水相中金属铜表面生成亚铜—邻菲罗啉配合物的反应

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本文研究了零价铜在邻菲罗啉水溶液中的反应。当溶液敞露于空气并存在有机阴离子 X^- 时, 例如苯甲酸盐(Bz)、对甲基苯磺酸盐(Ts)等, 铜的表面生成了致密的反应产物的薄层, 经 IR、UV/VIS、MS 和元素分析证明了该薄层为相当纯的亚铜的邻菲罗啉配位化合物, 结构为 $[Cu(phen)_2]^+X^-$。在乙醇/甲苯混合溶剂中得到了表面反应产物的晶体 $[Cu(phen)_2](CH_3C_4H_6SO_3)C_2H_5OH$, 并用 X-ray 测得了结构。本工作表明溶液中的 Cu^{II} 离子抑制 Cu^0 氧化成 Cu^I 而影响反应层的形成, 同时又促进 Cu^I 氧化成 Cu^{II} 的过程。

关键词:　亚铜-邻菲罗啉配合物　铜表面反应　晶体结构

FORMATION OF BIS(1, 10-PHENANTHROLINE) CUPROUS COMPLEXES ON METALLIC COPPER SURFACE IN AQUEOUS SOLUTION

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The formation of cuprous complex on metallic copper surface in 1, 10-phenanthroline (phen) aqueous solution has been investigated as exposed in air and in the presence of common organic anions (X^-) such as benzoate (Bz^-) and toluene sulphonate (Ts^-). The complexes deposited on the surface of metallic copper have been proved to be rather pure cuprous phenanthroline complexes having the structure $[Cu(phen)_2]X$ based on the elemental analysis, IR, UV/VIS spectroscopy and mass spectroscopy (FAB). The crystal structure of the complex $[Cu(phen)_2](CH_3C_6H_4SO_3)\cdot C_2H_5OH$ was determined by X-ray diffraction analysis. The work demonstrated that the Cu^{II} ion in the reaction solution hindered the process of Cu^0 to Cu^I and in the meanwhile accelerated the process of Cu^I to Cu^{II}.

Keywords:　cuprous phenanthroline complex　copper surface reaction　crystal structure

Introduction

Copper compounds are important catalysts for the oxidation and oxygenation of organic compounds both in chemical and biological systems. Recently, much attention has been paid to cuprous phenanthroline complexes in degrading DNA and probing structure[1]. The bind-

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ing and activation of molecular oxygen of copper complexes have been extensively studied. But the systematics in reactivity of copper complexes/O_2 systems and the mechanism in Cu/O_2 chemistry still remain not clearly understood[2].

Cuprous complexes are mostly prepared from $[Cu(NCMe)_4]X$ because of the stabilization of copper (Ⅰ) ion by MeCN. A "stronger" ligand such as 1, 10-phenanthroline and Ph_3P can substitute methyl nitrile ligands. Reduction methods are also used for the preparation. But in most cases, experiments must be carried out under a nitrogen or an argon atmosphere. In our study, a convenient preparative method of cuprous phenantroline (phen) complexes was first introduced starting from metallic copper. The reaction was performed in the phen aqueous solution with some common organic anions (such as carboxylates or sulfonates) and exposed in air at room temperature.

Metallic copper is not reactive in either water or methanol in an oxygen atmosphere[3]. It has been reported that, in the presence os bipyridyl ligands, metallic copper is oxidized in an aqueous solution, and binuclear hydroxybridged divalent copper complexes are formed[4]. A direct preparation of Cu^{2+} catecholates from copper and phenols can be performed in the presence of O_2 and catalytic amount of CuCl[5]. Gargano have studied the reactivity of metallic copper with several acidic organic compounds in the pyridine/methanol solution and an oxygen atmosphere, resulting in divalent copper compounds[3]. Benzimidazole reacted with metallic copper and produced Cu^{2+} bisbenzimidazolate[6]. To our knowledge, little has been reported on the preparation of air sensitive cuprous complexes from metallic copper in the oxygen-containing aqueous solution.

