

Direct electrochemical synthesis and crystal structure of a copper(II) complex with a chiral (*S*)-2-(diphenylmethanol)-1-(2-pyridylmethyl)pyrrolidine

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Abstract

A new chiral binuclear copper(II) complex of (*S*)-2-(diphenylmethanol)-1-(2-pyridylmethyl)pyrrolidine (*S*-dmpmpH) was prepared by direct electrochemical oxidation of Cu electrode in acetonitrile solutions. The final product, $\text{Cu}_2(\text{S-dmpmp})_2\text{Cl}(\mu\text{-OH})$ was crystallized and characterized by microanalysis, Raman spectroscopy together with X-ray crystallographic determinations. © 2005 Elsevier B.V. All rights reserved.

Keywords: Chiral ligand; Copper; Direct electrochemical oxidation; Raman spectroscopy

Chiral amino alcohols are widely used as original reactant and effective catalysts in asymmetric synthesis. For example, several chiral 2-aminoalkanesulfonic acids, which have been found in many mammalian tissues and were involved in various important physiological processes [1], were synthesized expeditiously from chiral amino alcohols [2]. As an effective catalyst, the nucleophilic addition of dialkylzincs to aldehydes in hydrocarbon solvents was accelerated in the presence of *p*-amino alcohols or relevant complexes [3,4]. Therefore, the studies on the preparation and properties of chiral amino alcohols and relevant complexes are still an active research issue.

In the past decades, transition metal complexes with chiral ligands have attracted considerable attention because of their high catalytic activity in the asymmetric cyanosilylation of ketones or aldehydes [5], chiral selectors in chiral capillary electrophoresis (CE) [6], and probes in electron-transfer reactions involving metallo-

proteins [7]. The special properties of the chiral complexes differed from the kind of the ligand. For example, there has been increasing interest in the multifunctional structure of pyridinylmethyl pyrrolidinemethanol derivatives with more than two dissimilar coordination sites in which the nitrogen atom and oxygen atom might easily coordinate with many metals such as Cu, Zn, Li, Rh, Ti and Ni [8]. Moreover, with the introduction of a pyridinyl moiety onto the amino alcohols, the cooperation of pyridine unit and chiral prolinol unit in the ligand, such as (*S*)-2-(diphenylmethanol)-1-(2-pyridylmethyl)pyrrolidine (*S*-dmpmpH) might result in unique properties for certain catalytic reactions. To our best knowledge, there is no report on the preparation and properties of metal complexes with pyridinylmethyl pyrrolidinemethanol.

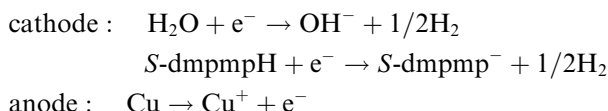
It should be of interest to prepare the metal complexes with an asymmetric chiral ligand of *S*-dmpmpH in order to produce new potential catalyst for other asymmetric synthesis. Very recently, a chiral Cu(II) complex of *S*-(1-benzyl-pyrrolidin-2-yl)-diphenylmethanol was prepared successfully by direct electrochemical oxidation of Cu in acetonitrile solutions in our lab [9]. In

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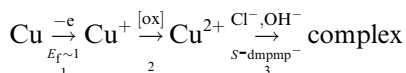
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the present work, Cu(II) complex with *S*-dmpmpH was synthesized by the same technique, and its structure was characterized by Raman spectroscopy and X-ray crystallographic determination.

The chiral tridentate ligand, *S*-dmpmpH, was prepared as shown in Scheme 1 [10]. Chiral copper(II) complex $\text{Cu}_2(\text{S-dmpmp})_2\text{Cl}(\mu\text{-OH})$ was prepared in 14.5% yield by using direct electrochemical synthesis as described in Tuck's work and our previous work [11,12]. It should be pointed out that crystal was selected as the final product to calculate the yield which resulted in the low yield. The electrochemical system can be represented as: $(-)\text{Pt}|\text{PPh}_3, \text{S-dmpmpH} \cdot \text{HCl}, \text{Et}_4\text{N-ClO}_4(\text{as electrolyte}), \text{CH}_3\text{CN}(\text{solvent with trace H}_2\text{O})|\text{Cu}(+)$. The electrochemical oxidation of copper obviously provided a convenient and clean (the electron used as oxidizer/reducer) route to produce Cu ions and deprotonated ligand anions without the necessary of additional reagent. The electrochemical efficiency E_f (defined as moles of metal dissolved per Faraday of charge), was about 1.00 mol/F, indicating the formation of Cu(I) ion at the initial step of the electrochemical reaction on the electrode surface. It can be described as the following:



