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基于{Er_2}和{Cu_2}单元构建的超分子网络

方伟慧　王志龙　杨国昱*

(中国科学院福建物质结构研究所,结构化学国家重点实验室,福州　350002)

摘要：利用水热法成功合成了一个新颖的稀土–过渡金属有机骨架 $Er(pyba)_3(H_2O)_2CuI$(Hpyba=4-吡啶-3-苯甲酸),并通过元素分析、红外光谱、X-射线粉末衍射、单晶 X-射线衍射及热分析等对其进行了表征。结构分析表明:2 种不同的{Er_2}和{Cu_2}单元经配体连接形成一维链,这些一维链通过氢键和 π-π 堆积作用进一步连接形成三维超分子网络。

关键词：水热；稀土–过渡金属有机骨架；一维链；铜；铒

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A Supramolecular Network Constructed from {Er_2} and {Cu_2} Units

FANG Wei-Hui　WANG Zhi-Long　YANG Guo-Yu*

(*State Key Laboratory of Structural Chemistry, Fujian Institute of Research on the Structure of Matter, Chinese Academy of Sciences, Fuzhou* 350002)

Abstract: A novel transition-lanthanide-organic chain, $Er(pyba)_3(H_2O)_2CuI$ (Hpyba=4-pyridin-3-yl-benzoic acid), has been hydrothermally synthesized and structurally characterized. Structure analysis shows that two types of units, {Er_2} and {Cu_2}, interconnect each other by ligands to form 1D chains, which are further linked by hydrogen bond and π-π stacking interactions to form a 3D supramolecular network. CCDC: 778355.

Key words: hydrothermal; transition-lanthanide-organic; one-dimentional chain; erium; copper

The current increasing interest in the construction of 3*d*-4*f* heterometallic complexes has been significantly provoked not only by their impressive structural diversity in architectures but also by the versatile applications in optoelectronic, magnetic, and porous materials[1-5]. As a result, a large number of 3*d*-4*f* heterometallic complexes[6-10] have been successfully synthesized, especially lanthanide-copper (Ln-Cu) coordination polymers[11-21]. Previously, our group reported a series of Ln-Cu frameworks[16-21] by isonicotinic acid (Hin), a rigid linear ligand containing O and N donors on the opposite sides, which can construct the extended frameworks with high structural stability and special topologies.

As a continuation of our search for new transition metal (TM)-Ln organic frameworks built by Ln and TM clusters, we chose 4-pyridin-3-yl-benzoic acid (Hpyba) as the multifunctional bridging ligand based on the following considerations: (1) It is a rigid ligand with oxygen and nitrogen donors on opposite sides, enabling the ligand to act as a linear bridge. (2) The carboxyl group may induce the oxophilic lanthanide ions to undergo hydroxo lanthanide cluster aggregation, the nitrogen atoms can coordinate to TM ions, and thus

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*通讯联系人。E-mail:ygy@fjirsm.ac.cn;会员登记号:01M030311215。

第一作者:方伟慧,女,28 岁,博士研究生,会员登记号:01P090421728;研究方向:金属–氧簇化学。

extended solids containing hydroxo lanthanide cluster cores and TM ions might be obtained. (3) Hpyba as a lengthened ligand may lead to more open frameworks under rationally hydrothermal conditions. Here we report the first 3*d*-4*f* lanthanide-organic frameworks Er(pyba)$_3$(H$_2$O)$_2$CuI constructed by 4-pyridin-3-yl-benzoic acid ligand.

1 Experimental

1.1 Materials and instrumentation

All chemicals were commercially purchased and used without further purification. IR spectra (KBr pellets) were recorded on an ABB Bomem MB102 spectrometer over a range 400~4 000 cm^{-1}. Powder X-ray diffraction (PXRD) data were collected on a Rigaku Mini FlexII diffractometer using Cu *Kα* radiation (λ = 0.154 056 nm) under ambient conditions. The thermogravimetric analysis was performed on a Mettler Toledo TGA/SDTA 851^e analyzer in air atmosphere with a heating rate of 10 ℃·min^{-1} from 30 to 1 000 ℃. The elemental analysis was carried out using the combustion method on an Elemental Vario EL Ⅲ CHNOS elemental analyzer.