Experimental

Copper surface reaction in aqueous solution

All solvents are of an analytical grade. 1, 10-phenanthroline (phen) and sodium benzoate (NaBz) are of an analytical grade and sodium *p*-toluene sulphonate (NaTs) is chemically pure. 1, 10-phenanthroline was dissolved in distilled water for: 5.6×10^{-3} mol/L, sodium benzoate (NaBz), sodium *p*-toluene sulphonate (NaTs) were added respectively into the solution at about 1.0×10^{-2} mol/L. Pure metallic copper foil was cleaned in 20% sulphuric acid to remove the oxide on the surface and rinsed with distilled water. Dip the cleaned copper foil steadily in the phen aqueous solution in the presence of NaBz or NaTs at room temperature. In half a minute, the reacted film could be observed on the surface of the copper foil. The thickness of the film increases with the time delay. After about three hours, a dark violet thick layer of the reaction product was tightly adhered on the surface. The foil was removed from the solution, then the residual solution was absorbed and dried the foil in a P_2O_5 vacuumed desicator. The surface reaction product could be easily separated by dissolving in deoxygenated ethanol at an argon atmosphere. After removing the solvent by suction, a dark violet powder product was obtained for measurement without any further purification. The product is stable in dry and inert atmosphere.

For investigating the influence of $[Cu(phen)_2]^{2+}$ $(Cu)^{II}$ on the surface reaction, we added different amounts of $CuBz_2\cdot3H_2O$ (in conc. range 0.0-1.6×10^{3} mol/L) to the phen/Bz^- solution, in which still only the Bz^- as anion was present. A definite size (*S*) of the cop-

per foil (weight M) was dipped in the solution for 2.7 hours, then the foil was taken out, dried and weighed together with the deposited cuprous complex film (Cu^{I}) to obtain M_a. The actual deposited weight $m_a = M_a - M_e$, there M_e was the net weight of the copper foil after dissolving the deposited complex by ethanol. The total loss of the copper foil was $m(Cu) = M - M_a$. Fig. 1 showed m_a and m_t (the theoretical yield of corresponding (Cu^{I}) calculated from m (Cu) for different Cu^{II} concentrations in solution.

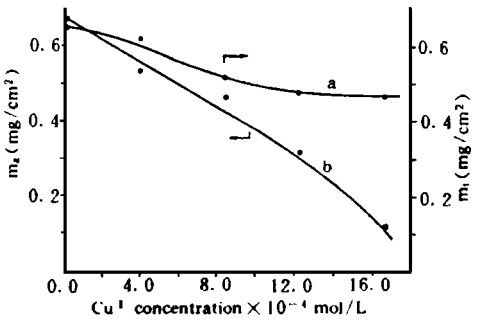

Fig. 1　Actual deposited weight m_a and theoretical deposited weight m_t on unit area of copper foil at different concentrations of Cu^{II}, reaction time 2.7 hrs

Spectrocopy and X-ray crystallography

Infrared spectra were measured with a Digilab FTS-20E infrared spectrometer by reflection absorption (incident angle = 80° and 26°) on the copper foil substrate. IR spectra were also measured by casting the ethanol solution of the product on BaF_2 or KRS-5 crystal. The KBr pellet sampling method is not always suitable because of the ion exchange. The UV/VIS spectra were recorded by a Perkin-Elmer Lamda-5 spectrophotometer using the deoxygenated ethanol solution. Mass spectra were measured using the FAB source on a VG Quattro MS-spectrometer.

A reddish brown crystal of $[Cu(phen)_2]Ts \cdot C_2H_5OH$ was obtained from the ethanol/toluene solution. A prismatic crystal having an approximate dimension of 0.2×0.2×0.3 mm was mounted in a glass capillary. All measurements were carried out on a Rigaku RASA-7R diffractrometer using a graphite monochromatized Mo-$K\alpha$ radiation (λ = 0.71069 Å) and a 12 kW rotating anode X-ray generator. Crystal data: monoclinic, space group $P2_1/c$ (# 14), a = 13.04(2), b = 16.16(1), c = 15.351(8) Å. β = 112.38(5)° and Z = 4, V = 2991(3) Å^3, D_{calc} = 1.42 g/cm^3.

