

一维链状希夫碱铜配合物的高效光芬顿试剂活性

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摘要: 合成了 2 个希夫碱配合物 $[\text{Cu}(\text{HL}^1)\text{ClO}_4]_n$ (**1**) 和 $[\text{Cu}(\text{HL}^2)\text{NO}_3]_n$ (**2**) ($\text{H}_2\text{L}^1 = N-[(2\text{-oxy-acetate})\text{benzyl}]-2\text{-amino ethanol}$, $\text{H}_2\text{L}^2 = N\text{-salicylidene-3-amino propanol}$), 并将其在无酸化条件下用作甲基橙降解的光芬顿催化剂。**1** 和 **2** 均为一维链状结构且铜为六配位的拉长八面体配位构型。它们均具有优秀的均相光芬顿试剂活性且 **1** 的光催化活性更优秀。实验结果表明, 本研究中的配体结构对铜配合物的光催化活性有影响。

关键词: 希夫碱; 铜配合物; 光芬顿反应; 甲基橙

中图分类号: O614.121

文献标识码: A

文章编号: 1001-4861(2015)02-0399-06

DOI: 10.11862/CJIC.2015.028

1D Chains of Copper(II) Schiff Base Complexes as Efficient Photo-Fenton-Like Catalysts

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Abstract: Two copper(II) Schiff base complexes $[\text{Cu}(\text{HL}^1)\text{ClO}_4]_n$ (**1**) and $[\text{Cu}(\text{HL}^2)\text{NO}_3]_n$ (**2**) ($\text{H}_2\text{L}^1 = N-[(2\text{-oxy-acetate})\text{benzyl}]-2\text{-amino ethanol}$, $\text{H}_2\text{L}^2 = N\text{-salicylidene-3-amino propanol}$) have been synthesized and explored as photo-Fenton-like catalysts for the degradation of methyl orange (MO) without acidification process. **1** and **2** show 1D chain motifs and each copper(II) ion is six-coordinated in elongated octahedral environment. They are the first 1D chains of copper(II) Schiff base complexes with excellent photocatalytic performance. **1** has advantages on catalyzing efficient MO degradation through homogeneous photo-Fenton-like reaction. The results indicate that the coordinated ligands have some effect on the photocatalytic activity of copper(II) complexes in this study. CCDC: 996021, **1**; 996020, **2**.

Key words: schiff base; copper(II) complex; photo-fenton-like; methyl orange

0 Introduction

Schiff base metal complexes have experienced booming development in the fields of bioinorganic

chemistry, catalysis, magnetism and material chemistry^[1-2], while their usage in relevance to environmental remediation was rare. Azo dye represents an important class of environmental water contaminations

收稿日期: 2014-09-19。收修改稿日期: 2014-10-17。

江苏省普通高校研究生科研创新计划(No.CXLX13_517), 江苏省高校自然科学研究面上项目(No.13KJB220006), 南京林业大学引进高层次人才留学回国人员科研基金项目, 南京大学配位化学重点实验室开放基金项目和江苏省高校优势学科建设工程资助项目(PAPD)资助。

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due to their toxicity and slow degradation^[3]. To avoid the dangerous accumulation of such dye in the environment, it is urgent to develop effective methods to degrade this type of pollutant to less harmful compounds or more desirable mineralization products.

Advanced oxidation processes (AOPs) degrading organic compounds to less toxic molecules or even to CO₂ and H₂O in perfect conditions, such as, Fenton (Fe²⁺/H₂O₂), photo-Fenton (Fe²⁺/H₂O₂/UV) and related reactions are considered as potentially convenient, economical and green ways for the remediation of dye-containing industry effluents^[4-5]. However, the strict requirement for acidic conditions with a distinct optimum pH value range of 2.8~3.0 combined with the removal of the sludge containing iron ions complicating the overall process and made Fenton and Photo-Fenton reactions uneconomical^[6], because most organic wastewater has pH values ranging from 5 to 7^[7-8]. To solve this problem, catalysts based on other transition metal ions and organic ligands have been developed^[9]. This type of catalyst behaves similarly to Fentons reagents and the mixtures of these metal compounds with H₂O₂ were defined as homogeneous Fenton-like reagents^[5]. The main advantage of such systems is the broad substrate specificity and the wide-working pH value range (pH 3~9) compared to the conventional Fenton catalyst^[7-9]. To the best of our knowledge, no report about 1D chains of copper(II) Schiff base complexes as Fenton-like catalyst has appeared. So, we evaluated the catalytic behaves of two 1D chains of Cu(II) Schiff base complexes in photo-Fenton-like reaction for methyl orange (MO) degradation.

