

具有新颖拓扑结构的吡啶基羧酸配体钇配合物的合成、晶体结构和拓扑学分析

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摘要: 利用水热合成制备了一个新的吡啶基多羧酸钇配合物 $Y_L(HL) \cdot 2H_2O$ (**1**) ($H_2L=5-((\text{吡啶基}-3\text{-亚甲基})\text{氨基})\text{间苯二甲酸}$)。利用元素分析及 X-射线单晶衍射对其进行了表征。结构分析结果表明标题化合物 **1** 属于三斜晶系, $P\bar{1}$ 空间群, 晶胞参数为 $a=1.015\ 35(11)\ \text{nm}$, $b=1.083\ 33(12)\ \text{nm}$, $c=1.287\ 40(14)\ \text{nm}$, $\alpha=70.9430(10)^\circ$, $\beta=127.689(3)^\circ$, $\gamma=84.0680(10)^\circ$, 晶胞体积 $V=1.317\ 0(2)\ \text{nm}^3$, $Z=2$, $D_c=1.680\ \text{g} \cdot \text{cm}^{-3}$, $F(000)=680$, $\mu=2.284\ \text{cm}^{-1}$, $R=0.056\ 2$, $wR=0.1600$ 。在化合物 **1** 中, 每个 Y 的配位环境为八配位的反四棱柱配位构型。该配合物的二维结构是少见的 $(4^2.6)(4^2.6^7.8)$ 层状拓扑。我们对配合物 **1** 的粉末衍射数据和热重分析也进行的讨论。

关键词: 晶体结构; 钇配合物; 拓扑; 羧酸配体

中图分类号: O614.32²

文献标识码: A

文章编号: 1001-4861(2012)11-2407-06

An Yttrium(III) Complex Based on Pyridyl-Carboxylate Ligand Exhibiting Distinctive New Topology

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Abstract: By using hydrothermal method, the reaction of 5-((pyridine-3-ylmethyl)amino)isophthalic acid (H_2L) with yttrium nitrate led to the formation of a novel yttrium(III) complex, namely, $Y_L(HL) \cdot 2H_2O$ (**1**), with interesting two-dimensional (2D) topology. The title complex was characterized by elemental analysis and IR spectroscopy and its structure was determined by single crystal X-ray structural analysis. The result of structural analysis shows that the **1** crystallizes in triclinic, space group $P\bar{1}$ with $a=1.015\ 35(11)\ \text{nm}$, $b=1.083\ 33(12)\ \text{nm}$, $c=1.287\ 40(14)\ \text{nm}$, $\alpha=70.9430(10)^\circ$, $\beta=127.689(3)^\circ$, $\gamma=84.0680(10)^\circ$, $V=1.317\ 0(2)\ \text{nm}^3$, $Z=2$, $D_c=1.680\ \text{g} \cdot \text{cm}^{-3}$, $F(000)=680$, $\mu=2.284\ \text{cm}^{-1}$, $R=0.056\ 2$, $wR=0.160\ 0$. The Y(III) atoms was eight-coordinated with carboxylate O atoms in square-antiprismatic geometry. In complex **1**, the 2D layer comprised of μ_2/μ_3 -ligands and 5-connected Y(III) centers is rare example of 2-nodal net of $(4^2.6)(4^2.6^7.8)$ topology. The XPRD and TGA analysis were also investigated. CCDC: 864386.

Key words: crystal structure; Y(III) complex; topochemistry; carboxylate ligand

收稿日期: 2012-02-16。收修改稿日期: 2012-06-26。

国家自然科学基金(No.20901004, 20801025)资助项目。

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0 Introduction

During the past decades, rational design and construction of novel complexes with diverse structures, especially interesting topologies, and applications have attracted more and more attentions of chemists^[1-3]. Many research groups have devoted their efforts on the development, design, and synthesis of novel metal-organic frameworks (MOFs) and significant results have been achieved by using transition/lanthanide metal salts and corresponding organic ligands^[4-6]. On the other side, mimicking of natural minerals topologies and constructions of novel complexes with new interesting topologies have attracted more and more attentions of chemists. Because of the limitations in the symmetry or steric hindrance associated with connected nodes, the use of five-, seven-, or eight-connected blocks are quite rare with comparing to the connectivity of three-, four-, or six-connected blocks^[7-8]. Up to now, although various complexes with fascinating structural diversities as well as their interesting properties have been synthesized, controllable synthesis of metal-organic frameworks (MOFs) with designed structure is still a great challenge^[9-11].