1.2 Synthesis of Er(pyba)$_3$(H$_2$O)$_2$CuI (1)

A mixture of Er_2O_3 (0.4 mmol, 0.150 0 g), CuI (0.4 mmol, 0.076 0 g), Hpyba (2 mmol, 0.398 7 g), H_2O (10.0 mL, 0.22 mmol) and one drop of $[Et_3NH][HSO_4]$[22] with the pH value of about 2.0 was sealed in a 30 mL Teflon-lined bomb at 190 ℃ for 7 d, and then cooled to room temperature. Yellow prismatic crystals of **1** were recovered by filtration, washed with distilled water and dried at ambient temperature (yield 45% based on Er_2O_3). Elemental Analysis: Calcd. for $C_{36}H_{28}CuErIN_3O_8$ (%): C 43.71, H 2.83, N 4.25; found (%): C 43.19, H 2.81, N 4.09.

1.3 Crystal structure determination

The intensity data was collected on a Scxmini CCD diffractometer with a graphite-monochromatized Mo *Kα* (λ =0.071 073 nm) radiation at room temperature. All absorption correction were performed using the SADABS program. The structure was solved by direct methods and refined by full-matrix least squares on F^2 with the SHELX-97 program[23]. All hydrogen atoms bond C were generated geometrically, H atoms associated with water molecules were located in a difference Fourier map and refined with fixed isotropic displacement parameters.

Crystal data for **1**: $C_{36}H_{28}CuErIN_3O_8$, triclinic, space group $P\bar{1}$, M_r=988.31, a=0.840 9 (2) nm, b=1.428 1(4) nm, c=1.572 5(2) nm, α=74.150(1)°, β=77.635(1)°, γ=73.832(1)°, V=1.725 2(7) nm^3, Z=2, F(000)=958, T=298 K, D_c=1.902 g·cm^{-3}, 15 099 reflections measured, 7 791 unique (R_{int}=0.047 6), 6 373 observed reflections with $I>2\sigma(I)$, R_1=0.063 1, wR_2=0.186 2, S=1.027. the highest difference peak and the deepest hole is 1 590 and −1 690 e·nm^{-3}. Selected bond distance and angle data for **1** is listed in Table 1. The experimental PXRD pattern of **1** corresponds well with the simulated pattern (Fig.1), revealing the purity of the compound.

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Table 1 Selected bond distances (nm) and angles (°) for 1

Er-O(1)	0.240 8(5)	Er-O(3)	0.239 2(5)	Cu-I	0.260 1(6)
Er-O(1W)	0.239 0(5)	Er-O(4)	0.239 6(6)	Cu-I^{ii}	0.266 0(3)
Er-O(2)	0.232 2(6)	Er-O(5)	0.230 2(6)	Cu-N(2)^{i}	0.212 1(7)
Er-O(2W)	0.230 7(5)	Er-O(6)^{i}	0.226 3(5)	Cu-N(3)	0.208 1(8)
O(1W)-Er-O(1)	126.0(2)	O(4)-Er-O(1)	84.4(2)	C(1)-O(1)-Er	90.9(4)
O(1W)-Er-O(3)	74.7(2)	O(5)-Er-O(1)	73.5(2)	C(1)-O(2)-Er	94.0(4)
O(1W)-Er-O(4)	128.8(2)	O(5)-Er-O(1W)	72.7(2)	C(13)-O(3)-Er	92.7(5)
O(2)-Er-O(1)	54.8(2)	O(5)-Er-O(2)	79.2(2)	C(13)-O(4)-Er	92.3(5)
O(2)-Er-O(1W)	78.3(2)	O(5)-Er-O(2W)	83.8(2)	C(25)-O(5)-Er	138.6(6)
O(2)-Er-O(3)	77.2(2)	O(5)-Er-O(3)	142.9(2)	C(25)-O(6)-Er^{i}	159.3(5)
O(2)-Er-O(4)	94.9(2)	O(5)-Er-O(4)	156.4(2)	N(2)^{i}-Cu-Cu^{ii}	134.7(2)

