

基于均苯三酸和柔性双咪唑配体的一个铜的 金属有机骨架合成、表征及催化性质

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摘要: 水热条件下, 合成了新的金属有机骨架 $[\text{Cu}(\text{Hbtc})(\text{bmix})_{0.5}]_n$ (**1**) (H_3btc =1,3,5-苯三甲酸, bmix =1,4-二(2-甲基咪唑基-1-亚甲基)苯)。单晶 X 射线衍射分析表明, 该配合物属正交晶系, $Pbcn$ 空间群, 晶胞参数为 $a=1.436\ 30(9)\ \text{nm}$, $b=1.477\ 15(11)\ \text{nm}$, $c=1.543\ 48(10)\ \text{nm}$, $V=3.274\ 7(4)\ \text{nm}^3$, $Z=8$ 。配合物 **1** 中, Hbtc^{2-} 以四连接方式与铜中心配位, bmix 桥连配体进一步修饰网络结构, 最终 **1** 显示为 1 个(4,5)节点的三维的网络结构, 其 Schläfli 符号为 $(4^2\cdot5\cdot6^2\cdot8)(4^2\cdot5^3\cdot6^3\cdot7\cdot8)$ 。此外还研究了配合物的热稳定性和对光助类芬顿反应降解甲基橙的催化性质。

关键词: 铜(II)配合物; 晶体结构; 催化; 柔性双咪唑

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Synthesis, Characterization and Catalysis of a Copper(II) MOF Based on 1,3,5-benzenetricarboxylic Acid and Flexible Bis(imidazole) Ligands

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Abstract: A metal-organic framework $[\text{Cu}(\text{Hbtc})(\text{bmix})_{0.5}]_n$ (**1**) (H_3btc =1,3,5-benzenetricarboxylic acid, bmix =1,4-bis (2-methylimidazole-1-ylmethyl)benzene) has been hydrothermally synthesized and characterized. **1** crystallizes in the orthorhombic system, space groups $Pbcn$, $a=1.436\ 3(1)\ \text{nm}$, $b=1.477\ 2(1)\ \text{nm}$, $c=1.543\ 5(1)\ \text{nm}$, $V=3.274\ 7(4)\ \text{nm}^3$, $Z=8$. In **1**, Hbtc^{2-} as a four-connector bridges Cu(II) node, and bmix ligand as a strut modifies its network structure. Eventually, the complex **1** displays a 3D (4,5)-connected net topology with a Schläfli symbol of $(4^2\cdot5\cdot6^2\cdot8)(4^2\cdot5^3\cdot6^3\cdot7\cdot8)$. In addition, the thermal and catalytic degradation of methyl orange in photo Fenton like process associated with complex **1** also were investigated. CCDC: 791521.

Key words: copper(II) complex; crystal structure; catalysis; flexible di(imidazole)

The rational design and synthesis of metal-organic framework (MOFs) with a regular array of well-defined pores has attracted tremendous attention, that is driven by their structural complexity and aesthetic topologies, as well as versatile functionalities in gas absorption and separation, catalysis, ion exchange and so on^[1-3]. The MOFs have some distinct advantages over tradition pore

materials such as zeolites in processability, structural diversity, and potential for postsynthetic modification, especially controllable porosity. For example, Yaghi and coworkers have obtained a great success on systematically decorating MOF-5 to yield a series of homologous frameworks with diversity of the pore size and functionalities by using a wide variety of

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carboxylate links diverse in their functional groups and lengths^[4]. All these superiorities for the porous MOFs contribute their potential application in a wide field. However, the construction of robust MOFs with suitable pores and excellent properties remains a highly challenging task.

Based on the similarity to zeolites, a logical application of MOFs could be as solid catalysts. Until now, many chemical reactions such as cyanosilylation of aldehyde, Friedel-Crafts *tert*-butylation of both toluene and biphenyl, rearrangement of α -pinene oxide, and the cyclization of citronellal have been demonstrably accelerated by MOFs^[5]. Of particularly interest are those coordinatively unsaturated Cu complexes with multicarboxylate ligands, in which the Lewis acid Cu (II) ions combined with the Bronsted carboxylic acids can contribute to the acid-catalyzed reactions^[6]. On the other hand, azo dye as one of the worst environmental pollutants in industries may be destructively abated by Fenton or Photo-Fenton reaction^[7]. Recently, more attentions have focused on the persulfate technique^[8], which, as a Fenton-like reaction to oxidize contaminants of concern, is largely dependent on metal-based catalyst. Likewise, it seems that MOFs-catalysts have the potential to provide faster degradation of the pollutants and produce less concentrations of the intermediates and those that can be easily separated from the system, however, there are less reports on this field.

