

一个由 4,4'-(丁烷-1,4-二氧基)-二苯甲酸和双咪唑配体 构筑的三重穿插金属有机骨架化合物

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摘要: 采用水热法合成了 1 个二维缠结金属有机框架化合物 $[\text{Cu}(\text{bbi})_{0.5}(\text{boba})]_n$ (**1**) ($\text{bbi}=1,1'-(1,4\text{-丁烷基})\text{-二(咪唑)}$; $\text{H}_2\text{boba}=4,4'-(\text{丁烷-1,4-二氧基})\text{-二苯甲酸}$), 并通过元素分析、红外光谱和单晶 X-射线衍射对其进行了结构表征。结构分析显示: 化合物 **1** 是具有聚轮烷和聚锁链结构特征的三重平行穿插网络。此外还研究了它的荧光和热稳定性。

关键词: 三重穿插; 4,4'-(丁烷-1,4-二氧基)-二苯甲酸; 晶体结构

中图分类号: O614.121 文献标识码: A 文章编号: 1001-4861(2014)08-1920-05

DOI: 10.11862/CJIC.2014.273

A 3-Fold Interpenetrating Metal-Organic Frameworks Constructed from 4,4'-(Butane-1,4-diylldioxy)dibenzoic Acid and Bis(imidazole) Ligands

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Abstract: A two-dimensional (2D) entangled MOF compound $[\text{Cu}(\text{bbi})_{0.5}(\text{boba})]_n$ (**1**) ($\text{bbi}=1,1'-(1,4\text{-butanediyl})\text{-bis(imidazole)}$; $\text{H}_2\text{boba}=4,4'-(\text{butane-1,4-diylldioxy})\text{-dibenzoic acid}$) was successfully synthesized by hydrothermal reaction and structurally characterized by elemental analysis, IR spectrum, and single-crystal X-ray diffraction. The structure analysis shows that compound **1** possesses a 3-fold parallel interpenetrating net with polyrotaxane and polycatenane characters. In addition, the fluorescence properties and thermogravimetric (TG) analysis are discussed. CCDC: 951513.

Key words: 3-fold interpenetration; 4,4'-(butane-1,4-diylldioxy)-dibenzoic acid; crystal structure

0 Introduction

Entangled systems of metal-organic frameworks (MOFs) have undergone revolutionary growth over the past decades because of their undisputed aesthetic topological structures and potential applications^[1-7]. Interpenetrating networks, among different types of entanglements, have been extensively studied^[8-9].

However, the polyrotaxane frameworks, especially those having both polyrotaxane and polycatenane characters, are still quite rare^[10-15]. According to the previous literature^[16-18], the synthetic strategy for the polyrotaxane networks is mainly dependent on the ligands selected with both flexible and long rigid characters. Therefore, 4,4'-(butane-1,4-diylldioxy)-dibenzoic acid (H_2boba) and 1,1'-(1,4-butanediyl)-bis

收稿日期: 2013-08-22。收修改稿日期: 2014-03-24。

四平市科技局基金(No.2012032, No.2013055)资助项目。

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(imidazole) (bbi) were used as the bridging ligands for building copper MOFs. In this paper, we successfully obtain an unusual 2D \rightarrow 2D example with 3-fold parallel interpenetrating network. Notably, it also shows both polyrotaxane and polycatenane features. Furthermore, TG analysis and fluorescence properties of this compound have been investigated.

1 Experimental

1.1 Generals

The 4,4'-(butane-1,4-diylidioxy)-dibenzoic acid and 1,1'-(1,4-butanediyl)-bis (imidazole) were synthesized by a procedure reported earlier^[19-20], and other reagents and solvents employed were commercially available and were used as received. Elemental analysis (C, H, N) were carried out with a Perkin-Elmer 2400 CHN elemental analyzer. Infrared (IR) spectrum was obtained on a Perkin-Elmer FT/IR instrument as KBr pellets (4 000~400 cm^{-1}). The TG analysis is conducted on a Diamond TG/DTA 6300 thermal analyzer (Perkin-Elmer Company, USA).