We concentrate our efforts on design and construction of MOFs with interesting topologies and properties by using N- or O-containing ligands^[12,13]. According to different coordination affinities of N, O atoms for transition and lanthanide metals, the system composed of ligands containing both N, O as coordination donors, like the pyridyl-carboxylate ligands, are now often used to synthesize heterometallic *d-f* metal complexes^[14,15]. In order to further investigate the self-assemblies of pyridyl-carboxylate with transition/lanthanide metal salts, we used pyridyl-containing carboxylate ligand, namely, 5-((pyridin-3-ylmethyl)amino)isophthalic acid (H_2L) as starting ligand. Due to the flexibility resulting from the methylene group and varied coordination modes of carboxylate groups, crystals with diverse structures, especially interesting topologies, can be easily formed. In this paper, we report a coordination framework with interesting new

topology based on N,O-bifunctional pyridyl-carboxylate ligand and yttrium metal salt, namely, $YL(HL) \cdot 2H_2O$ (**1**) ($H_2L=5-((\text{pyridine-3-ylmethyl})\text{amino})\text{isophthalic acid}$), which may provide useful strategy for construction of new coordination frameworks.

1 Experimental

1.1 General

All chemicals and solvents in this work were commercially obtained and used as received without further purification. The concerning ligand 5-((pyridine-3-ylmethyl)amino)isophthalic acid was synthesized according to the reported literatures^[12-13]. C, H and N analyses were made on Elementar Vario EL-III elemental analyzer. Infrared (IR) spectrum was recorded on Avatar 360 FT-IR spectrophotometer by using KBr disc. Powder X-ray diffraction patterns were recorded on a RigakuD/max-RA rotating anode X-ray diffractometer with graphite monochromatic $Cu K\alpha$ ($\lambda=0.154\ 2\ \text{nm}$) radiation at room temperature. Thermogravimetric analysis was performed on a simultaneous NETZSCH STA 409 PC LUX thermal analyzer. Powder samples were loaded into alumina pans and heated under flowing N_2 at a heating rate of $10\ ^\circ\text{C} \cdot \text{min}^{-1}$.

1.2 Structure determinations

A suitable single crystal of **1** with dimensions of $0.15\ \text{mm} \times 0.10\ \text{mm} \times 0.10\ \text{mm}$ was selected for data collection at 293 K, using a Bruker Smart Apex II CCD equipped with a $Mo K\alpha$ radiation ($\lambda=0.071\ 073\ \text{nm}$). The structures were solved by direct methods using SHELXTL and refined by full-matrix least-squares methods anisotropically for non-hydrogen atoms^[16]. The hydrogen atoms except for those of water molecules were generated geometrically. Calculations were performed on a personal computer with the SHELXTL program package^[16]. Details of the crystal parameters, data collection, and refinement are summarized in Table 1. Selected bond lengths and angles of complexes **1** with their estimated standard deviations are listed in Table 2 and hydrogen bonding distances are given in Table 3.

CCDC: 864386.

Table 1 Crystallographic data for complex 1

Empirical formula	C ₂₈ H ₂₅ N ₄ O ₁₀ Y	Z	2
Formula weight	666.43	D _c / (g·cm ⁻³)	1.68
Temperature / K	293(2)	Absorption coefficient / cm ⁻¹	2.284
Crystal system	Triclinic	F(000)	680
Space group	<i>P</i> $\bar{1}$	θ range / (°)	1.69~25.00
<i>a</i> / nm	1.015 35(11)	Reflections collected	9 361
<i>b</i> / nm	1.083 33(12)	Independent / observed reflections	4 584 / 4 094
<i>c</i> / nm	1.287 40(14)	<i>R</i> _{int}	0.022 4
α / (°)	70.943 0(10)	Goodness of-fit on <i>F</i> ²	1.05
β / (°)	80.153 0(10)	<i>R</i> (<i>I</i> >2 σ (<i>I</i>))	0.056 2
γ / (°)	84.068 0(10)	<i>wR</i> (<i>I</i> >2 σ (<i>I</i>)) ^a	0.160 0
<i>V</i> / nm ³	1.317 0(2)		

^a $w=1/[\sigma^2(F_o^2)+(0.125\ 0P)^2+1.645\ 6P]$ where $P=(F_o^2+2F_c^2)/3$.