In this work, our interest is to explore the formation of novel coordination architectures based transition metal with aromatic multicarboxylate and flexible bis(imidazole) ligands, and they are expected to display catalytic activity in degradation of methyl orange in photo-Fenton like process. With this in mind, herein, we report synthesis, characterization and catalysis of a new coordination framework, $[\text{Cu}(\text{Hbtc})(\text{bmix})_{0.5}]_n$ (**1**) (H_3btc =1,3,5-benzenetricarboxylic acid, bmix =1,4-bis(2-methylimidazole-1-ylmethyl)benzene).

1 Experimental

1.1 Materials and general methods

All starting reagents are commercially available,

analytical grade and used without further purification. The ligand *bmix* was prepared according to the literature method^[9]. The methyl orange (MO) has a λ_{max} of 506 nm in the acidic solution. Elemental analyses were made on a Perkin-Elmer automatic analyzer. IR spectra were recorded on a FTIR Avatar 360 (Nicolet) spectrophotometer in 4 000~400 cm^{-1} region by using KBr pellets method. Powder X-ray diffraction measurement was executed on a D/MAX 2500PC X-ray diffractometer using Cu $K\alpha$ radiation ($\lambda=0.15418$ nm) in the 2θ range of $3^\circ\sim50^\circ$ with a step size of 0.02° and a scanning rate of $4^\circ\cdot\text{min}^{-1}$. The TG measurements were carried out on a NETZSCH TG 209 thermal analyzer from room temperature to 800 $^\circ\text{C}$ under N_2 atmosphere with a heating rate of $10^\circ\text{C}\cdot\text{min}^{-1}$. The absorptivity values of methyl orange solution were measured by a 722S Vis spectrophotometer at maximum wavelength of 505 nm.

1.2 Synthesis of complex 1

A mixture of copper nitrate trihydrate (1.0 mmol, 241.6 mg), *bmix* ligand (1.0 mmol, 266.4 mg), 1,3,5-benzenetricarboxylic acid (1.0 mmol, 210.0 mg), NaOH (2.0 mmol, 80.0 mg), and H_2O (10 mL) was placed in a Teflon-lined stainless vessel and heated to 170 $^\circ\text{C}$ for 72 h under autogenous pressure, and then cooled to room temperature at a rate of $5^\circ\text{C}\cdot\text{h}^{-1}$. The blue crystal of **1** was obtained in 65 % yield based on Cu. Element anal. calcd. for $\text{C}_{17}\text{H}_{13}\text{CuN}_2\text{O}_6$ (%): C 50.49, H 3.24, N 6.93; found (%): C 50.79, H 3.03, N 6.61. FTIR (KBr pellet, cm^{-1}): 3 430 (s), 1 680 (m), 1 630(s), 1 540 (w), 1 440 (w), 1 380 (m), 1 280 (m), 1 110 (m), 997 (w), 758 (w), 683 (w), 542 (w).

1.3 Catalysis experiment

The **1** (100 mg) and sodium persulfate (20 mg) was added into 200 mL methyl orange solution ($10\text{ mg}\cdot\text{L}^{-1}$) of which the pH value was adjusted with sulfuric acid ($1\text{ mol}\cdot\text{L}^{-1}$) to 2~3. Afterwards the reaction system was directly exposed to the UV light, and maintained the temperature at 25 $^\circ\text{C}$ using thermostat. At a given interval, aliquots of the mixture were periodically taken, and analyzed with the Vis spectrophotometer at an absorption wavelength of 506 nm. This procedure was repeated except the absence of **1**.