1 Experimental

1.1 Materials and physical measurements

All chemicals were commercial available and used without further purification unless otherwise noted. *O*-oxy-acetatebenzaldehyde was prepared according to literature and characterized by IR, ¹H NMR, MS and C, H, N analysis^[10].

1.2 Synthesis of the complexes

[Cu(HL¹)ClO₄]_n (**1**): An absolute methanol solution

(5 mL) of *O*-oxy-acetatebenzaldehyde (0.018 g, 1 mmol) was added dropwise to a vigorously stirred solution of ethanolamine (0.062 g, 1 mmol) in 5 mL absolute methanol under refluxing. The resulting yellow solution was refluxed for 6 h before cooling to room temperature. To this yellow H₂L¹ solution, a solution of copper(II) perchlorate (0.263 g, 1 mmol) in 5 mL methanol/acetonitrile (1:1, V/V) was added slowly under vigorously stirring. The resulting solution was stirred for 1 h at 30 °C. Blue needle single crystals suitable for X-ray analysis were obtained on slow diffusion of ether into the solution after one week. Yield: 11.74%. Anal. Calcd. for C₄₄H₄₈Cl₄Cu₄N₄O₃₂: C 34.30, H 3.14, N 3.64. Found: C 34.68, H 3.16, N 3.42. IR (KBr pellet, cm⁻¹): 3 432 (br, s), 1 658 (s), 1 384 (m), 1 287 (w), 1 215 (m), 1 102 (s), 623 (m), 524 (w), 406 (m).

[Cu(HL²)NO₃]_n (**2**): An absolute methanolic solution (5 mL) of salicylaldehyde (0.122 g, 1 mmol) was added dropwise to a vigorously stirred solution of propanol amine (0.075 g, 1 mmol) in 5 mL absolute methanol under refluxing. The resulting yellow solution was refluxed for 6 h before cooling to room temperature. To this yellow H₂L² solution, a solution of copper(II) nitrate (0.243 g, 1 mmol) in 5 mL methanol was added slowly under vigorously stirring. The resulting solution was stirred for 1 h at 30 °C. Green block single crystals suitable for X-ray analysis were obtained on slow diffusion of ether into the solution after one week. Yield: 42.94%. Anal. Calcd. for C₁₀H₁₁CuN₂O₅: C 39.67, H 3.66, N 9.25. Found: C 39.59, H 3.78, N 9.26. IR (KBr pellet, cm⁻¹): 3 433 (br, s), 1 630 (s), 1 463 (s), 1 448 (s), 1 404 (m), 1 384 (m), 1 278 (s), 1 210 (m), 546 (w), 435 (m).

1.3 X-ray crystallography

The data were recorded on a Bruker SMART APEX II CCD area-detector with graphite-monochromated Mo K α radiation ($\lambda=0.071\ 073$ nm for **1** and **2**) at 293 K. Empirical absorption correction was applied. The structure of **1** and **2** were solved by direct methods of SHELXS-97 and refined by full-matrix least-squares techniques using the SHELXL-97 program^[11]. All the non-hydrogen atoms were refined

anisotropically. Details of the crystallographic data and structure refinement parameters for complexes **1** and **2** are given in Table S1.

CCDC: 996021, **1**; 996020, **2**.

1.4 Photoreactor and light source

The reactor used in all experiments was a XPA-VII type photochemical apparatus (Xujiang Machine Factory, Nanjing, China). A 300 W high pressure mercury lamp equipped with cool water circulating filter to absorb the near IR radiation was used as the UV light source. The lamp was always allowed to stabilize before use.

1.5 Evaluation of Photocatalytic Activity

To evaluate the photo-Fenton-like catalytic behaviors of **1** and **2**, MO was selected as model dye due to its environmental significance and non-biodegradation. The photoreaction was carried out under the natural pH value of the catalyst/MO/H₂O₂ system (around 6) unless otherwise noted.

Freshly prepared aqueous solutions of MO (20 $\mu\text{mol}\cdot\text{L}^{-1}$, 250 mL) in the presence of **1** (0.001 0 g) or **2** (0.001 0 g) and H₂O₂ (16 $\text{mmol}\cdot\text{L}^{-1}$) were magnetically stirred for 30 min in the dark. Then the solutions were started to photocatalytic degradation under aerated conditions at ambient temperature in

