第 28 卷第 9 期
2012 年 9 月

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CHINESE JOURNAL OF INORGANIC CHEMISTRY

Vol.28 No.9
2005-2010

# 两个一维铜配位聚合物的合成、晶体结构及其与双氧水的氧化反应

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**摘要**：本文利用柔性的 *N*,*N*,*N*′,*N*′-间-二甲苯二胺四乙酸($H_4L$)及不同的氮杂环配体如刚性的 4-4′-联吡啶(4,4′-bipy)及柔性的间-二(咪唑-1-亚甲基)苯(mbix)构筑了 2 个新的一维铜配位聚合物$\{[Cu_2L(4,4'\text{-bipy})(H_2O)_2]\cdot 2.5H_2O\}_n$ (**1**)和$\{[Cu_2L(mbix)(H_2O)_2]\cdot 3H_2O\}_n$ (**2**),并对其进行了元素分析、红外光谱和 X-ray 单晶衍射表征。另外利用紫外-可见光谱的方法对 2 个化合物与 $H_2O_2$ 的氧化反应进行了研究,结果表明虽然化合物 **1** 和 **2** 在高浓度的 $H_2O_2$ 条件下均发生了分子断裂,但仍能使配体 $L^{4-}$中二甲苯基联接体 C2 位置发生羟基化。

**关键词**：铜；聚合物；氧化反应；双氧水

**中图分类号**：O614.121 **文献标识码**：A **文章编号**：1001-4861(2012)09-2005-06

## Syntheses, Structure and Oxidation Reaction of Two 1D Copper(Ⅱ) Coordination Polymers with $H_2O_2$

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**Abstract:** Two 1D copper coordination polymers, $\{[Cu_2L(4,4'\text{-bipy})(H_2O)_2]\cdot 2.5H_2O\}_n$ (**1**) and $\{[Cu_2L(mbix)(H_2O)_2]\cdot 3H_2O\}_n$ (**2**) ($H_4L$=*N*,*N*,*N*′,*N*′-m-xylylenediamine tetracetic acid, mbix=*m*-bis(imidazol-1-ylmethyl)benzene) have been synthesized for the continuance of our research work on the coordination frameworks and oxidation reaction of copper(Ⅱ) complexes with ligand $L^{4-}$. Compound **1** crystallizes in monoclinic system with space group $P2_1/c$ and compound **2** crystallizes in space group $P\bar{1}$ with triclinic system, and they both form a 1D zigig-like chain. Interchain hydrogen-bonding interactions further extend the 1D arrangement to generate a 3D supramolecular architecture for **1** and **2**. UV-Vis spectra shows that compound **1** and **2** both can hydroxylate the xylyl linker in the supporting ligand $L^{4-}$ in spite of chemical degradation of the two compounds by reaction with $H_2O_2$. CCDC: 888051, **1**; 888052, **2**.

**Key words:** copper(Ⅱ); polymer; oxidation reaction; $H_2O_2$

Hydroxylation of alkanes and arenes catalyzed by copper complexes is of current interest for understanding the dioxygen activation mechanisms of many copper-containning metalloenzymes such as hemocyanin, tyrosinase, and catechol oxidases[1]. Since Karlin and co-works had firstly demonstrated that the copper (Ⅰ) complex, $[Cu_2(m\text{-XYLpy}_2)](PF_6)_2$ (*m*-XYLpy$_2$=*N*,*N*,*N*′,*N*′-tetra-(2-pyridylethyl)-*m*-xylylene diamine) was capable of performing hydroxylation of the xylyl linkers of the supporting ligands in the presence of dioxygen[2], many model compounds have been developed and their reactivity toward various substrates has been