Continued Table 1

O(2W)-Er-O(1)	85.7(2)	O(6)^{i}-Er-O(1)	160.1(2)	N(2)^{i}-Cu-I	112.6(2)
O(2W)-Er-O(1W)	130.0(2)	O(6)^{i}-Er-O(1W)	71.1(2)	N(2)^{i}-Cu-I^{ii}	108.8(2)
O(2W)-Er-O(2)	140.0(2)	O(6)^{i}-Er-O(2)	145.1(2)	N(3)-Cu-Cu^{ii}	127.0(2)
O(2W)-Er-O(3)	131.8(2)	O(6)^{i}-Er-O(2W)	74.5(2)	N(3)-Cu-I	111.1(2)
O(2W)-Er-O(4)	86.5(2)	O(6)^{i}-Er-O(3)	78.8(2)	N(3)-Cu-I^{ii}	104.1(2)
O(3)-Er-O(1)	113.6(2)	O(6)^{i}-Er-O(4)	91.4(2)	Cu-I-Cu^{ii}	60.12(4)
O(3)-Er-O(4)	54.5(2)	O(6)^{i}-Er-O(5)	106.6(2)	I-Cu-I^{ii}	119.88(4)

Symmetry transformations: ^{i} $-x+2, -y+1, -z$; ^{ii} $-x+4, -y, -z-1$.

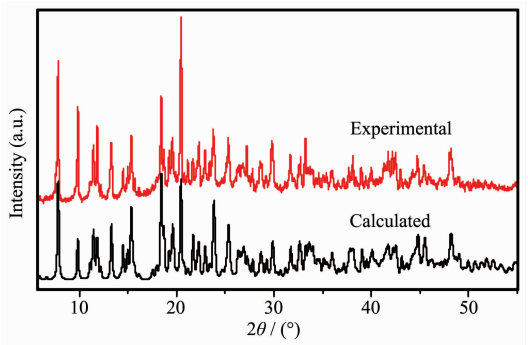


Fig.1　Calculated and experimental XRD powder patterns of compound **1**

2　Results and discussion

2.1　Synthesis

In order to construct 3*d*-4*f* heterometallic structures, cuprous halide was adopted as a 3*d*-component, lanthanide oxide, rather than lanthanide salts, as the source of lanthanides, and 4-pyridin-3-yl-benzoic acid as an organic ligand which shows good coordinating appetency to lanthanide and transition metals under hydrothermal conditions. The acidity of the mixed solution must be adjusted carefully to pH=2 by adding [Et_3NH][HSO_4] and the pH of the final solution turned into 4.9 after heating at 190 ℃ for 7 d. [Et_3NH][HSO_4] is crucial for the formation of **1**, no single crystals were obtained without it or using other acid, such as H_2SO_4, HAc and $HClO_4$, under similar conditions.

2.2　Crystal structures

As shown in Fig.2, the asymmetric unit of **1** contains one unique Er^{3+} ions, one Cu^{+}, one I^{-}, two coordinated water molecules and three pyba^{-} ligands with three different coordination modes in the ratio of 1∶1∶1 (Scheme 1). Er1 ion is eight-coordinated, and the coordination geometry is close to that of a bicapped trigonal prism: six O_{COO}^{-} (O1/O2 in mode Ⅰ, O3/O4 in mode Ⅱ, O5/O6 in mode Ⅲ) from three pyba^{-} ligands and two coordinated water (O1w, O2w). Two Er^{3+} ions are linked by -O5-C25-O6- to give a unit of {$Er_2(COO^{-})_2$} that was further stabilized by six carboxyl groups of six pyba^{-} ligands, forming a {Er_2} unit (Fig.3a). The Er-O bond distances range from 0.226 3(5) to 0.240 8(5) nm. The Cu^{+} ion is four-coordinate in distorted tetrahedral geometry, comprising two μ_2-I atoms and two N atoms from two bridging pyba^{-} ligands. Two Cu^{+} ions are bridged by edge-sharing two μ_2-I atoms to form a {Cu_2} unit, which coincides with our former work[24] and then bonds to four N atoms of four pyba^{-} ligands (Fig.3b).