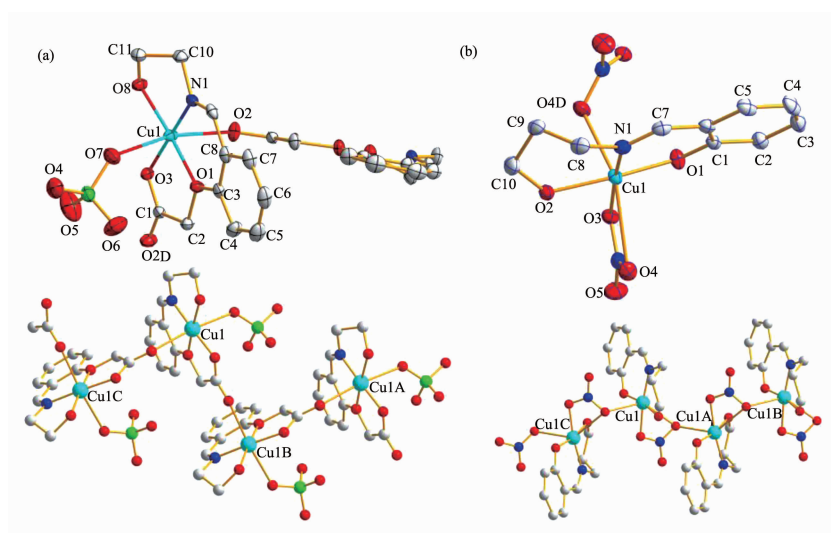
the presence/absence of UV light irradiation. The solutions were magnetically stirred throughout the experiment. At given time intervals, 3 mL aliquots were sampled and subsequently analyzed by TU-1901 UV-Visible spectrophotometer (Beijing Purkinje General Instrument Co., Ltd.) to record the temporal UV-Visible spectral variations of the dye. The MO concentration was determined by measuring the maximum absorbance at 465 nm as a function of irradiation time using the UV-Visible spectrophotometer. All the tests were carried out three times to ensure the reproducibility.

2 Results and discussion

2.1 Description of the structures

The complexes **1** and **2** crystallized in monoclinic space group $P2_1/c$ and orthorhombic space group $Pbca$, with $Z=1$ and $Z=8$, respectively. The coordination environment of each copper(II) ion in **1** and **2** with the partial atomic numbering scheme is shown in Fig.1. Selected bond lengths and bond angles are given in Table S2 (1) and Table S3 (2).

As displayed in Fig.1(a), copper(II) ion in **1** is six-coordinated by one imine nitrogen atom (N1) and five O atoms from one hydroxyl (O8), one deprotonated



Hydrogen atoms are omitted for clarity; Symmetry code: A: $x, y, -1+z$; B: $x, 1/2-y, -1/2+z$; C: $x, 1/2-y, 1/2+z$; D: $x, y, 1+z$ for **1**; A: $1/2+x, 1/2-y, -z$; B: $1+x, y, z$; C: $-1/2+x, 1/2-y, -z$; D: $-3/2+x, 1/2-y, -z$ for **2**

Fig.1 ORTEP views of coordination environment of copper(II) ion in **1** ((a), top) and **2** ((b), top) with the ellipsoids drawn at the 30% probability level and ball-and-stick representations of **1** ((a), bottom) and **2** ((b), bottom)

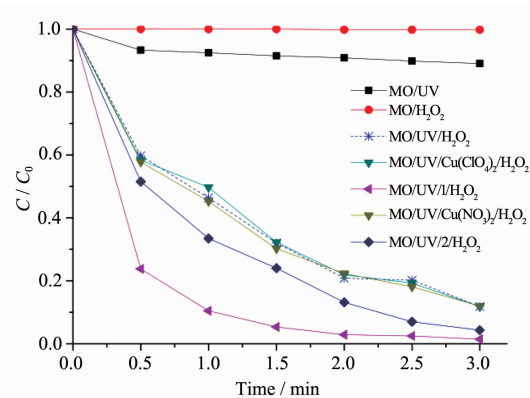
phenolic hydroxyl (O1), one perchlorate (O7) and two carboxylates (O2 and O3), respectively. The coordination geometry around Cu1 could be described as octahedron with N1-O1-O3-O8 as the basal plane (total bond angle at Cu1 in the basal plane is 359.40°), and O2 and O7 atoms on the axial sites. The octahedron of Cu1 can be described as a Jahn-Teller weakly distorted octahedral geometry, with a CuNO5 chromophore resulting from two short ($d_{\text{Cu1-O3}} = 0.190\ 5(2)$ nm, $d_{\text{Cu1-N1}} = 0.191\ 2(3)$ nm), two long ($d_{\text{Cu1-O2}} = 0.240\ 6(2)$ nm, $d_{\text{Cu1-O7}} = 0.267\ 29(30)$ nm), and two intermediate ($d_{\text{Cu1-O1}} = 0.199\ 6(2)$ nm, $d_{\text{Cu1-O8}} = 0.197\ 2(2)$ nm) bond lengths (Table S2). The average basal $d_{\text{Cu-O}}$ (0.219 0 nm) is much shorter than the average apical one (0.258 5 nm), which is expected for the Cu(II) ion in an elongated octahedral environment. What's more, each ligand links two Cu(II) ions through carboxylic oxygen atoms generating a 1D chain (Fig.1(a)), The Cu...Cu separation within the chain is 0.619 93(7) nm.