1.2 Synthesis

A mixture of $\text{CuSO}_4 \cdot 5\text{H}_2\text{O}$ (0.2 mmol), bbi (0.3 mmol), H_2boba (0.2 mmol), NaOH (0.12 mmol), water (7 mL) and $\text{CH}_3\text{CH}_2\text{OH}$ (3 mL) was placed in a Teflon reactor (20 mL) which was then sealed and heated to 150 $^\circ\text{C}$ for three days. The reaction system was slowly cooled to room temperature. Pale blue crystals suitable for single crystal X-ray diffraction analysis were collected from the final reaction system by filtration, washed several times with distilled water

and dried in air at ambient temperature. Yield: 28% based on Cu. IR (KBr, cm^{-1}): 2 950s, 1 606s, 1 570s, 1 524s, 1 396s, 1 308s, 1 250s, 1 117w, 1 112w, 1 026 m, 1 000m, 857m, 783w, 718s, 701s, 659s. Anal. Calcd. for $\text{C}_{23}\text{H}_{23}\text{CuN}_2\text{O}_6$ (%): C, 56.73; H, 4.76; N, 5.75. Found (%): C, 56.68; H, 4.81; N, 5.71.

1.3 X-ray structure determination

A single crystal with dimensions of 0.29 mm \times 0.25 mm \times 0.24 mm was selected and mounted on a Bruker CCD diffractometer equipped with a graphite-monochromatized Mo $K\alpha$ ($\lambda=0.071\ 073\ \text{nm}$) radiation by using an ω scanning method at 293(2) K. The structure was solved by Direct Method with SHELXS-97 program^[21] and refined with SHELXL 97^[22] by full-matrix least-squares techniques on F^2 . All non-hydrogen atoms were refined anisotropically and hydrogen atoms of the ligands were refined as rigid groups. Selected bond lengths and angles for compound 1 are given in Table 1.

CCDC: 951513.

Crystal data for compound 1: $\text{C}_{23}\text{H}_{23}\text{CuN}_2\text{O}_6$, triclinic, space group $P\bar{1}$, $M_w=486.97$, $a=0.786\ 0(5)\ \text{nm}$, $b=1.152\ 2(7)\ \text{nm}$, $c=1.354\ 5(8)\ \text{nm}$, $\alpha=101.295\ 0(10)^\circ$, $\beta=98.503\ 0(10)^\circ$, $\gamma=105.145\ 0(10)^\circ$, $V=1.135\ 21(12)\ \text{nm}^3$, $Z=2$, $F(000)=504$, $\mu(\text{Mo } K\alpha)=1.003\ \text{mm}^{-1}$, $D_c=1.425\ \text{g}\cdot\text{cm}^{-3}$, 6 285 reflections measured in the $1.57^\circ \leq \theta \leq 26.04^\circ$ range, 4 430 unique ($R_{\text{int}}=0.015\ 4$), 3 843 observed reflections with $I>2\sigma(I)$, the final $R=0.035\ 1$ and $wR=0.078\ 6$ ($w=1/[\sigma^2(F_o^2)+(0.028\ 7P)^2+0.701\ 7P]$, where $P=(F_o^2+2F_c^2)/3$), $S=1.050$, $(\Delta\rho)_{\text{max}}=264\ \text{e}\cdot\text{nm}^{-3}$, $(\Delta\rho)_{\text{min}}=-359\ \text{e}\cdot\text{nm}^{-3}$ and $(\Delta/\sigma)_{\text{max}}=56$.