Results and Discussion

The surface deposition reaction on the metallic copper surface is highly repeatable in the phen aqueous solution at an ambient temperature range 10-30℃ and in presence of some organic salts such as carboxylates or sulphonates. Here we focus on the results using the Bz^- and Ts^- anion.

Stoichiometry of the surface reaction products

The surface reaction product using Bz^- as anion shows MLCT absorption maximum at 438.8 nm and the molar absorptivity of which is about 6830 $mol^{-1} \cdot L \cdot cm^{-1}$. It is consistent with the reported data[7] of $[Cu(phen)_2]^+$. IR spectra of the product show phen absorptions at 722 (vs), 839 (m), 1423 (s), 1505 (w), 1561 (vs) cm^{-1} and $\nu_{as}(COO^-)$ and $\nu_s(COO^-)$ at 1608 (vs) and 1352 (m) cm^{-1} respectively. The FAB MS spectrum gives m/z (%): 544 ($[Cu(phen)_2]Bz^+$, 5), 439 ($[OCu(phen)_2]^+$, 2), 423 ($[Cu(phen)_2]^+$, 80), 365 ($[Cu(phen)C_6H_5COOH]^+$, 10) and 243 ($[Cu(phen)]^+$, 100). Elemental analysis of the

film product, found: C, 67.82; H, 3.79; N, 10.18. $C_{31}H_{21}CuN_4O_2$ requires for C, 68.30; H, 3.88; N, 10.29. All results support the molecular formula $[Cu(phen)_2]\cdot(C_6H_5COO)$ for the product available.

The crystal structure of $[Cu(phen)_2]Ts\cdot C_2H_5OH$

The crystal structure of the complex is consistent with the stoichiometry and connectivity expected for $[Cu(phen)_2]Ts\cdot C_2H_5OH$. The molecule consists of a monovalent cation $[Cu(phen)_2]^+$, a large anion $CH_3C_6H_4SO_3^-$ and a nonbonding solvent C_2H_5OH in the lattice. The perspective view of the molecule is presented in Fig. 2, together with the atomic numbering scheme. The selected bond distances and angles are given in Table 1. The coordination around the cuprous ion is completed by four nitrogen atoms from two phenanthroline ligands with Cu-N bond distances ranging from 1.95(3)-2.09(2) Å, and N-Cu-N bond angles about 82.° Both Cu-N distances and N-Cu-N bond angles are consistent with crystal structure of $[Cu(phen)_2]ClO_4$ and $[Cu(phen)_2](CuBr_2)$ reported in Ref. 8, which has the same cation as that in our work. The interligand dihedral angle 79.27 °is not quite far from 90 °, with interligand N-Cu-N angles differing from 113.0 °to 137.5.° It seems that different anion affects the interligand dihedral angles. Our case is comparable with the structure of the cation $[Cu(phen)_2](CuBr_2)$ which shows the interligand dihedral angle 76.8 °, but in contrast to that of $[Cu(phen)_2]ClO_4$ with 49.9.° The dihedral angles between the planar anion $CH_3C_6H_4SO_3^-$ and the two phen ligands in the cation are nearly equal, which are 65.09 °and 63.44 °, respectively.

Table 1 Selected Atomic Distances (Å) and Bond Angles (°) for $[Cu(phen)_2]Ts\cdot C_2H_5OH$

Cu-N (1)	2.05(2)	N (1)-Cu-N (2)	82.3(9)
Cu-N (2)	1.95(3)	N (1)-Cu-N (3)	113.0(9)
Cu-N (3)	2.09(2)	N (1)-Cu-N (4)	123.3(9)
Cu-N (4)	2.04(2)	N (2)-Cu-N (3)	137.5(9)
C_1-N (3)	1.31(4)	N (2)-Cu-N (4)	122(1)
C_{12}-N (3)	1.40(3)	N (3)-Cu-N (4)	82(1)
C_{11}-N (4)	1.41(3)	Cu-N (1)-C_{22}	130(2)
C_{10}-N (4)	1.27(3)	Cu-N (1)-C_{23}	112(1)
C_{22}-N (1)	1.33(3)	Cu-N (2)-C_{13}	131(2)
C_{23}-N (1)	1.35(3)	Cu-N (2)-C_{24}	112(1)
C_{24}-N (2)	1.44(3)	Cu-N (3)-C_1	132(2)
C_{13}-N (2)	1.32(4)	Cu-N (3)-C_{12}	108(2)
		Cu-N (4)-C_{10}	134(2)
		Cu-N (4)-C_{11}	113(1)