Table 2 Selected bond lengths (nm) and bond angles (°) for complex 1

Y1-O1	0.241 3(4)	Y1-O2	0.238 1(4)	Y1-O3 ^{#1}	0.222 8(4)
Y1-O4 ^{#2}	0.222 3(4)	Y1-O5	0.242 3(3)	Y1-O6	0.238 6(3)
Y1-O7 ^{#3}	0.247 9(6)	Y1-O8 ^{#3}	0.233 8(4)		
O1-Y1-O2	53.56(12)	O1-Y1-O3 ^{#1}	129.45(13)	O1-Y1-O4 ^{#2}	149.04(14)
O1-Y1-O5	87.31(16)	O1-Y1-O6	73.17(12)	O1-Y1-O7 ^{#3}	87.7(2)
O1-Y1-O8 ^{#3}	79.8(2)	O2-Y1-O3 ^{#1}	75.99(13)	O2-Y1-O4 ^{#2}	156.15(16)
O2-Y1-O5	87.05(16)	O2-Y1-O6	115.49(14)	O2-Y1-O7 ^{#3}	84.5(2)
O2-Y1-O8 ^{#3}	117.99(19)	O3 ^{#1} -Y1-O4 ^{#2}	81.33(14)	O3 ^{#1} -Y1-O5	93.84(16)
O3 ^{#1} -Y1-O6	142.74(15)	O3 ^{#1} -Y1-O7 ^{#3}	84.07(19)	O3 ^{#1} -Y1-O8 ^{#3}	128.51(18)
O4 ^{#2} -Y1-O5	87.2(2)	O4 ^{#2} -Y1-O6	78.99(15)	O4 ^{#2} -Y1-O7 ^{#3}	100.5(2)
O4 ^{#2} -Y1-O8 ^{#3}	82.1(2)	O5-Y1-O6	54.05(12)	O5-Y1-O7 ^{#3}	171.54(17)
O5-Y1-O8 ^{#3}	133.49(14)	O6-Y1-O7 ^{#3}	130.49(13)	O6-Y1-O8 ^{#3}	79.46(13)
O7 ^{#3} -Y1-O8 ^{#3}	51.96(15)				

Symmetric code: ^{#1} -*x*+1, -*y*+1, -*z*+1; ^{#2} -*x*+1, *y*-1/2, -*z*+1/2; ^{#3} *x*-1, *y*, *z*.

Table 3 Hydrogen bond lengths and bond angles

D-H...A	<i>d</i> (D-H) / nm	<i>d</i> (H...A) / nm	<i>d</i> (D...A) / nm	\angle DHA/(°)
O1W-H1WA...O1 ^{#1}	0.085	0.227	0.312 2(8)	176
O1W-H1WB...O8 ^{#2}	0.085	0.233	0.317 6(7)	176
O2W-H2WA...O5 ^{#3}	0.085	0.216	0.298 6(9)	165
O2W-H2WB...O7 ^{#4}	0.085	0.252	0.334 4(10)	165
N1-H1...O1W ^{#5}	0.086	0.228	0.304 3(7)	147
N2-H2A...O7 ^{#6}	0.086	0.232	0.315 5(12)	164
N3-H3...O1 ^{#7}	0.086	0.244	0.318 2(6)	146

Symmetry transformation used to generate equivalent atoms: ^{#1} -*x*, 1-*y*, 1-*z*; ^{#2} -1+*x*, *y*, *z*; ^{#3} *x*, *y*, -1+*z*; ^{#4} 1-*x*, 1-*y*, 1-*z*; ^{#5} *x*, -1+*y*, *z*; ^{#6} 1-*x*, -*y*, 1-*z*; ^{#7} 1-*x*, 1-*y*, 1-*z*.