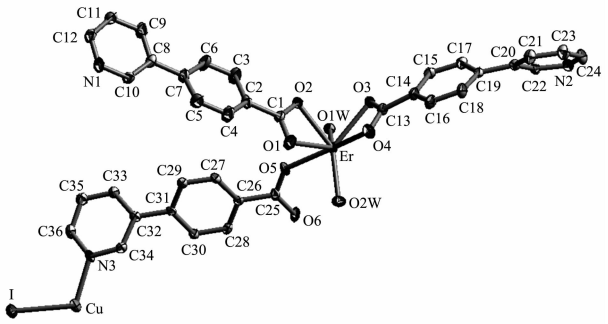
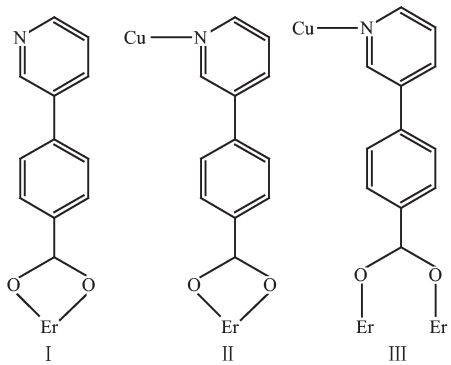


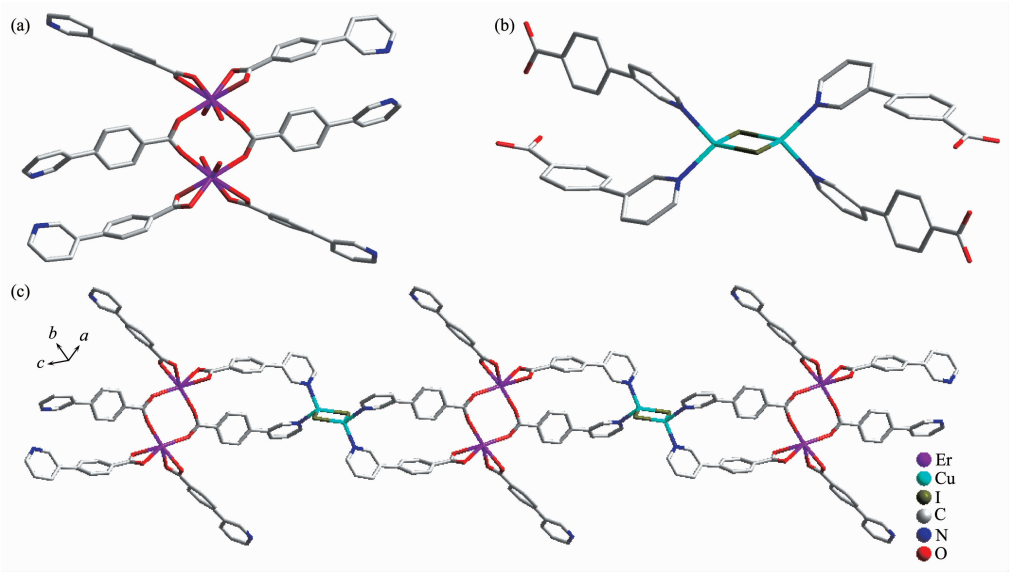
Fig.2　ORTEP view (30% thermal ellipsoids) showing the crystal structure of **1**



Scheme 1　Coordination modes of the pyba^{-} ligands in **1**

The Cu-N and Cu-I bond lengths vary from 0.208 1(8)~0.212 1(7) and 0.260 1(6)~0.266 0(3) nm, respectively. These values are consistent with the reported literatures[16-21]. In the structure, the $\{Er_2\}$ and $\{Cu_2\}$ units connected each other through four $pyba^-$ ligands, two in mode Ⅱ and two in mode Ⅲ, result in a 1D chain (Fig.3c). The deprotonated $pyba^-$ ligands in mode Ⅰ are regularly appended up and down of the 1D chain, linked via carboxylate oxygen atoms from ligands.