收稿日期:2012-03-23。收修改稿日期:2012-05-17。

国家自然科学基金(No.20801035,20971084)资助项目。

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investigated[3-7]. For example, Cramer group found an efficient aromatic ligand hydroxylation took place to give phenolate-copper(Ⅱ) complexes by reaction of the tripyridyl-nitrogen chelating copper(Ⅰ) complexes with $H_2O_2$[8], and Poater and co-works showed a hexaazamacrocyclic dicoppper(Ⅰ) complex mediated intramolecular aromatic hydroxylation through $O_2$ activation[9]. Apart from many excellent systems of copper complexes with different *N*-heterocylces ligands for hydroxylation of arenes, a few of examples for efficient hydroxylation of arene groups by iron complexes have also been known[10]. Suzuki et al. reported a regioselective hydroxylation of a xylyl linker by the reaction of a diiron(Ⅲ) complex bearing carboxylate-rich ligand $L^{4-}$ ($H_4L$ =*N*,*N*,*N*′,*N*′-*m*-xylylenediamine tetracetic acid) with $H_2O_2$[11]. In view of no examples being reported on the hydroxylation of substrates by the copper complexes with carboxylate ligand, we had previously investigated the oxidation reaction of dicopper(Ⅱ) complex based on the same ligand $L^{4-}$ used by Suzuki[12]. We found that the dicopper(Ⅱ) complex could also exhibited hydroxylation of the xylyl linker of the supporting ligand in the presence of $H_2O_2$ as its diiron(Ⅲ) analogue did[12].

As the continuance of our research work on the oxidation reaction of copper complexes with ligand $L^{4-}$ used by Suzuki and ours, as well as thinking of the study on the extended solid forming ability of the ligand $L^{4-}$ in the presence of a donor amine being less known yet, in this paper, two new one-dimensional copper coordination polymers built up from ligand $L^{4-}$ and different *N*-heterocylces such as rigid pyridyl-based 4,4′-bipy and flexible imidazole-based mbix (mbix=*m*-bis(imidazol-1-ylmethyl)benzene), $\{[Cu_2L(4,4'\text{-bipy})(H_2O)_2]\cdot 2.5H_2O\}_n$ (**1**), $\{[Cu_2L(mbix)(H_2O)_2]\cdot 3H_2O\}_n$ (**2**) have been prepared and characterized by single crystal X-ray diffraction and IR spectrum. The reaction of compound **1** and **2** with $H_2O_2$ has also been studied by UV-Vis spectra.

## 1 Experimental

### 1.1 Materials and general methods

The ligand $H_4L$ was prepared according to the reported procedure in our previous work[11]. Other chemicals were of reagent grade and used as received without further purification. Elemental analyses were performed on a Vario EL III elemental analyzer. Infrared spectra were recorded with a Nicolet A370 FT-IR spectrometer by KBr pellets in the range 400~4 000 $cm^{-1}$. UV-Vis spectra were recorded on a Shimadzu RF-5301 spectrophotometer.

### 1.2 Synthesis of complexes

$\{[Cu_2L(4,4'\text{-bipy})(H_2O)_2]\cdot 2.5H_2O\}_n$ (**1**): $Cu(NO_3)_2\cdot 6H_2O$ (0.8 mmol, 0.237 6 g) in water (2 mL) was added to a hot aqueous solution (15 mL) of $H_4L$ (0.4 mol, 0.147 2 g) and 4,4′-bipy (0.4 mol, 0.062 4 g) in the presence of NaOH (1.6 mmol) and stirred for 1 min. The resulting solution was cooled slowly and allowed to stand at room temperature. Blue crystals suitable for single crystal X-ray structure analysis formed within 48 h. Yield: 0.182 g, 55%. Anal. Calcd. for $C_{26}H_{33}Cu_2N_4O_{12.5}$ (%): C, 42.80; H, 4.56; N, 7.63. Found(%): C, 42.82; H, 4.53; N, 7.68.

$\{[Cu_2L(mbix)(H_2O)_2]\cdot 3H_2O\}_n$ (**2**): Compound **2** was synthesized by a similar procedure as described for **1** except using mbix (0.4 mol, 0.095 2 g) instead of 4,4′-bipy. Yield: 0.262 g, 72%. Anal. Calcd. for $C_{30}H_{40}Cu_2N_6O_{13}$(%): C, 43.95; H, 4.85; N, 10.28. Found(%): C, 43.92; H, 4.88; N, 10.25.