1.3 Synthesis of YL(HL)·2H₂O (1)

To a suspension of H₂L (40.8 mg, 0.15 mmol) in 15 mL water was added Y(NO₃)₃·6H₂O (38.3 mg, 0.1

mmol) and LiOH (0.012 g, 0.30 mmol). After being stirred for 30 min, the resulting solution was sealed into a bomb equipped with a Teflon liner and heated

at 100 °C for 72 h. After slow cooling of the reaction mixture to room temperature, pale yellow crystals of **1** were obtained in ca. 40% yield. Anal. Calcd. for compound **1**, $C_{28}H_{25}N_4O_{10}Y$ (%): C 50.46, H 3.79, N 8.41; found(%): C 50.74, H 3.62, N 8.35. FT-IR (KBr pellet, cm^{-1}): 3 450 br, 1 702 m, 1 633 m, 1 606 m, 1 543 vs, 1 428 s, 1 410 s, 1 386 vs, 1 258 s, 1 109 w, 1 044 w, 742 m, 624 m.

2 Results and discussion

2.1 Structure description

Crystals of structure **1** form under hydrothermal condition as air-stable pale yellow blocks. The crystallographic analysis reveals that the compound crystallizes in triclinic system, space group $P\bar{1}$. The asymmetric unit of **1** consists of one yttrium atom, two ligands, and two distinct water molecules (Fig.1). In complex **1**, the Y(III) ions are eight-coordinated by carboxylic O atoms from five different ligands with Y-O bond lengths varying from 0.222 3(4) to 0.247 9(4) nm, which is comparable to other reported Y-O distances^[17]. The O-Y-O coordination angles are in the range of 51.96(15)° to 171.54(17)°. Thus, the coordination environment around the Y(III) ions can be regarded as distorted square-antiprismatic geometry. There are two kinds of ligands in the structure of **1**: (1) One links three different Y(III) ions (μ_3 -L), whose carboxylate groups adopt μ_2 - η^1 : η^1 and μ_1 - η^1 : η^1 coordination modes, respectively (e.g. the ligands containing O1, O2, O3 and O4), and the dihedral angle between the pyridine ring and benzene ring is 5.5°.

(2) The other ligands (e.g. the ligands containing O6, O5, O7 and O8) serve as μ_2 -pillar linking two Y(III) atoms, where the two carboxylate groups all adopt μ_1 - η^1 : η^1 coordination mode, and the corresponding dihedral angle between pyridine and benzene is 80.6°.

In **1**, with ignoring the coordination of the μ_2 -ligand, each μ_3 -L connects three yttrium atoms and each Y(III) links three different μ_3 -L to form a one dimensional (1D) ladder-like structure with Y...Y distances of 0.557 and 0.822 nm, respectively (Fig. 2). The chain units were further connected by μ_2 -ligands to form a two-dimensional network (Fig.3), which stack along the ac plane to give the whole three-dimensional framework. In addition, the adjacent pyridine rings of the μ_2 - and μ_3 -ligand on the same sheet as well as the pyridine rings and benzene rings of adjacent net are offset stacked with centroid...centroid distances of 0.349, 0.360, 0.351 nm and dihedral angles of 2.88°, 5.94°, 5.24°, respectively, indicating strong $\pi \cdots \pi$ interactions between these aromatic groups, which play important roles in the stabilization the 2D and 3D structure of **1** (Fig.4). Although the N donors did not coordinate to any metal ions in **1**, probably due to the “hard-soft acid-base” theory, they are still important by forming hydrogen bonds to stabilize the whole framework of the title complex (Table 3). Meanwhile, the uncoordinated water molecules occupy the voids between the 2D layers and form O-H...O hydrogen bonds with corresponding carboxylate O atoms, which also further

