>

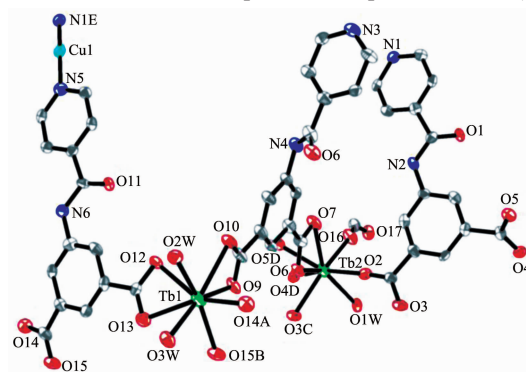
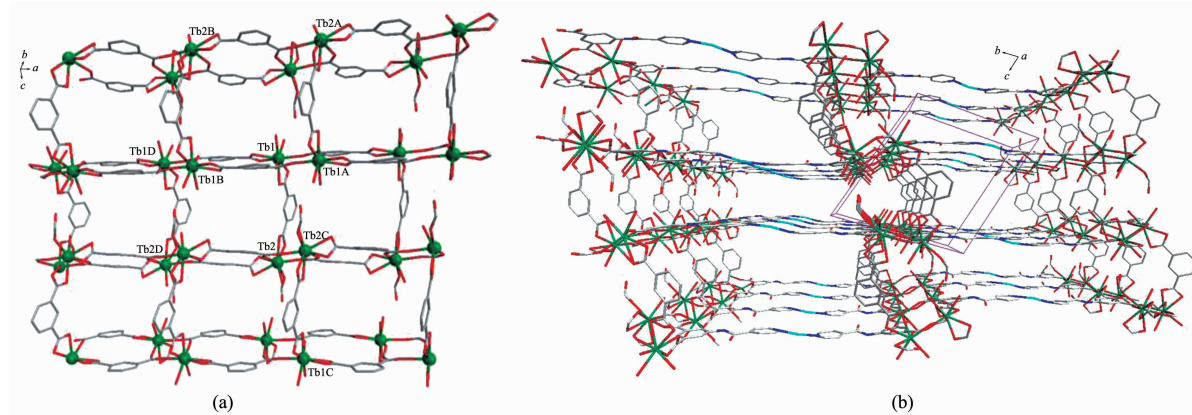


Fig.1 Coordination environment of Cu(I) and Tb(III) in complex **1** with 30% thermal ellipsoids



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

Fig.2 2D bi-layer structure linked by INAIP<sup>2-</sup> ligands and Tb(III) centers (a) and 3D layer-pillered structure (b)

(ina)<sub>2</sub> (H<sub>2</sub>O)<sub>2</sub>Cu<sup>I</sup>·Cl]<sup>[21]</sup>. In complex **1**, it is noted that three INAIP<sup>2-</sup> ligands exhibit two coordination modes, one ligand coordinate to three Tb(III) atoms using its two carboxylate groups in  $\mu_2$ - $\eta^1$ : $\eta^1$ -bimonodentate and  $\mu_1$ - $\eta^1$ : $\eta^1$ -chelate modes and one Cu(I) atom through its pyridyl nitrogen atom, the other only coordinates to two Tb(III) atoms using its two carboxylate groups in the  $\mu_1$ - $\eta^1$ : $\eta^1$ -chelate mode with free coordination of the pyridyl group, which is different from the complexes [LnAg(INAIP)<sub>2</sub>]·3H<sub>2</sub>O<sup>[22]</sup>. If the coordination interactions between the Cu-N and Cu-O are neglected, the neighboring binuclear subunits are connected via the INAIP<sup>2-</sup> ligands to form a two-dimensional (2D) bilayer network (Fig.2a). Then, the 2D layers are further connected together via the Cu-N coordination interactions to generate the 3D layer-pillared framework as illustrated in Fig.2b. It is clear that there is a large 1D channel along the a-axis, in order to minimize the hollow cavities and stabilize the framework, the potential voids formed via a single 3D framework show combination with another identical one, giving a two-fold interpenetrated structure of **1**.