1.4 Crystallography data and crystal structure determination of complex 1

The suitable single crystal of the title complex was mounted on the top of a glass fiber with epoxy cement for the X-ray measurement. The crystallographic data collections for complex **1** were carried out on a Bruker Smart 1000 CCD diffractometer with graphite-monochromated Mo $K\alpha$ radiation ($\lambda=0.071\ 073$ nm) and ω - 2θ scan mode at 293 K. The absorption corrections were applied using SADABS program^[10]. The structure were solved by direct methods and refined anisotro-

pically by the full-matrix least-squares technique using the Bruker's SHELXTL program package^[11]. All non hydrogen atoms were refined with anisotropic displacement parameters. Hydrogen atoms were included in calculated positions and refined with isotropic thermal parameters riding on the corresponding parent atoms. A summary of crystallography data are given in Table 1. The selected bond lengths and angles are listed in Table 2.

CCDC: 791521.

Table 1 Crystallographic data and detail of refinement of **1**

Complex	1	Crystal size	0.25×0.30×0.14
Empirical formula	C ₁₇ H ₁₃ CuN ₂ O ₆	$F(000)$	1 648
Formula weight	404.83	θ range / (°)	3.06 to 25.01
Wavelength / nm	0.071 073	Reflections collected	7 883
Crystal system	Orthorhombic	Independent reflections (R_{int})	2 895 (0.038 4)
Space group	$Pbcn$	Completeness / %	99.8
a / nm	1.436 3(1)	Absorption coefficient / mm ⁻¹	1.372
b / nm	1.477 2(1)	T / K	293
c / nm	1.543 5(1)	Goodness of fit on F^2	0.818
V / nm ³	3.2747(4)	Final R indices ($I>2\sigma(I)$) ^[a,b]	$R_1=0.029\ 0$, $wR_2=0.055\ 9$
Z	8	R (all data) ^[a,b]	$R_1=0.056\ 2$, $wR_2=0.058\ 7$
D_c / (g·cm ⁻³)	1.642	Largest diff. peak and hole / (e·nm ⁻³)	302 and -356

^[a] $R_1 = \sum ||F_o| - |F_c|| / \sum |F_o|$; ^[b] $R_1 = \{ \sum [w(F_o^2 - F_c^2)^2] / \sum [w(F_o^2)] \}^{1/2}$.

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

Cu1-O1	0.232 7(2)	Cu1-O3 ⁱⁱⁱ	0.193 1(2)	Cu1-O6 ^{iv}	0.194 4(2)
Cu1-O5 ⁱⁱ	0.196 3(2)	Cu1-N1	0.197 5(2)		
O3 ⁱⁱⁱ -Cu1-O6 ^{iv}	157.75(8)	O3 ⁱⁱⁱ -Cu1-O5 ⁱⁱ	86.48(8)	O6 ^{iv} -Cu1-O5 ⁱⁱ	86.80(8)
O3 ⁱⁱⁱ -Cu1-N1	96.10(8)	O6 ^{iv} -Cu1-N1	92.16(9)	O5 ⁱⁱ -Cu1-N1	175.36(9)
O3 ⁱⁱⁱ -Cu1-O1	101.39(7)	O6 ^{iv} -Cu1-O1	98.88(8)	O5 ⁱⁱ -Cu1-O1	83.46(8)
N1-Cu1-O1	92.24(8)				

Symmetry codes: ⁱⁱ $x, -y, z-1/2$; ⁱⁱⁱ $-x+1/2, -y+1/2, z-1/2$; ^{iv} $-x, y, -z+1$.

2 Results and discussion

The complex **1** was obtained by hydrothermal reaction of copper nitrate trihydrate, 1,3,5-benzenetri-carboxylic acid, bmix ligand, and sodium hydroxide at a molar ratio of 1:1:1:2. Complex **1** is stable in air and insoluble in common solvents such as water, ethanol, methanol, and acetic acid. The results of elemental analyses for this complex were in good agreement with

the theoretical requirements of their compositions (X-ray analysis results).