Fig.1(b) shows the ORTEP diagram of the coordination environment of copper(II) ion in **2**. Each copper(II) ion coordinates with one H_2L^2 ligand in its deprotonated form (HL^2) and two nitrates. The copper(II) ion exhibits a six-coordinated motif; in the equatorial plane, Cu1 is coordinated by one imine nitrogen atom (N1) and three O atoms from one deprotonated hydroxyl (O2), one phenolic hydroxyl (O1) and one nitrate (O7) (total bond angle at Cu1 in the basal plane is 344.34°), respectively. The apical positions are occupied by two oxygen atoms from two nitrates with significantly larger axial distances compared with the equatorial ones, which would be consistent with a very weak metal ion interaction due to the Jahn-Teller effect. The coordination environment around Cu1 can be described as a distorted octahedral geometry, with a CuNO5 chromophore resulting from two short ($d_{\text{Cu1-O1}} = 0.189\ 20(17)$ nm, $d_{\text{Cu1-N1}} = 0.194\ 3(2)$ nm), two long ($d_{\text{Cu1-O4}} = 2.647\ 6(18)$ nm, $d_{\text{Cu1-O4A}} = 0.251\ 95(17)$ nm), and two intermediate ($d_{\text{Cu1-O2}} = 0.197\ 71(18)$ nm, $d_{\text{Cu1-O3}} = 0.201\ 83(18)$ nm) bond lengths (Table S3). The average basal $d_{\text{Cu-O}}$ (0.195 76 nm) is much shorter than the average apical one (0.258 35 nm), which is expected for the Cu(II) ion in an elongated octahedral environ-

ment. Two copper (II) centers with the separation of 0.435 39(7) nm are jointed together through the bridging nitrate and extend into a 1D chain (Fig.1(b)).

2.2 Kinetics of MO Degradation

The changes of MO concentration as a function of reaction time under different conditions are illustrated in Fig.2. It is observed that H_2O_2 alone had no evident effect on the degradation. MO degraded very slowly under UV light illumination; whereas the reaction rate was evidently enhanced in the presence of H_2O_2 and UV light together. It is noticed that the inorganic salts $\text{Cu}(\text{NO}_3)_2$ and $\text{Cu}(\text{ClO}_4)_2$ could be basically regarded as no use to the system of MO/UV/ H_2O_2 . The best results came out with the combined effect of H_2O_2 , catalyst (**1** or **2**) and UV light. A comparison of the different processes leads us to conclude that the involvement of catalyst **1** or **2** sharply improved the degradation efficiency; and **1** displayed better catalytic activity than **2** under the same concentration. The crystal structure analysis indicates that the coordination number of copper(II) ion is both six in **1** and **2**; their structural differences are the coordinated anion and ligand. Thus, the difference in their catalytic ability was caused by the different coordinated ligands. It is noticed that the copper(II) centers in **1** were bridged by the organic ligand, while the bridge of **2** is inorganic nitrate anion, thus **1** should have stronger stability. The stronger stability of **1** caused its stronger ability to



Experimental conditions: MO: $20\ \mu\text{mol}\cdot\text{L}^{-1}$; H_2O_2 : $16\ \mu\text{mol}\cdot\text{L}^{-1}$; **1** or **2**: 0.001 0 g; pH=6.14 for **1**; pH=6.48 for **2**; UV light, 300 W

Fig.2 Degradation kinetics of MO in different reaction systems

active H_2O_2 to form the intermediate product $[\text{Cu}^+\text{O}_2\text{H}(\text{HL})]\text{ClO}_4$ (See Supporting Information, Proposed reaction pathways section), which results in better catalytic ability. This result is consistent with Wus conclusion, i.e., ligand structure influences the stability constants of copper complexes and may result in different physiochemical properties^[12]. The present research tells us that different ligand could tune the catalytic activity of coordination complexes composed of the same metal ion to a certain degree.

Because the two complexes have similar structure (with a CuNO_5 chromophore) and **1** has slight advantage, we just discussed the results of **1** in detail here, the relative data for **2** were provided in the Supporting Information.

