Synthesis and electrochemical behaviors of dinuclear copper(I) complexes of trimethylenedioxy-bridged dinucleating ligands

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Introduction. Copper complexes have been studied as catalysts in the electrolytic reduction of carbon dioxide, and the relationship between their structures and electrochemical behaviors is of interest. As an example, reactions catalyzed by dinuclear copper(I) complexes have been reported.[1] In this study, a dinucleating ligand having two bipyridine moieties was synthesized, and the electrochemical behaviors of the complexes obtained by reaction with CuCl or $[Cu(NCCH_3)_4]BF_4$ were evaluated.

Synthesis. Ligand L1 (Fig. 1) was obtained by reaction of 6-bromo-2,2'-bipyridine and disodium 2,2-dimethyl-1,3-propanediolate in DMF at 80°C for 3 days. Copper complexes were obtained by reaction of L1 with CuCl or $[Cu(NCCH_3)_4]BF_4$ in acetone at room temperature overnight. The structure of the CuCl-derived complex was determined by single-crystal X-ray diffraction analysis, and it was found that a binuclear complex $[Cu_2L1_2]^{2+}$ was obtained in which two copper atoms were bridged by two molecules of L1 (Fig. 2). Both complexes showed similar ^{1}H NMR and ESI-MS(+) spectra, so it is expected that both have the structure $[Cu_2L1_2]^{2+}$ but have different counter anions.

Electrochemistry. Fig. 3 shows the cyclic voltammograms for the complexes obtained from L1 and CuCl or $[Cu(NCCH_3)_4]BF_4$. The CuCl-derived complex showed two sets of redox waves in the potential range of −0.5 to 0.5 V, whereas the complex derived from $[Cu(NCCH_3)_4]BF_4$ showed only one set. These redox waves are attributed to the Cu^I/Cu^{II} redox processes in different environments. In addition, for both complexes, a redox wave was observed at the low potential side (−1.5 to −0.5 V), which is associated with formation and dissolution of Cu^0.

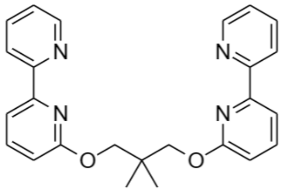

Figure 1. The structure of L1.

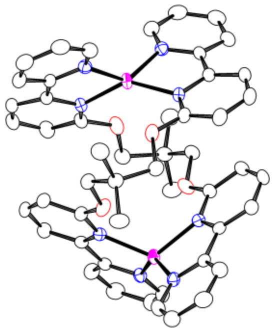

Figure 2. X-ray structure of $[Cu_2L1_2]^{2+}$ (The counteranion and hydrogen atoms are omitted).

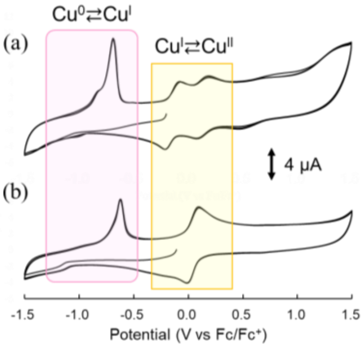

Figure 3. Voltammograms of (a) the CuCl-derived complex, and (b) the complex derived from $[Cu(NCCH_3)_4]BF_4$.

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[1] N. Sakamoto *et al. Nat. Catal.*, **2024**, *7*, 574-584.