Table 1 Selected bond distances (nm) and angles ($^\circ$) for 1

Cu(1)-O(5)#2	0.197 80(17)	Cu(1)-O(2)#3	0.199 22(17)	Cu(1)-O(1)	0.199 77(17)
Cu(1)-N(1)	0.211 03(19)	Cu(1)-O(6)#1	0.195 49(18)	O(2)-Cu(1)#3	0.199 22(17)
Cu(1)-Cu(1)#3	0.268 72(6)				
O(6)#1-Cu(1)-O(5)#2	166.64(7)	O(6)#1-Cu(1)-O(2)#3	88.44(8)	O(5)#2-Cu(1)-O(2)#3	89.24(8)
O(6)#1-Cu(1)-O(1)	88.39(8)	O(5)#2-Cu(1)-O(1)	90.84(8)	O(2)#3-Cu(1)-O(1)	166.58(7)
O(6)#1-Cu(1)-N(1)	99.67(8)	O(5)#2-Cu(1)-N(1)	93.69(7)	O(2)#3-Cu(1)-N(1)	101.69(8)
O(1)-Cu(1)-N(1)	91.70(7)	O(6)#1-Cu(1)-Cu(1)#3	84.87(5)	O(5)#2-Cu(1)-Cu(1)#3	81.87(5)
O(2)#3-Cu(1)-Cu(1)#3	87.16(5)	O(1)-Cu(1)-Cu(1)#3	79.57(5)	N(1)-Cu(1)-Cu(1)#3	170.09(6)

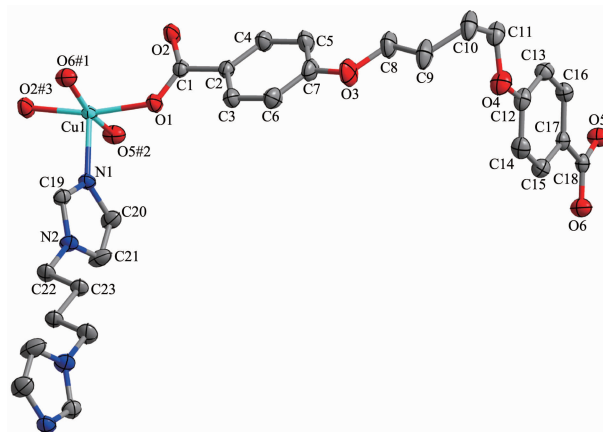
Symmetry transformations used to generate equivalent atoms: #1: $x+1, y-1, z$; #2: $-x+1, -y+2, -z$; #3: $-x+2, -y+1, -z$.

2 Results and discussion

2.1 Description of crystal structure

As shown in Fig.1, the asymmetric unit of compound **1** contains one Cu^{2+} ion, one boba^{2-} anion, and half bbi ligand. The five-coordinated Cu^{2+} ion is surrounded by four carboxylate oxygen atoms from four different boba^{2-} anions and one nitrogen atoms from one bbi ligand, which belongs to square-pyramidal coordination geometry. Each boba^{2-} anion connects to four Cu^{2+} ions, and both carboxylate groups adopt a $\mu^2\text{-}\eta^1\text{:}\eta^1$ fashion. As a result, each pair of Cu^{2+} ions is bridged by four carboxylate groups to generate 1D beaded chain with a $\text{Cu} \cdots \text{Cu}$ separation of 0.268 71(4) nm. The adjacent 1D beaded chains are further linked together through bbi ligands to yield a 2D sheet (Fig.2a). Notably, the sheet has two different rectangle windows of $[\text{Cu}_4(\text{boba})_2]$ and $[\text{Cu}_8(\text{boba})_4(\text{bbi})_2]$. The $[\text{Cu}_4(\text{boba})_2]$ window is built up by four Cu^{2+} ions and two boba^{2-} anions with dimensions of 1.055 63(4) nm \times 1.102 11(5) nm, while the $[\text{Cu}_8(\text{boba})_4(\text{bbi})_2]$ window is built up by eight Cu^{2+} ions, four boba^{2-} anions, and two bbi ligands with dimensions of 1.555 19(7) nm \times 1.688 91(8) nm (Fig.2b). The windows in the single sheet are so large that they allow 3-fold interpenetration to occur in a parallel