There are obvious H-bonded interactions in the structure of compound **1** (Table 2). The 1D chains converted into 2D network structure by intermolecular



Coordinated water are omit for clarity

Fig.3 (a) Coordination enviroments of $\{Er_2\}$ unit; (b) Coordination enviroments of $\{Cu_2\}$ unit; (c) View of the 1D chain based on $\{Er_2\}$ and $\{Cu_2\}$ units

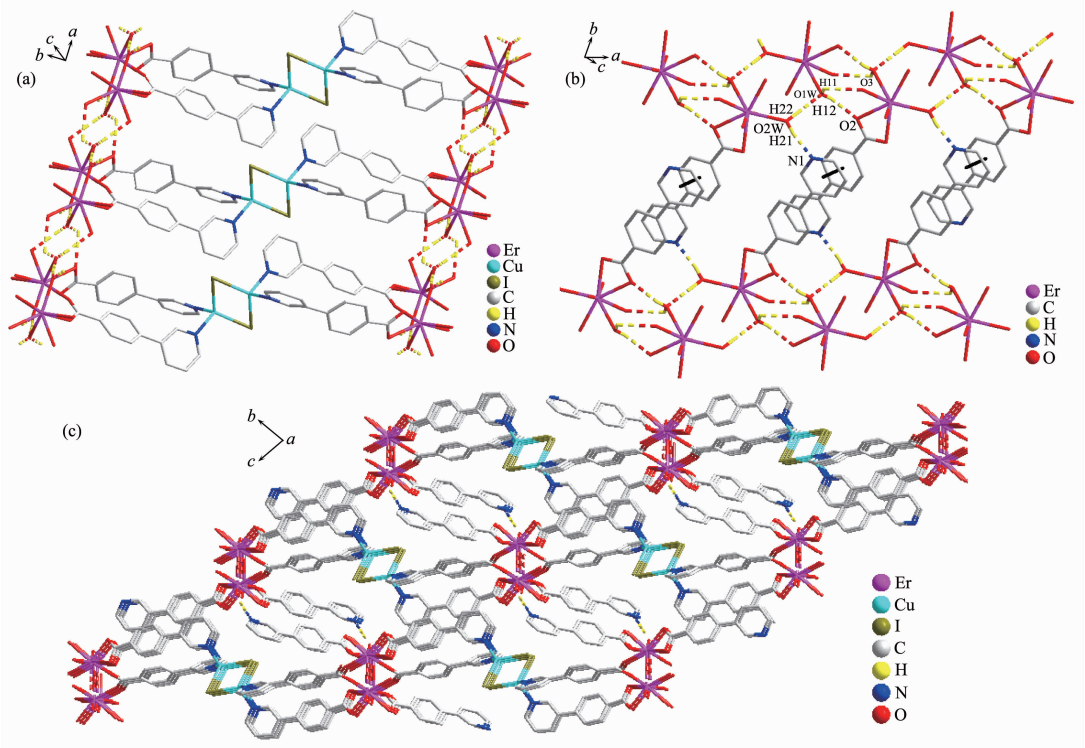


Fig.4 (a) 2D network structure constructed by hydrogen bond in **1**; (b) Hydrogen bond and π-π stacking interactions in **1**; (c) 3D supramolecular network of **1**