Formation of the cuprous complex film on metallic copper surface

The deposition of bis (1, 10-phenanthroline) cuprous complex on the copper surface in the aqueous solution, intrinsically is an oxidation reaction of copper by the molecular oxygen in the presence of 1, 10-phenanthroline. The reaction cannot take place in a strictly deoxygenated solution and an inert atmosphere.

For one dipping reaction of a copper foil, the thickness of the deposited cuprous complex film reached the maximum (ca. 10 μm) after about 8 hours, yielding about 1.0-2.0 mg/cm^2.

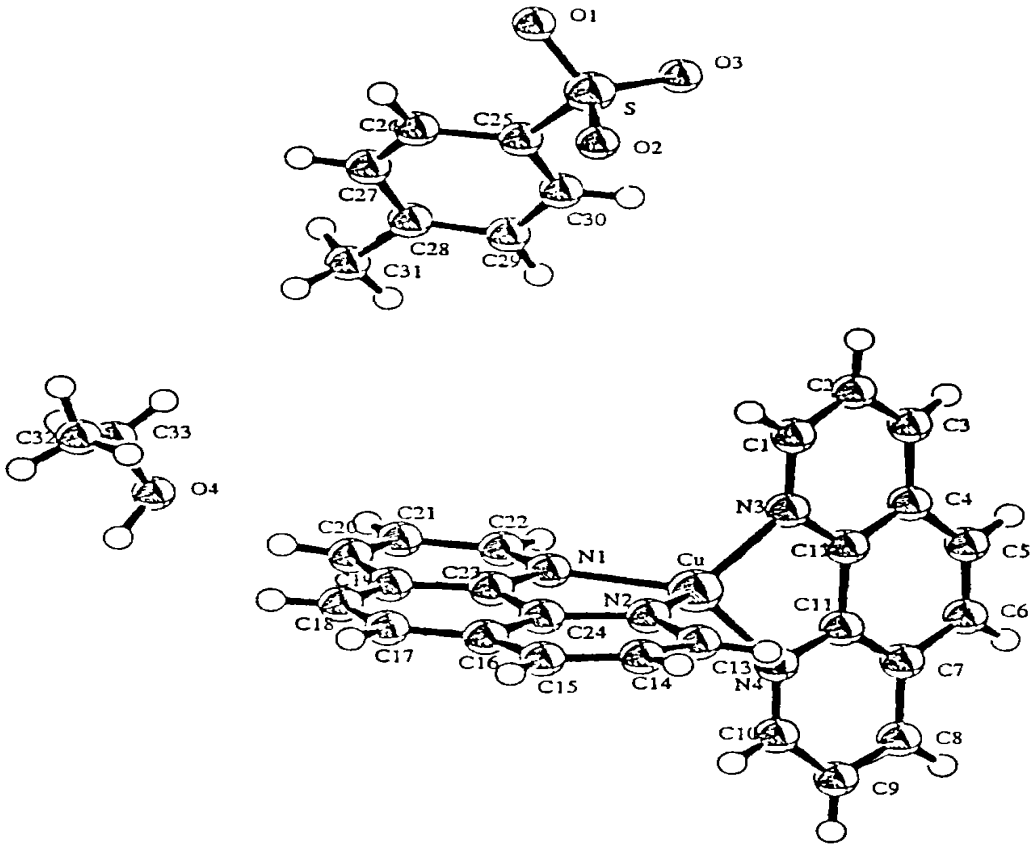

Fig. 2　An ORTEP view of $[Cu(phen)_2]Ts \cdot C_2H_5OH$, showing the atomic numbering

Later, the thickness began to decrease, because the cuprous complex on the foil began to be oxidized to $[Cu(phen)_2]^{2+}$ and dissolved into the solution. After about two days, all deposited cuprous complex was dissolved into the solution. It implies that $[Cu(phen)_2]^{2+}$ may influence the formation of $[Cu(phen)_2]X$ in the system.