fashion (Fig.3). Moreover, this network also presents both polyrotaxane and polycatenane characters. As illustrated in Fig.3b, Every one $[\text{Cu}_4(\text{boba})_2]$ window of each sheet is threaded by two armed rods of the bbi ligands from two adjacent sheets in a parallel fashion, and a large window of $[\text{Cu}_8(\text{boba})_4(\text{bbi})_2]$ from one sheet is interlocked by two $[\text{Cu}_4(\text{boba})_2]$ windows from the other two identical layers. The structure is similar to that found in the related compound $[\text{Zn}(\text{bpib})_{0.5}(\text{L})]$ (bpib = 1,4-bis (2-(pyridin-2-yl)-1*H*-imidazol-1-yl)butane, H_2L =4,4'-(2,2'-oxybis(ethane-2,1-diyl)bis(oxy))



H atoms were omitted for clarity; Symmetry code: #1 $x+1, y-1, z$; #2 $-x+1, -y+2, -z$; #3 $-x+2, -y+1, -z$; Displacement ellipsoids are drawn at 40% probability

Fig.1 Coordination environment of Cu(II) atoms in **1**

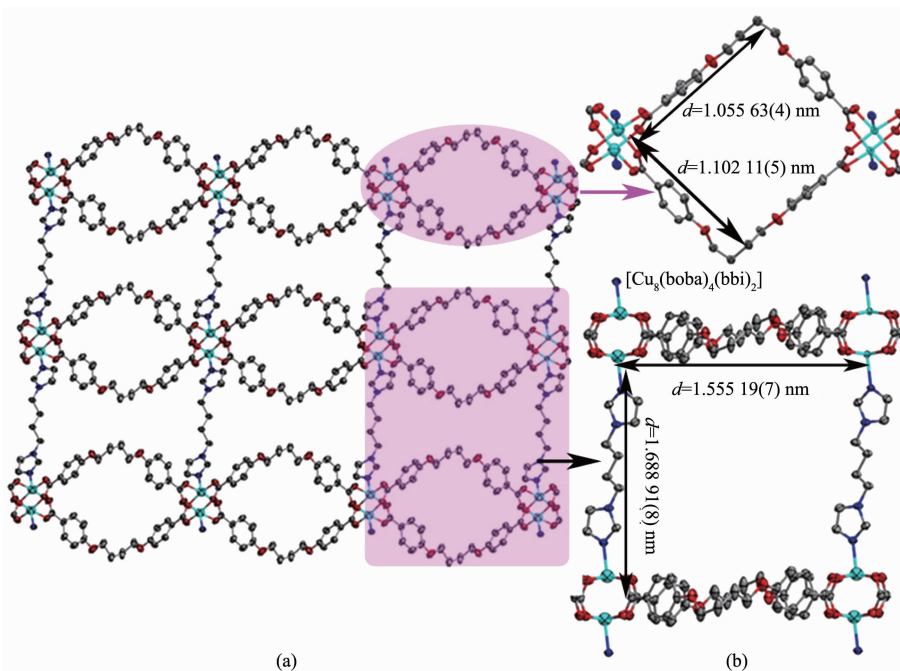


Fig.2 (a) View of the 2D sheet in **1**; (b) Two different rectangle of windows in 2D sheet

dibenzoic acid)^[13]. Compare to the reported structure [Zn(bpib)_{0.5}(L)], it is totally different specially the metal center. The ligands are analogue between [Zn(bpib)_{0.5}(L)] and compound **1**.