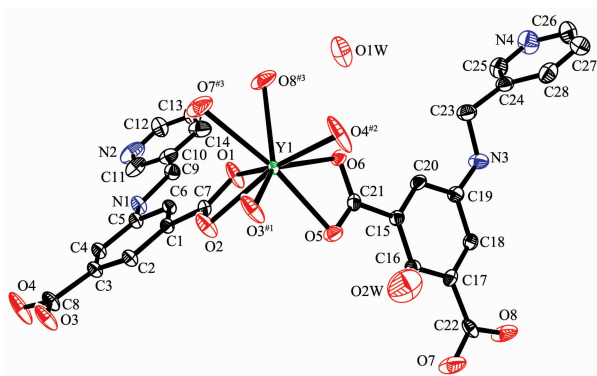


Fig.1 Asymmetric unit of complex **1**, with additional atoms completing the coordination environments of yttrium atom

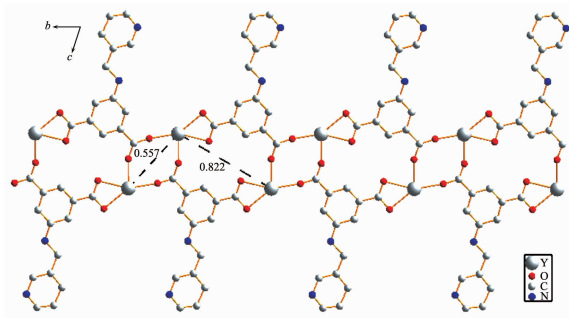


Fig.2 One-dimensional chain in **1** with Y...Y distances marked (nm) viewing along the *a* axis

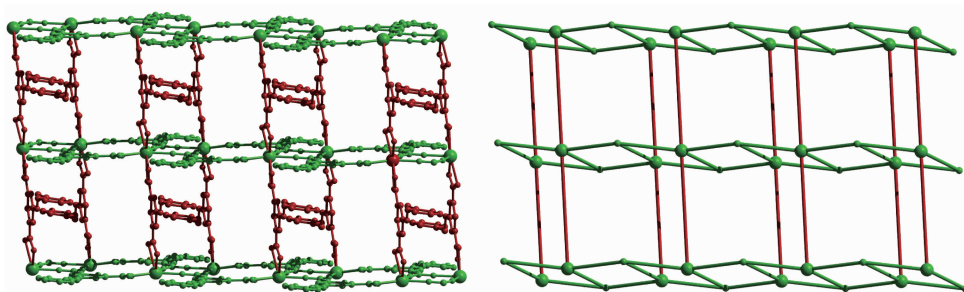
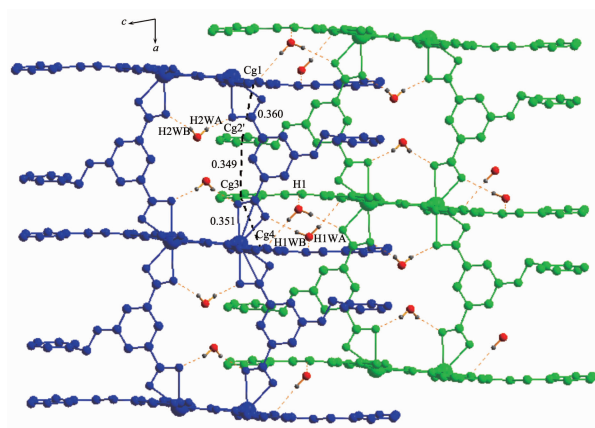


Fig.3 (Left) Two dimensional net structure of **1**; (right) schematic drawing of the 2D $(4^2.6)(4^2.6^7.8)$ topological sheet in **1**, where the μ_3 -ligand and Y(III) atoms are represented by three- and five- spokes radiation from a solid point, respectively



Corresponding H atoms and centers of aromatic rings were also marked

Fig.4 Three-dimensional framework stacked by 2D sheets in **1** viewing along the *b* axis, in which the hydrogen bonds and $\pi \cdots \pi$ interactions were also marked (nm)

stabilize the stacks of these 2D sheets (Table 3, Fig.5)^[18].