The overall reaction procedure was described as:

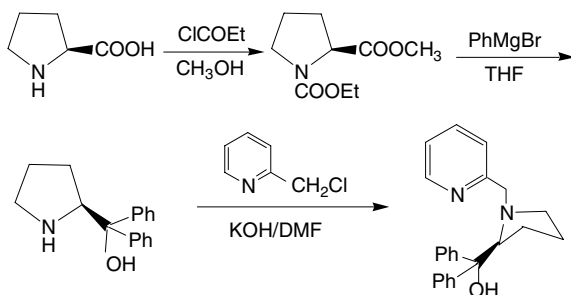


In the most of our previous electrochemical synthesis by constant current electrolysis, the metal was firstly oxidized to its low valence, i.e. E_f was about 1.0 mol/F for copper, and 0.5 mol/F for iron, nickel, zinc and some rare earth elements (such as Sm, Nd). Therefore, in the present case, the Cu(I) ion was formed on the copper anode surface in the initial step because of the electrolysis. In order to stabilize the Cu(I) ion, triphenylphosphine (PPh_3), which is normally used as a common ligand in organometallic and coordination chemistry and is one of the most common ligands found in homogeneous

transition metal catalysts for the binding and transformations of organic substrates, was introduced to the solution. As a consequence, the Cu(I) was stabilized by PPh_3 to form $\text{Cu}(\text{PPh}_3)_n^+$. After that, the ion of $\text{Cu}(\text{PPh}_3)_n^+$ was oxidized by air rather than the further electrochemical oxidization. It coordinated with the ligand anions from the cathode and other anions of Cl^- and OH^- to produce the final Cu(II) complex [12]. During the coordination processes, the stabilization reagent PPh_3 was replaced by the deprotonated ligand anion because of the steric interactions. Therefore, the ligand of PPh_3 was absent in the final complex. We have observed similar phenomenon in the synthesis of chiral Cu(II) complex of *S*-(1-benzyl-pyrrolidin-2-yl)-diphenyl-methanol [9]. In order to analyze the effect of PPh_3 , similar electrochemical synthesis was carried out in the nonaqueous solution without PPh_3 . The E_f of about 1.0 mol/F suggested the formation of Cu(I) ion. However, the color of the solution around the anode changed quickly as soon as the current was applied, and the copper anode surface became black. The final product was a light brown precipitation with copper powder. It was mainly because the naked Cu(I) ions were unstable and disproportionated to Cu(0) and Cu(II).

The final complex was crystallized by vapor diffusion of diethyl ether into acetonitrile solution. The elemental analysis confirmed the formula of $\text{C}_{46}\text{H}_{47}\text{ClCu}_2\text{N}_4\text{O}_3$ [13]. Its stereo structure was determined by X-ray crystallographic diffraction analysis. An ORTEP drawing of the complex is shown in Fig. 1. The structure reveals the presence of two Cu(II) centers linked through a bridging chlorine anion and a hydroxyl group. Each copper atom locates in a distorted trigonal-bipyramidal environment of a hydroxyl oxygen atom and two N atoms (from pyridine ring and pyrrolidine ring), two bridging ligands of chlorine ion and hydroxyl group. The Cu1–N1 and Cu1–N2 bond distances (2.051(3) Å) are slightly longer than that of the Cu2–N3 and Cu2–N4 distances (2.041(3) and 2.016(3) Å). However, these Cu–N distances are somewhat shorter than the Cu–N lengths of 2.098 Å in similar complex of $\text{CuL}_2(\text{HL}=\text{S}-(1\text{-benzyl-pyrrolidin-2-yl})\text{-diphenyl-methanol})$ [9]. The Cu–O distances are unequal (1.918(3) Å and 1.895(3) Å for Cu1–O1 and Cu2–O2, respectively). And these values are also longer than the Cu(II)–O (1.8574(16) Å) in CuL_2 [9]. The torsion angles between the pyridine and pyrrolidine rings are $-33.5(5)^\circ$ (N1–C6–C7–N2) and $-34.7(5)^\circ$ (N3–C29–C30–N4), respectively. The four-membered $\text{Cu}(\text{OH})\text{CuCl}$ ring is nearly planar with the Cu...Cu separation of 3.235 Å. The structure is stabilized not only by two bridging groups but also by two weak intramolecular hydrogen bonds (C11–H11...O2 and C34–H34...O1).

In order to analyze the interaction between the metal center and ligand, the Raman spectroscopic studies were



Scheme 1. Synthesis of the chiral ligand *S*-dmpmpH.

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