To get better insight into the intricate framework structure of **1**, topological analysis was carried out. As described above, each Tb<sub>2</sub> is surrounded by six INAIP<sup>2-</sup> ligands, so each Tb<sub>2</sub> subunit is a six-connected node. On the other hand, since the INAIP<sup>2-</sup> ligand links two Tb<sub>2</sub> subunits and one Cu(I) atom, it can be considered as a three-connecting node. Consequently, according to the calculation of TOPOS<sup>[23]</sup>, the final framework of **1** belongs to a binodal (3, 6)-connected

two-fold **sqc27** type of topology net, with Schflfi symbol of (4·6<sup>2</sup>)<sub>2</sub>(4<sup>4</sup>·6<sup>10</sup>·8<sup>3</sup>) (Fig.3).

## 2.2 IR and photoluminescence property

The infrared spectra of the title complexes have been recorded and some important assignments are shown above. No strong IR band from -COOH appeared at nearly 1 700 cm<sup>-1</sup>, indicating that the H<sub>2</sub>INAIP ligands are entirely protonated in it, and peaks at 3 424 cm<sup>-1</sup> could be assigned to characteristic peaks of the  $\nu$ (O-H) absorptions of water molecules. These IR results are coincident with the crystallographic structural analyses. The thermogravimetric analysis (TGA) of **1** reveals that there are three stages of weight loss in the temperature range of 20 ~650 °C (Fig.4). The first stage, occurring between 20 and 95 °C, is attributed to the loss of three free water molecules per formula (observed weight loss 3.90%; calcd. 3.90%). The second stage, occurring from 95 to 160 °C, is attributed to the loss of three coordinated water molecules per formula (observed weight loss 3.94%; calcd. 3.90%). After the loss of all the water molecules, the supramolecular framework is stable up to 300 °C, followed by another weight loss at high temperature.

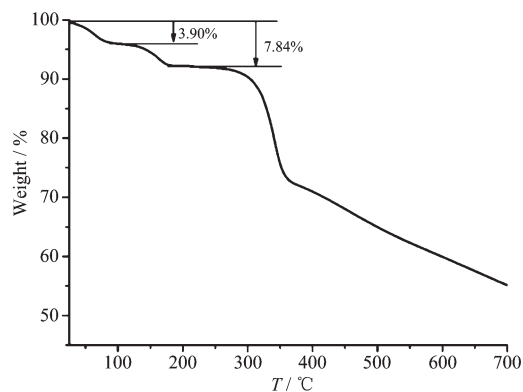


Fig.4 TGA curve of complex **1**

Due to the excellent luminescent properties of Tb(III) ions, the room temperature photoluminescence in the solid state of **1** was investigated. The emission spectrum of **1** (Fig.5) upon excitation at 362 nm exhibits the characteristic transitions of  $^5D_4 \rightarrow ^7F_J$  ( $J=3\sim 6$ ) of Tb(III), which the bands are at 490, 543, 585 and 622 nm can be attributed to the corresponding transitions<sup>[24,25]</sup>. The most intense transition is  $^5D_4 \rightarrow ^7F_3$  at 543 nm, which implies green emission light of **1**.

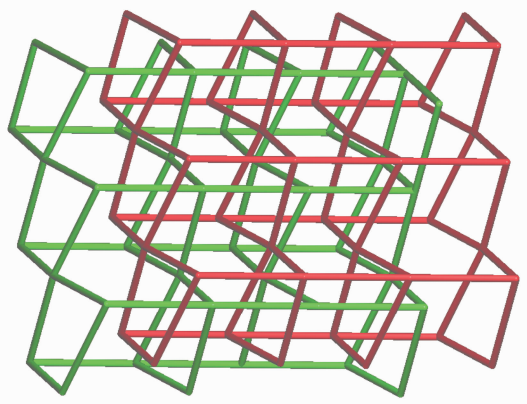
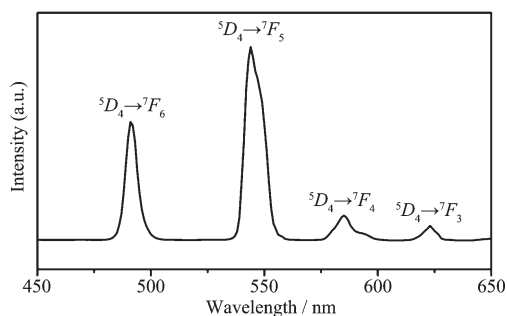


Fig.3 Topologically representation of the two-fold interpenetrated **sqc27** structure of **1**

Fig.5 Solid-state emission spectrum of the title complex **1**

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