### 1.3 X-ray crystallography

The well-shaped single crystals of **1** and **2** were selected for X-ray diffraction study. The diffraction data were collected on a Bruker Smart Apex-II CCD diffractometer with graphite monochromated Mo $K\alpha$ radiation ($\lambda$=0.071 073 nm) at 293(2) K. Determinations of the crystal system, orientation matrix and cell dimensions were performed according to the established procedures. Empirical absorption corrections were applied using the SADABS program. The structures were solved by direct method with SHELXS-97 program and refined by full-matrix least squares on $F^2$ with SHELXL-97 program[13]. All non-hydrogen atoms were refined anisotropically, and hydrogen atoms were located and included at their calculated positions. The crystal data and structure refinement results are summarized in Table 1.

CCDC: 888051, **1**; 888052, **2**.

**Table 1　Crystal data and structure refinement information for compound 1 and 2**

| Compound | **1** | **2** |
|---|---|---|
| Empirical formula | $C_{26}H_{33}Cu_2N_4O_{12.50}$ | $C_{30}H_{40}Cu_2N_6O_{13}$ |
| Formula weight | 728.64 | 819.76 |
| Crystal system | Monoclinic | Triclinic |
| Space group | $P2_1/c$ | $P\bar{1}$ |
| $a$ / nm | 1.257 12(12) | 1.185 6(2) |
| $b$ / nm | 1.836 25(17) | 1.202 9(2) |
| $c$ / nm | 2.039 37(14) | 1.632 3(3) |
| $\alpha$ / (°) | | 74.232(3) |
| $\beta$ / (°) | 126.714(4) | 81.171(3) |
| $\gamma$ / (°) | | 61.009(2) |
| $V$ / nm$^3$ | 3.773 8(6) | 1.958 9(6) |
| $Z$ | 4 | 2 |
| Calculated density / (g·cm$^{-3}$) | 1.282 | 1.390 |
| Final $R$ indices ($I>2\sigma(I)$) | $R_1$=0.055 1, $wR_2$=0.112 9 | $R_1$=0.057 8, $wR_2$=0.122 6 |
| $R$ indices (all data) | $R_1$=0.073 7, $wR_2$=0.115 8 | $R_1$=0.078 3, $wR_2$=0.126 9 |

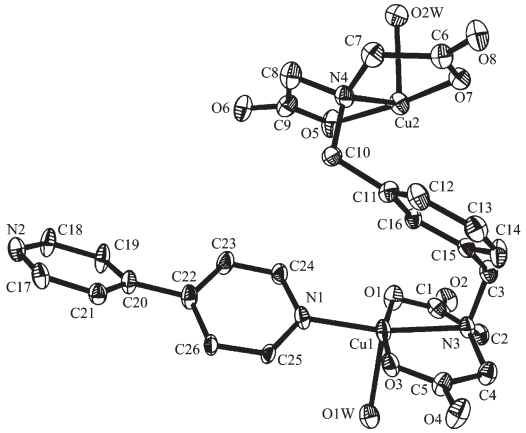
## 2　Results and discussion

### 2.1　Description of crystal structures

Compound **1** and **2** are obtained as well formed crystals directly from the reaction mixtures. These crystals, whose size is dependent on the rate of crystallization and the concentration of the initial solution, are insoluble in water as well as common organic solvents.

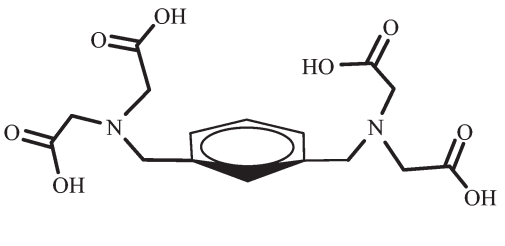
Due to the presence of methylene groups between the central benzene ring and terminal iminodiacetic group in $H_4L$, there can be two conformations when they coordinate with metal ions, namely, *cis*, *cis*-conformation (V-form) and *trans*, *trans*-conformation (Z-form) (Scheme 1). Crystallographic analysis reveals that the two iminodiacetate groups in compound **1** and **2** are all in opposite directions to the central benzene ring (Fig.1). Therefore, the conformations of the resulting compound **1** and **2** are in Z-form. Selected bond lengths and angles are given in Table 2.