The influence of $[Cu(phen)_2]^{2+}$ ion to the surface reaction in the solution are shown in Fig. 1. Curve (a) shows m_t decreases with the increasing concentration of Cu^{II} in the solution. This indicates that Cu^{II} ion hinders the oxidation of Cu^0. Both the oxidation process $Cu^0 \rightarrow Cu^I$ (deposited on the foil) and $Cu^I \rightarrow Cu^{II}$ (dissolved into the solution) contribute to the copper consumption m (Cu). We could find that m_t is not always equal to actual yield of Cu^I m_a, generally $m_a < m_t$, because a part of the deposited cuprous complex is dissolved by oxidation for Cu^{II}. In Fig. 1 we could find that m_a equals to m_t without adding Cu^{II} within at least 2.7 hours. It implies that in several hours the surface reaction has little by-product at very low Cu^{II} ion concentration. The more the Cu^{II} ion concentration increases, the more m_a deviates from m_t. And the yield of the deposited Cu^I sharply decreases. Apparently a part of the cuprous complex was dissolved to Cu^{II} by oxidation at a higher Cu^{II} concentration.

We suppose that in our reaction system two oxidation processes compete in the whole

process described above. $Cu^0 \rightarrow Cu^I$ process is predominated in the early stage. It keeps consuming molecular oxygen in the solution for a rather long time (about 8 hours) till the film thickness of the surface product increases to the maximum value. In this period the molecular oxygen "penetrates" through the Cu^I film reaching the copper surface to maintain the process. The penetration process might be a transportation of molecular oxygen by exchanging binding complex $[O_2Cu(phen)_2]^+$ through the Cu^I layer to the copper surface. When the Cu^I layer was thickened to some extent, the penetration of oxygen became slower than the consumption of oxygen in $Cu^0 \rightarrow Cu^I$ process. Then $Cu^I \rightarrow Cu^{II}$ process became predominated in the solution.

The basic study on the reaction of copper (Ⅰ) complex with molecular oxygen is of great importance for understanding the pathway of oxygen in copper-catalyzed auto oxidation reactions in both chemical and biological systems. The oxidation of 1, 10-phenanthroline copper (Ⅰ) complex by molecular oxygen in the aqueous solution and with many different ligands has been investigated in detail by Goldstein[9, 10]. They concluded in their research that the reduction of molecular oxygen by $[Cu(phen)_2]^+$ (Cu^I) proceeds via the formation of an intermediate with a copper-oxygen bond, i.e. via Cu^I-O_2. Depending on the concentration of Cu^{II} present in the solution, this transient may either react with another Cu^I or decompose to Cu^{II} and O_2, as shown in Eq. (1) and Eq. (2).

$$Cu^I + O_2 = Cu^I - O_2 \xrightarrow{Cu^I} 2Cu^{II} + O_2^{2-} \quad (1)$$

$$Cu^I - O_2 \rightarrow Cu^{II} + O_2^- \xrightarrow{Cu^I} 2Cu^{II} + O_2^{2-} \quad (2)$$

$Cu^I \rightarrow Cu^{II}$ in our system is not a simple process. Our experimental results are consistent with Goldstein's conclusion. When extra molecular oxygen is present in the solution, the transient complex Cu^I-O_2 may decompose to Cu^{II} (Eq. 2). When the Cu^{II} concentration becomes higher in the solution, the transient may react with another Cu^I to produce Cu^{II}. The Cu^{II} ion accelerates the oxidation of Cu^I to Cu^{II}.

Conclusion

The cuprous complex film could be formed in the aqueous solution on a clean metallic copper surface in the presence of a nitrogen-containing heterocyclic ligand such as 1, 10-phenanthroline and a proper organic anion (Bz^- and Ts^- for instance). The deposited cuprous complex has proved to have a slightly distorted tetrahedral skeleton $[Cu(phen)_2]^+$. When the deposited Cu^I film increased to a maximum thickness, it started to be oxidized to cupric compound. The Cu^{II} ion in the solution hindered the process of Cu^0 to Cu^I, and in the meanwhile accelerated the process of Cu^I to Cu^{II}.

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