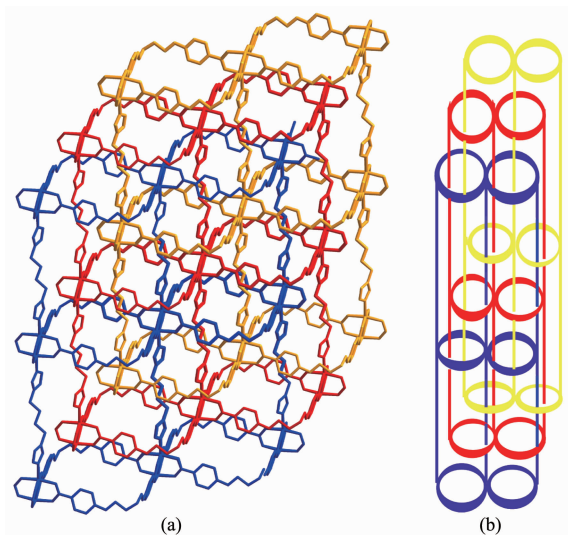


Fig.3 (a) View of the 3-fold interpenetration architecture;
(b) Both polyrotaxane and polycatenane characters
of **1**

2.2 IR analysis

The COO⁻ is coordinated with its asymmetric and symmetric stretching appearing at 1 570 cm⁻¹ ($\nu(\text{OCO})_{\text{asym}}$) and 1 396 cm⁻¹ ($\nu(\text{OCO})_{\text{sym}}$)^[23-24], respectively. The $\Delta\nu(\nu(\text{OCO})_{\text{asym}} - \nu(\text{OCO})_{\text{sym}})$ is 174 cm⁻¹ (<200 cm⁻¹), showing the presence of bridging mode carboxylates in the dianions. Therefore, the carboxylates coordinate to the Cu center as the bridging mode ligands via the carboxyl groups^[25]. The IR analysis result is also in good agreement with the X-ray crystal structure of compound **1**.

2.3 Thermogravimetric analysis

Thermogravimetric analysis (TGA) was performed to examine the thermal stability of the compound **1**. The crushed single crystal sample was heated up to 600 °C under N₂ gas at a heating rate of 10 °C·min⁻¹. As shown in Fig.4, the first weight loss of 83.66% occurs between room temperature and 481.5 °C, corresponding to the removal of half bbi ligand and boba²⁻ anions (Calcd. 83.67%). Upon further heating, after 481.5 °C no weight loss is observed, indicating the complete decomposition of **1**. The residual weight 16.34% (Calcd. 16.33 %) corresponding to CuO. The

above thermal behaviors may be attributed to the structural features and the TGA results basically agree with the formula of **1**.

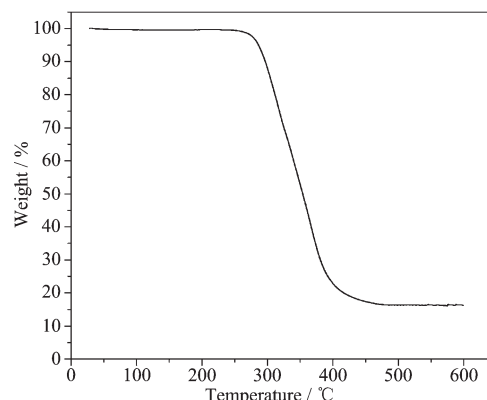


Fig.4 TG curve of **1** from room temperature to 600 °C

2.4 Photoluminescent properties

The fluorescence emission spectrum of compound **1** in the solid state at room temperature is shown in Fig.5. The emission peaks of bbi and H₂boba are at 377 and 382 nm, respectively. The emission bands of the free ligands could be caused by π^*-n or $\pi^*-\pi$ transition^[26]. The emission peak of compound **1** is located at 361 nm ($\lambda_{\text{ex}}=332$ nm). The emission band is near to that of the free ligands, so the fluorescence emission can probably be attributed to the intraligand transitions^[27].

