

Synthesis of Novel Copper Complexes with Distorted Structures and Electroreduction of Carbon Dioxide

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Background Electrolytic reduction is one of the methods for utilizing CO₂ as a useful carbon resource. It has been reported that hydrocarbons can be selectively obtained when a copper complex is used as a catalyst for electrolytic reduction¹⁾. During the catalytic cycle, the oxidation state of the copper center is expected to change, which is accompanied with change of the coordination geometry. A copper complex having a planar structure has a problem in that the ligand may be dissociated when the structure is changed. In this study, a copper complex with a distorted structure was synthesized and its electrochemical properties were examined, with the aim that the structural change is smoothly accommodated during the redox process.

Synthesis The Cu²⁺ complex was synthesized by stirring copper (II) perchlorate hexahydrate and 6,6'-bis(2-pyridylthio)-2,2'-bipyridine²⁾ in methanol for 30 minutes at room temperature (Fig.1). The synthesized Cu²⁺ complex was found to have a distorted structure by X-ray single crystal structure analysis.

Electrochemistry The redox behavior of the synthesized Cu²⁺ complexes was investigated by CV measurements in CH₃CN solutions. The highly reversible Cu⁺/Cu²⁺ redox wave was observed at -0.1 V (vs. ferrocene) when measured in the range from -1.0 V to +1.0 V (Fig.2 dashed line). When the scan range was extended to -2.5 V, an additional reduction wave was observed at -2.3 V (Fig.2 solid line). This wave was attributed to the reduction of the ligand. Other redox waves and the voltammogram under CO₂ will be discussed in detail during the presentation.

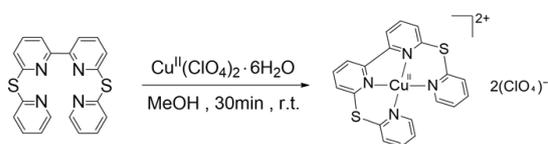


Fig.1 Synthesis of the Cu²⁺ complex

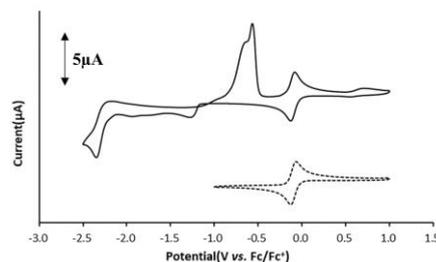


Fig.2 Cyclic voltammograms of the Cu²⁺ complex in CH₃CN/0.1 M Et₄NClO₄

1) Zhe Weng et al., *J. Am. Chem. Soc.*, **2016**, *138*, 8076–8079

2) Y. Uchida et al., *Heteroatom Chem*, **1994**, *5*, 409-413