Compound **1** crystallizes in monoclinic system

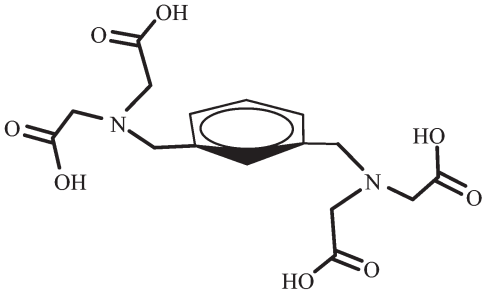



Hydrogen atoms and free water molecules omitted for clarity

Fig.1　ORTEP drawing of compound **1** with 30% thermal ellipsoids probability




V-form




Z-form

Scheme 1　V-form and Z-form conformations of $H_4L$

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

| | | | | | |
|---|---|---|---|---|---|
| **1** | | | | | |
| Cu(1)-O(3) | 0.193 5(3) | Cu(1)-O(1W) | 0.234 5(3) | Cu(2)-N(4) | 0.200 7(3) |
| Cu(1)-O(1) | 0.195 3(3) | Cu(2)-O(7) | 0.193 2(2) | Cu(2)-O(2W) | 0.231 4(3) |
| Cu(1)-N(1) | 0.198 2(3) | Cu(2)-O(5) | 0.196 7(3) | Cu(1)-N(3) | 0.200 4(3) |
| Cu(2)-N(2)#1 | 0.200 2(3) | | | | |
| O(3)-Cu(1)-O(1) | 167.42(11) | O(3)-Cu(1)-O(1W) | 91.41(11) | N(2)#1-Cu(2)-N(4) | 163.28(15) |
| N(1)-Cu(1)-N(3) | 167.18(13) | O(7)-Cu(2)-O(5) | 166.97(10) | O(7)-Cu(2)-O(2W) | 90.37(11) |
| **2** | | | | | |
| Cu(1)-O(3) | 0.191 9(4) | Cu(1)-O(1W) | 0.233 3(4) | Cu(2)-N(6)#1 | 0.201 9(3) |
| Cu(1)-O(1) | 0.196 1(3) | Cu(2)-N(3) | 0.193 6(4) | Cu(2)-O(2W) | 0.232 8(4) |
| Cu(1)-N(1) | 0.200 1(4) | Cu(2)-O(8)#1 | 0.194 9(3) | Cu(1)-N(5) | 0.201 4(4) |
| Cu(2)-O(6)#1 | 0.197 2(3) | | | | |
| O(3)-Cu(1)-O(1) | 168.49(16) | O(3)-Cu(1)-O(1W) | 88.74(14) | N(3)-Cu(2)-N(6)#1 | 160.23(16) |
| N(1)-Cu(1)-N(5) | 158.87(14) | O(8)#1-Cu(2)-O(6)#1 | 167.82(14) | O(8)#1-Cu(2)-O(2W) | 90.63(14) |

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

with space group $P2_1/c$. As shown in Fig.1, each Cu(Ⅱ) ion in **1** has a $N_2O_3$ coordination environment that can be described as slightly distorted square-pyramidal geometry (type 4+1, $\tau_1$=0.006 $\tau_2$=0.07) according to the Addison-Reedijk geometric criterion. The equatorial plane is dened by one nitrogen atom and two oxygen atoms from iminodiacetate group and one nitrogen atom from 4,4′-bpy. The Cu1 atom is displaced out the best plane formed by N1, O1, N3 and O3 by 0.012 7 nm and the Cu2 atom is out the square plane (N2, O5, N4 and O7) by 0.013 5 nm. The Cu-O distance range from 0.193 5(3) to 0.196 7(3) nm. Bond lengths of Cu-N (bipy) and Cu-N (iminodiacetate) are 0.198 2(3) and 0.200 7(3) nm, respectively. These bond lengths are comparable to those reported values[11]. Water molecules occupied the apical position with a longer distances of 0.234 5(3) nm (Cu1-O1W) and 0.231 4(3) nm (Cu2-O2W). The Cu1⋯Cu2 separation is 0.549 5 nm. Each iminodiacetate group coordinates to Cu1 or Cu2 ion in mer-$NO_2$ tridentate chelating mode, which led to the formation of two five-member rings of $CuNC_2O$ with a dihedral angle of 6.29° for Cu1 and 7.89° for Cu2. Furthermore, two pyridyl rings in the rigid 4,4′-bipy spacer are out of coplanarity and twisted by 34.2°.