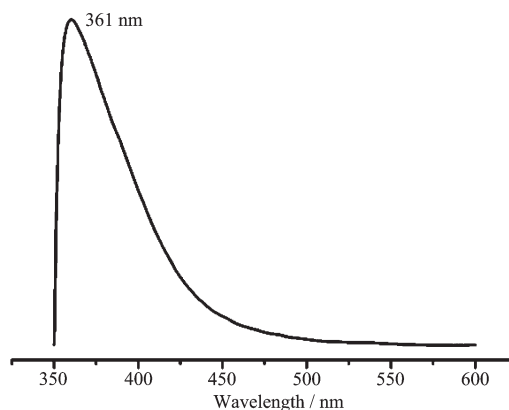


Fig.5 Emission spectrum of **1** in the solid state at room temperature

References:

- [1] Carlucci L, Ciani G, Proserpio D M. *CrystEngComm*, **2003**, *5*: 269-279
- [2] Bu X H, Tong M L, Chang H C, et al. *Angew. Chem. Int.*

- Ed.*, **2004**,**43**:192-195
- [3] Suhan N D, Loeb S J, Eichhorn S H. *J. Am. Chem. Soc.*, **2013**,**135**:400-408
- [4] Sun J K, Yao Q X, Tian Y Y, et al. *Chem. Eur. J.*, **2012**,**18**: 1924-1931
- [5] Eddaoudi M, Kim J, Rosi N, et al. *Science*, **2002**,**295**:469-472
- [6] Beves J E, Blight B A, Campbell C J, et al. *Angew. Chem. Int. Ed.*, **2011**,**50**:9260-9327
- [7] Zeng M H, Zhang W X, Sun X Z, et al. *Angew. Chem. Int. Ed.*, **2005**,**44**:3079-3082
- [8] Hoskins B F, Robson R, Slizys D A. *Angew. Chem. Int. Ed.*, **1997**,**36**:2336-2337
- [9] Goodgame D M L, Menzer S, Smith A M, et al. *Angew. Chem. Int. Ed.*, **1995**,**34**:574-575
- [10] Yang J, Ma J F, Batten S R, et al. *Chem. Commun.*, **2008**: 2233-2235
- [11] Wang G H, Li Z G, Jia H Q, et al. *Cryst. Growth Des.*, **2008**,**8**:1932-1939
- [12] Luo F, Yang Y T, Che Y X, Zheng J M. *CrystEngComm*, **2008**,**10**:981-982
- [13] Lan Y Q, Li S L, Qin J S, et al. *Inorg. Chem.*, **2008**,**47**: 10600-10610
- [14] Liu J Q, Wang Y Y, Zhang Y N, et al. *Eur. J. Inorg. Chem.*, **2009**:147-154
- [15] Cao X Y, Yao Y G, Batten S R, et al. *CrystEngComm*, **2009**,**11**:1030-1036
- [16] Batten S R, Robson R. *Angew. Chem. Int. Ed.*, **1998**,**37**: 1460-1494
- [17] Batten S R. *CrystEngComm*, **2001**,**3**:67-72
- [18] Kim K. *Chem. Soc. Rev.*, **2002**,**31**:96-107
- [19] Hou L M, Kan Y H. *Acta Cryst.*, **2007**,**E63**:o2157-o2158
- [20] Yang J, Ma J F, Liu Y Y, et al. *Eur. J. Inorg. Chem.*, **2005**, **11**:2174-2180
- [21] Sheldrick G M. *SHELXS 97, Program for the Solution of Crystal Structure*, University of Göttingen, **1997**.
- [22] Sheldrick G M. *SHELXS 97, Program for the Refinement of Crystal Structure*, University of Göttingen, **1997**.
- [23] Adams D M, Lock P J. *J. Chem., Soc. A*, **1971**:2801-2806
- [24] Schlafer H L, Fritz H P. *Spectrochim. Acta*, **1967**,**23A**:1409-1413
- [25] Nakamoto K. *Infrared and Raman Spectra of Inorganic and Coordination Compounds*, New York: Wiley and Sons, **1986**.
- [26] Kan W Q, Ma J F, Liu B, et al. *CrystEngComm*, **2012**:286-299
- [27] ZHAO Yue(赵越), ZHAI Ling-Ling(翟玲玲), SUN Wei-Yin(孙为银). *Chinese J. Inorg. Chem.*(无机化学学报), **2014**, **30**:99-105