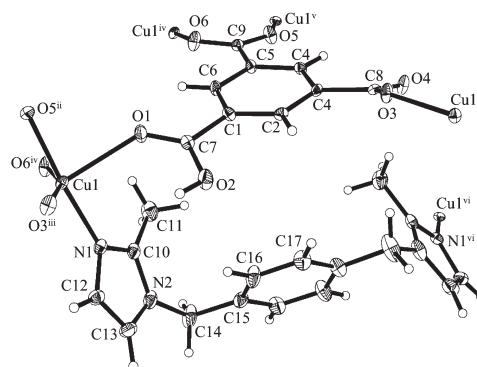
2.1 IR spectrum

For the IR spectrum of complex **1**, there is a broad strong peak at near $3\ 430\ \text{cm}^{-1}$, which corresponds to the asymmetric stretching vibrations of O-H on one carboxylate group of Hbtc²⁻ ligand. The three absorption bands of $1\ 540$, $1\ 280$, and $1\ 110\ \text{cm}^{-1}$ can be assigned to the vibrations of imidazole rings of bmix ligand. The

characteristic bands of deprotonated carboxylate groups are found at $1\,630\text{ cm}^{-1}$ for asymmetric stretching vibrations at $1\,440$ and $1\,380\text{ cm}^{-1}$ for symmetric vibrations. It should be noted that the medium peak at $1\,680\text{ cm}^{-1}$ arises from the vibrations of the undeprotonated carboxylate group for complex **1**^[12], indicating the incomplete deprotonation of the H₃btc ligand. Nevertheless, this value is slightly smaller than the reasonable value (near $1\,715\text{ cm}^{-1}$)^[12], due to the participation of the carboxylate group of Hbtc²⁻ in coordination.

2.2 Description of crystal structure

The single crystal X-ray diffraction analysis reveals that the complex **1** crystallizes in orthorhombic, space group *Pbcn*, and displays a 3D metal-organic framework topology. The asymmetric unit of **1** consists of one Cu(II) ion, one Hbtc²⁻ dianion, and a half bmix ligand. As shown in Fig.1, the coordination geometry around Cu(II) ion in **1** shows a severely distorted square-pyramidal sphere ($\tau=0.294$) with the basal plane constructed by one N atom from a bmix and three carboxylate O atoms from distinct Hbtc dianion (Cu1-N1 $0.197\,5(2)\text{ nm}$, Cu1-O3ⁱⁱⁱ $0.193\,1(2)\text{ nm}$, Cu1-O5ⁱⁱ $0.196\,3(2)\text{ nm}$ and Cu1-O6^{iv} $0.194\,4(2)\text{ nm}$), the apical position occupied by the carboxylate O atom from Hbtc dianion (Cu1-O1 $0.232\,7(2)\text{ nm}$). The Cu(II) atom is displaced by $0.013\,9\text{ nm}$ from the mean basal plane towards O1. All the coordination bond lengths are comparable to those of normal range^[13]. In **1**, the Hbtc²⁻ acts as a tetradentate ligand through its three carboxylate groups (Scheme 1). Two carboxylate groups of the Hbtc²⁻ (including one COO⁻ and one COOH) adopts monodentate coordination mode to bond one Cu(II) ion respectively, while the remaining deprotonated carboxylate group using its two O atoms combine two Cu(II) centers. Thus, one Hbtc²⁻ ligand bridges four Cu(II) atoms resulting in the formation of a 3D porous framework. The pores in the 3D architecture, however, are further decorated by strut of bmix ligand linking two Cu atoms, having a Cu...Cu separation of $1.253\,6\text{ nm}$. Wherein the dihedral angle between two imidazole rings within same bmix ligand is $21.8(1)^\circ$. Therefore, a MOF with 3D hybrid material was built up.

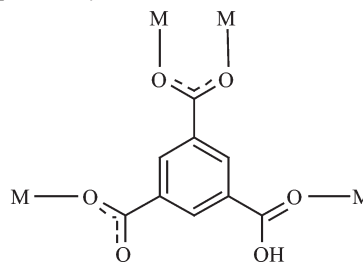


Symmetry transformations used to generate equivalent atoms:

ⁱ $-x+1/2, -y+1/2, z+1/2$; ⁱⁱ $x, -y, z-1/2$; ⁱⁱⁱ $-x+1/2, -y+1/2, z-1/2$;

^{iv} $-x, y, -z+1$; ^v $x, -y, z+1/2$; ^{vi} $-x, y, -z+3/2$

Fig.1 Coordination environment around Cu(II) center in complex **1** with thermal ellipsoids at 30 % probability level