Analysis of the crystal packing of compound **1** shows that One-dimensional zigig-like chains are linked into a two-dimensional layer supramolecular framework through the O(W)–H⋯O hydrogen-bonding interactions in $b$ direction (Fig.2). Two-dimensional layer supramolecular framework is further linked into a three-dimensional structure by the weak C–H⋯O hydrogen-bond interactions and $\pi$-$\pi$ interactions in $c$ direction.

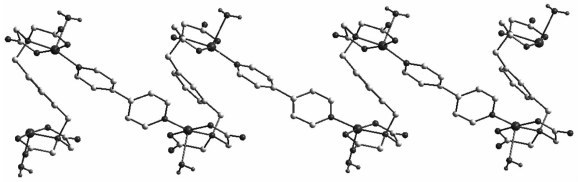
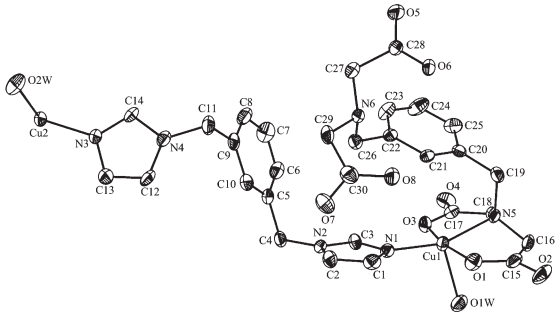


Fig.2 One dimensional zigig-like chain of **1**

For complex **2**, the flexible bridging ligand mbix was used instead of rigid 4,4′-bipy. It crystallizes in space group $P\bar{1}$ with triclinic system. As shown in Fig. 3, The Cu(Ⅱ) centers in **2** have the same $N_2O_3$ coordination environment with that in **1** described as slightly distorted square-pyramidal ($\tau_1$=0.16 $\tau_2$=0.11) geometry. Accordingly, the iminodiacetate group gives two nearly coplanarfive-member chelated ring of $CuNC_2O$ with a dihedral angle of 9.26° and 10.66° for Cu1 and Cu2, respectively, and the Cu-N (mbix) distance is 0.2001(4) and 0.1936(4) nm and Cu-N

(iminodiacetate group) distance is 0.201 4(4) and 0.201 9(3) nm, which also agreed well with the reported values[11]. The distance of Cu1-O1 and Cu1-O3 bond in basal plane are 0.196 1(3) to 0.191 9(4) nm, while the apical Cu1-O1W and Cu2-O2W bond has a distance with 0.233 3(4) and 0.232 8(4) nm. The Cu ⋯ Cu distance in **2** is 0.541 2 nm, which is shorter than that in **1**. The Cu1 atom is displaced out the best plane formed by N1, O1, N5 and O3 by 0.014 5 nm and the Cu2 atom is out the square plane(N3, O6, N6 and O8) by 0.016 5 nm.




Hydrogen atoms and free water molecules omitted for clarity

Fig.3　ORTEP drawing of compound **2** with 30% thermal ellipsoids probability

One-dimensional zigig-like chains of complex **2** (Fig.4) stacked into a 3D layer supramolecular structure by the O(W)–H⋯O hydrogen-bonding interactions in *a* direction and the O(W)–H⋯O hydrogen-bonding interactions in *c* direction.