Table 2 Hydrogen bond and angles for compound 1

D–H···A	*d*(D-H) / nm	*d*(H···A) / nm	*d*(D···A) / nm	∠DHA / (°)
O(1W)–H(11)···O(3)^{i}	0.081 8	0.200 9	0.270 1	142.1
O(1W)–H(12)···O(2)^{i}	0.082 0	0.193 1	0.271 0	158.6
O(2W)–H(21)···N(1)^{ii}	0.082 1	0.183 5	0.264 8	170.9
O(2W)–H(22)···O(1W)^{iii}	0.082 1	0.202 1	0.283 5	170.9

Symmetry transformations: ^{i} $-x+1, -y+1, -z$; ^{ii} $-x+2, -y, -z$; ^{iii} $-x+2, -y+1, -z$.

hydrogen bond (O(1W)–H(11)···O(3) and O(1W)–H(12)···O(2)) and intramolecular hydrogen bond (O(2W)–H(22)···O(1W)) (Fig.4a). The strong hydrogen bond interactions are found between the pyridyl nitrogen atoms (N1) from adjacent chain and the oxygen atoms from the coordinated water (O2W) (O(2W)–H(21)···N(1)), additionally, π-π contacts are also observed between the deprotonated pyba$^-$ ligands in mode Ⅰ, centroid-centroid distance: 0.359 and 0.391 nm (Fig. 4b). Thus, a 3D supramolecular network structure is constructed (Fig.4c).

2.3 IR spectroscopy

As shown in Fig.5, the characteristic features of pyba$^-$ ligand dominate the IR spectrum. The strong and acuity absorption band around 3 400 cm^{-1} were assigned as the characteristic peaks of OH vibration. The strong vibrations at 1 605, 1 526 and 1 415 cm^{-1} are corresponding to the asymmetric and symmetric stretching vibrations of the carboxylate group, respectively. Bands in the 1 000~1 400 cm^{-1} range are attributed to ν(C-N) and ν(C-C) vibrations. The $\Delta\nu_{O\text{-}C\text{-}C}$ vibration in plane occurs in middle intensity peaks around in 785 cm^{-1}. The absence of strong bands ranging from 1 690 to 1 730 cm^{-1} indicates that the ligands are deproponated.

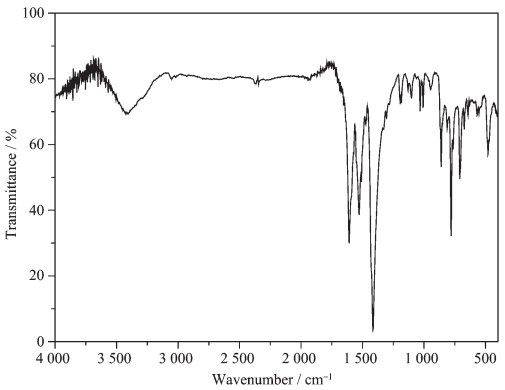


Fig.5 IR spectra of compounds **1**

2.4 Thermal properties

The thermogravimetric analysis was carried out in flowing dry air atmosphere with a heating rate of 10 ℃·min^{-1} in the temperature range of 30~1 000 ℃.The weight loss from 30 to 360 ℃ is attributed to the removal of the coordinated water molecules (calcd. 3.6%, found 3.7%). Above 300 until 450 ℃, one step of weight loss was observed, mainly corresponding to the successive release of organic ligands, and the coordination networks of compound **1** decompose completely.

3 Conclusions

We report the syntheses and structure of [Er(pyba)$_3$(H$_2$O)$_2$CuI]$_n$ by using lanthanide oxide, rather than lanthanide salts, as the source of lanthanides under hydrothermal conditions. Structure analysis shows that {Er_2} and {Cu_2} units interconnect by ligands to form 1D chains, which are further linked by hydrogen bond and π-π stacking interactions to make a 3D supramolecular network structure. This work provides a rational route for the construction of fascinating TM-Ln-organic frameworks based on {Er_2} and {Cu_2} units. Further work will be focused on the construction of high-D Ln-organic-TM frameworks involving the combination of Ln clusters and TM clusters.

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