Scheme 1

To clearly understand the framework of complex **1**, the topological analysis method was employed. The bmix ligand can be simplified as a long linear connector, then we define Cu(II) center as five-connected node, and Hbtc²⁻ ligand as 4-connected node. Accordingly, the 3D framework of **1** is depicted as a (4,5)-connected net. The topological analysis of **1** by OLEX program^[14] suggests a unusual binodal network with a Schläfli symbol of $(4^2 \cdot 5 \cdot 6^2 \cdot 8)(4^2 \cdot 5^3 \cdot 6^3 \cdot 7 \cdot 8)$ (Fig.2).

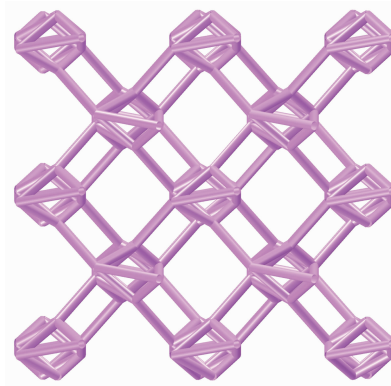


Fig.2 Topology view of **1** running along *c* axis drawn by OLEX program

2.3 Powder X-ray diffraction and thermal property of **1**

The powder XRD pattern and simulated XRD pattern of complex **1** are depicted in Fig.3. It is obvious that the measured powder XRD pattern is in good agreement with the simulated pattern by X-ray single crystal data, suggesting the bulk sample of **1** is highly pure.

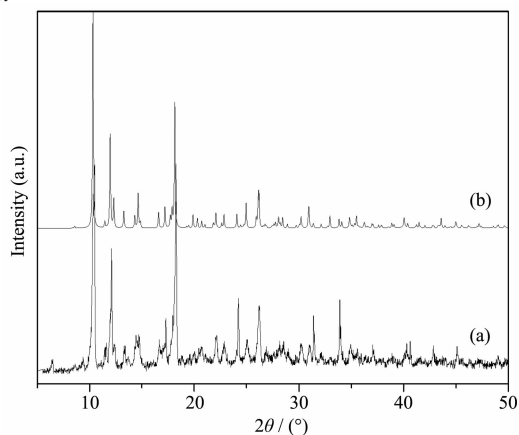


Fig.3 PXRD pattern of (a) the as synthesized **1**, (b) simulated

The thermal property of **1** was performed under N_2 atmosphere from room temperature to $800\text{ }^{\circ}\text{C}$. As depicted in Fig.4, the complex **1** is stable up to $293\text{ }^{\circ}\text{C}$, and then weight loss of 49.08% occurs at temperature between 293 and $339\text{ }^{\circ}\text{C}$, which is assigned to the decomposition of the Hbtc dianion (calcd. 47.46%). The removal of the bmix ligand taken place gradually in the range of 339 to $490\text{ }^{\circ}\text{C}$ with an observed weight loss of 30.51% (calcd. 32.89%). The residual mass of 19.41% corresponds to the CuO (calcd. 19.65%). The thermal analysis result reveals that the complex **1** displays a

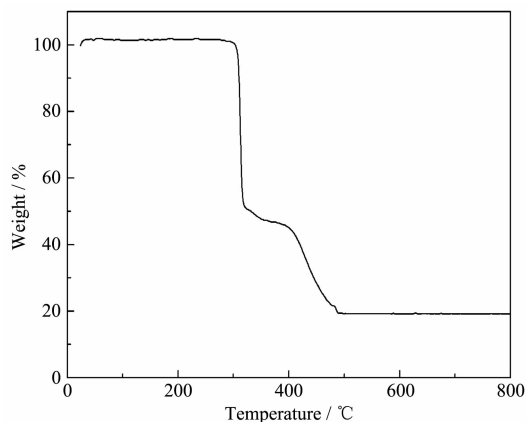


Fig.4 TG curve of complex **1**

good thermal stability.