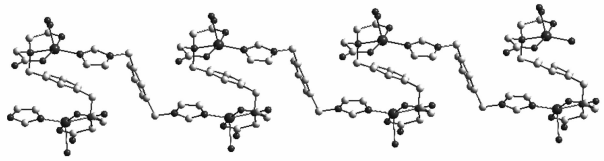


Fig.4　One dimensional zigig-like chain of **2**

## 2.3　IR spectra

For **1**, the absorption bands at 1 613 $cm^{-1}$ in IR spectra can be assigned to the asymmetric $\nu_{as}$(OCO) stretching bands and the band at 1 384 $cm^{-1}$ can be attributed to the symmetric $\nu_s$ (OCO) stretching bands. For **2**, the bands at 1 620 and 1 387 $cm^{-1}$ correspond to $\nu_{as}$(OCO) and $\nu_s$(OCO), respectively. The large differences between $\nu_{as}$(OCO) and $\nu_s$(OCO) of 229 $cm^{-1}$ for **1** and 233 $cm^{-1}$ for **2** indicating that carboxylates are all coordinated with Cu(Ⅱ) ions in a monodentate fashion in both complexes[14], which are consistent with their crystal structures.

## 2.4　Oxidation reaction of compound 1 and 2 by $H_2O_2$

It is reported that the diiron(Ⅲ) complex of $L^{4-}$ could hydroxylate the xylyl linker in the presence of $H_2O_2$[10]. On the basis of this result, we have previously demonstrated that the dicopper(Ⅱ) complex of this ligand could also do the same work as its diiron(Ⅲ) analogue did. In order to go on exploring the possibility of oxidation reaction of the one-dimensional copper(Ⅱ) polymer constructed by the $Cu_2L$ motif and *N*-heterocylces, we have investigated the reactions of complex **1** and **2** with $H_2O_2$ by UV-vis spectra. Addition of 300 equiv of $H_2O_2$ to the aqueous suspension of **1** and **2** and left them stood for 14 h, the blue solids slowly dissolved into the solution, and the color of solution experienced a change from blue to colorless to yellow. As can be seen from Fig.5, the same electronic absorption spectra of the resultant yellow solution of **1** and **2** (data not shown) show a new absorption band centered at ~380 nm, which indicates that the xylyl linker in $L^{4-}$ may also be hydroxylated by complex **1** or **2**/$H_2O_2$ system according to the similarity of 380 nm absorption to that of the dicopper (Ⅱ) complex of $L^{4-}$ in both wavelength and absorption coefficient. Indeed, the negative ion ESI-MS spectrum of the yellow solution of **1** and **2** by addition of $H_2O_2$ both showed a same signal at *m/z* 505.75 attributable to the hydroxylated specie $[Cu_2(L\text{-}O)]^-$. However, the ESI-MS observations also demonstrate that the

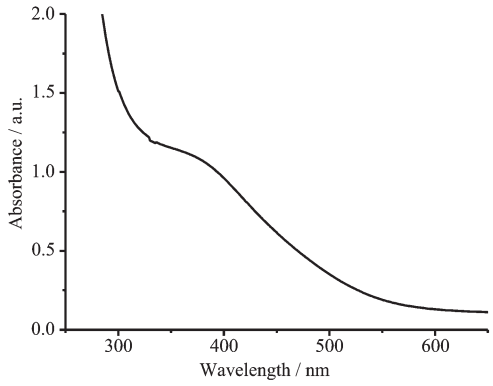



Fig.5　UV-Vis spectra of the reaction of compound **1** with 300 equiv $H_2O_2$ in water

hydroxylation process is companied by the dissociation of the bridging *N*-heterocylces ligand 4,4′-bipy or mbix from their respective one-dimensional polymer. Simultaneously, the ESI-MS spectrum in positive mode of compound **1** and **2** also displayed a same signal at *m/z* 195.17 that can be assigned to [iminodiacetate-Cu]$^+$, suggesting parts of $Cu_2L$ motif in polymer **1** or **2** have been further decomposed under the high concentration of $H_2O_2$.

In summary, two new 1D copper coordination polymers constructed from the carboxylate-rich ligand $L^{4-}$ and different *N*-heterocycles such as rigid 4,4′-bipy and flexible mbix have been structural characterized. Although compound **1** and **2** have undergone chemical degradation by reaction with 300 equiv of $H_2O_2$, they can both hydroxylate the xylyl linker in the ligand $L^{4-}$ similar to their $Cu_2L$ analogue.

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