2.3 UV-Vis spectra of MO during the photo-Fenton-like process

The temporal evolution of the spectral changes of MO for $\text{MO}/\text{UV}/\text{H}_2\text{O}_2/\mathbf{1}$ system is displayed in Fig.3. In general, the UV-Vis spectra of MO solution showed two characteristic absorption peaks at 272 and 465 nm. The UV band at 272 nm was ascribed to the $\pi \rightarrow \pi^*$ transition of the aromatic rings in the MO molecule, whereas the band in the visible region (465 nm) was attributed to the conjugated structure formed by the azo bond under the strong influence of the electron-donating dimethylamino group^[13]. The rate of degradation was recorded with respect to the changes

in intensity of absorption peak at 465 nm.

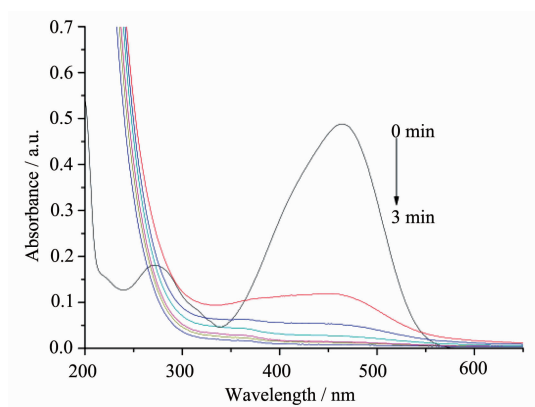
In the present study, the maximum absorption band of MO in the visible region decreased dramatically to about zero in 3 min, with no new adsorption band appearing in the visible region. This indicates that the decolorization of the MO was rather complete. And the absorption peak at 272 nm diminished all over the spectral window and no more specific peak can be detected under the current experimental condition. The disappearance of the absorption peaks corresponding to MO indicates that MO was degraded.

2.4 Mineralization studies

Complete decolorization of MO does not necessary mean that it has been completely oxidized into CO_2 and H_2O , that is mineralization, as reactive intermediates containing benzene rings can be formed during oxidation. Therefore, it is important to evaluate the mineralization of organic dye. The mineralization degree of MO was evaluated by monitoring the change in the total organic carbon (TOC) as shown in Fig.S12. The TOC analysis provides information on whether or not MO molecules are completely converted into CO_2 and H_2O . TOC_0 referred to the TOC content of the initial MO solution and TOC_t referred to the TOC content of the reaction solution at reaction time t . Fig. S12 shows about 57% mineralization in 25 min was obtained, the removal of TOC achieved confirmed that the photodegradation of MO was accompanied by partial mineralization and the decolorization rate was much faster than mineralization rate. Such high TOC removal rate indicates that some benzene substituted intermediates and some ring-open up degradation products of benzene such as formic acid, acetic acid maybe both present in the final solution^[14-15]. Anyway, the results demonstrate that **1** have some advantage on photocatalytic degradation of dye pollutants.

3 Conclusions

In conclusion, this report shows that the two 1D chains of copper(II) Schiff base complexes (**1** and **2**) were excellent homogeneous photo-Fenton-like catalyst and the catalytic property has a close relationship



Experimental conditions: MO: $20 \mu\text{mol} \cdot \text{L}^{-1}$; H_2O_2 : $16 \mu\text{mol} \cdot \text{L}^{-1}$; **1**: 0.001 0 g; pH=6.14; UV light, 300 W

Fig.3 Temporal absorption spectrum changes observed for the homogeneous photo-Fenton-like process catalyzed by **1**

with their structures, i.e., the composition of the coordinated ligands. No acidification process is an important advantage of the reactions; because it overcame one major drawback of homogeneous Fenton process, i.e. the narrow acidic pH range which is unfavorable in practice due to the costs of acidification during processing and neutralization after treatment. The present processes not only led to almost complete decolorization of MO in relatively short time (≈ 3 min) but also partially mineralized MO. The work represented the first example of 1D chains of copper(II) Schiff base complexes acting as efficient photo-Fenton-like catalyst. These experimental results not only are encouraging but also enlighten a new clue to develop practical highly active photo-Fenton-like catalysts using under neutral pH condition. The existing system may be applicable to color removal for textile waste water.

Acknowledgements: The authors gratefully acknowledge the financial support from State Key Laboratory of Coordination Chemistry of Nanjing University, Nanjing Forestry University and the Priority Academic Program Development of Jiangsu Higher Education Institutions, College and University Graduate Research Innovation Project of Jiangsu Province (No. CXLX13_517), and University Science Research Project of Jiangsu Province (No. 13KJB220006)

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