2.4 Catalytic activity for the degradation of methyl orange

The degradation experiment of methyl orange under UV irradiation was followed by Vis spectroscopy and the results are depicted in Fig.5 (the vertical axis shows the percentage of methyl orange remaining at time t). It can be obviously observed that the efficiency of methyl orange degradation within 150 min reaction is achieved by about 50% at the present of MOF-1 in the curve 1, and amounts up to 90% after 370 min. Notably, the experiment is conducted without MOF-1 catalyst in the curve 2, the efficiency of the reaction is reduced to 18% in 150 min, and the reaction almost shut down after 240 min, affording only 7.8% decrease of the MO concentration upon continuing to stand for 450 min. Thus, the metal-organic framework **1** can catalyzes the reaction of MO degraded by persulfate technique.

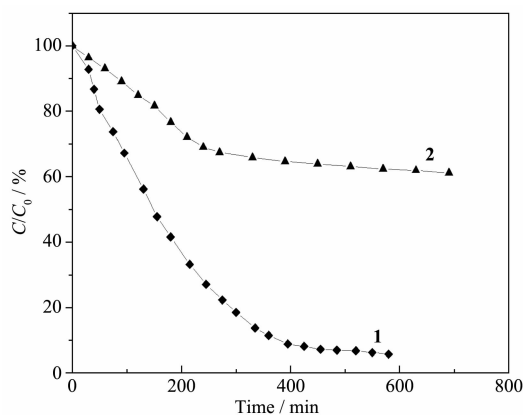


Fig.5 Contrast experiments of the degradation of methyl orange

3 Conclusions

A new metal-organic framework, $[\text{Cu}(\text{Hbtc})(\text{bmix})_{0.5}]_n$ (**1**), has been prepared by hydrothermal method. The **1** exhibits a 3D framework with permanent pore channels, which is constructed by Hbtc^{2-} linking $\text{Cu}(\text{II})$ nodes and modified by long flexible ligand bmix. The TG result reveals that this complex has a good thermal stability and can stable up to $293\text{ }^{\circ}\text{C}$, the **1** displays the catalytic activity on Fenton-like process to degrade methyl orange.

References:

- [1] (a) Kuppler R J, Timmons D J, Fang Q R, et al. *Coord. Chem. Rev.*, **2009**, **253**:3042-3066
(b) HU Zong-Zhi (胡宗智), ZHAO Jun (赵君), KE Xi-Jun (柯希俊), et al. *Chinese J. Inorg. Chem. (Wuji Huaxue Xuebao)*, **2011**, **27**(1):184-188
- [2] Plabst M, McCusker L B, Bein T. *J. Am. Chem. Soc.*, **2009**, **131**:18112-18118
- [3] Li J R, Kuppler R J, Zhou H C. *Chem. Soc. Rev.*, **2009**, **38**:1477-1504
- [4] Eddaoudi M, Kim J, Rosi N, et al. *Science*, **2002**, **295**:469-472
- [5] Lee J Y, Farha O K, Roberts J, et al. *Chem. Soc. Rev.*, **2009**, **38**:1450-1459
- [6] Alaerts L, Séguin E, Poelman H, et al. *Chem. Eur. J.*, **2006**, **12**:7353-7363
- [7] Feng J Y, Hu X J, Yue P L, et al. *Ind. Eng. Chem. Res.*, **2003**, **42**:2058-2066
- [8] Ocampo A M. *Thesis for the Doctorate of Washington State University*. **2009**.
- [9] Hoskins B F, Robson R, Slizys D A. *J. Am. Chem. Soc.*, **1997**, **119**:2952-2953
- [10] Sheldrick G M. *SADABS*, University of Göttingen, Göttingen, Germany, **1996**.
- [11] *SHELXTL* 6.10, Bruker Analytical Instrumentation, Madison, Wisconsin, USA, **2000**.
- [12] Li W, Li M X, Yang J J, et al. *J. Coord. Chem.*, **2008**, **61**:2715-2721
- [13] (a) Addison A W, Rao T N, Reedijk J, et al. *J. Chem. Soc., Dalton Trans.*, **1984**:1349-1356
(b) Wang P S, Moorefield C N, Panzer M, et al. *Chem. Commun.*, **2005**:465-480
- [14] Dolomanov O V, Blake A J, et al. *J. Appl. Cryst.*, **2003**, **36**:1283-1284