Topological study performed using the software package TOPOS 4.0^[19] reveal that this topology is an interesting two-nodal net. In **1**, each yttrium (III) connects five different ligands, while each ligand links three or two metal centers. Thus, the μ_3 -ligand and Y (III) units can be defined as 3- and 5-connected nodes, respectively. In the simplification way, with the μ_2 -ligand simplified as a pillar, the 2D network of **1** can be described as a two nodal 3,5-c net of $(4^2.6)(4^2.6^7.8)$ topology with “long” Schläfli symbol $(4.4.6_3)(4.4.6_3.6_3.6_3.6_4.6_4.8_{10})$, which is, to the best of our knowledge, a rare example of such topological 2D network.

2.2 XPRD and thermogravimetric analysis

The XPRD analysis of **1** has been performed to evaluate the purity of the as-synthesized sample of **1**. As shown in Fig.5, the positions of diffraction peaks

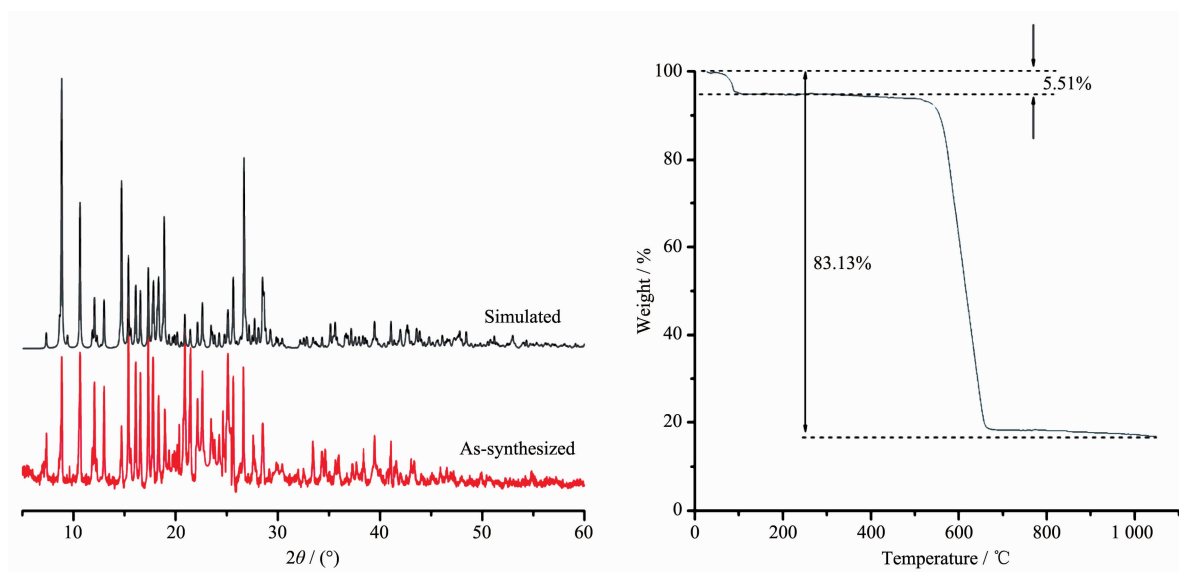


Fig.5 (Left) XPRD pattern and (right) TGA curve of complex **1**

are consistent with the simulated ones, indicating the phase purity of the as-synthesized sample.

The Thermogravimetric analysis of complex **1** was carried out in the range 20~1 100 °C under nitrogen atmosphere. The TGA data show that the initial weight loss of 5.51% (Calcd. 5.40%) occurred from 30 to 102 °C corresponding to the loss of the coordinated water molecules and the second begins at 360 °C where the decomposition of the residue starts with total weight loss of 83.13% (Calcd. 83.06% based on Y₂O₃).

3 Conclusions

In summary, by using pyridyl-carboxylate ligand and yttrium(III) nitrate, we successfully synthesized a novel polymer exhibiting interesting new 2D sheet structure of (4².6)(4².6⁷.8) topology, in which the metal centers acted as rare five-connecting blocks. The whole 3D framework of **1** was stabilized by abundant $\pi\cdots\pi$ and hydrogen bond interactions. This work may offer a strategy for preparing such MOFs with new topologies.

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