

Redox Chemistry of Novel Copper Complexes with Carbanion and Halogen Coordination

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Copper(II) ion with tripodal ligands forms stable trigonal bipyramidal structure which has received considerable attention in both biological model and basic coordination chemistry. We recently synthesized a novel tripodal ligand, tris(2-pyridylthio)methane (Htptm) which has a potential source of carbon atom for carbanion. The trigonal bipyramidal (*tbp*) complex of $[\text{Cu}(\text{tptm})\text{X}]$ was obtained by the reaction of Htptm with copper(I) within the presence of oxygen and halide ion, X. The central metal Cu(II) ion forms bonds to the three pyridine nitrogen atoms and, surprisingly, sp^3 -hybridized anionic carbon atom of the ligand. The complexes are stable as solids as well as in acetonitrile and dichloromethane solutions. The complete series of halogens from F to I coordinate to Cu(II) and the structures of these complexes have been determined by crystallographically (Fig.1). Other than halogen, pseudohalogen and hydroxo can coordinate to Cu(II) as X. The *tbp* structures for all $[\text{Cu}(\text{tptm})\text{X}]$ were maintained also in dichloromethane solution which was proved by ESR spectroscopy. In this paper we explored the redox chemistry of the copper(II) complex with halogen ligand by cyclic Voltammetry (CV) and *in-situ* spectroelectrochemistry. The redox properties of $[\text{Cu}^{\text{II}}(\text{tptm})\text{X}]$ were interpreted as an effect of coordinating halogen atoms. Presence of the corresponding halide ion in the solution affects considerably the redox process causing significant change of CV.

Electrochemical measurements were carried out in acetonitrile or dichloromethane. The working electrode for voltammetry was a platinum disk with a diameter of 1.6 mm and that for *in-situ* optically transparent thin-layer spectroelectrochemistry was a 150 mesh platinum net. The reference electrode was an $\text{Ag}|\text{Ag}^+$, the potential of which was corrected using an internal standard redox couple of ferrocenium/ferrocene.

All the copper(II) complexes $[\text{Cu}^{\text{II}}(\text{tptm})\text{X}]$ except X = I in acetonitrile undergo a one-electron reduction corresponding Cu(II) to Cu(I) and a one-electron oxidation corresponding Cu(II) to Cu(III) in both nonaqueous solvents containing tetrabutylammonium hexafluorophosphate as a supporting electrolyte. The X = I complex dissociates the iodide ion to form the X = CH_3CN complex in acetonitrile. As shown in Fig. 2 the formal redox potential in the reduction process depends largely on the axial halogen ligand, while that in the oxidation process is independence of the ligand of halogen atoms. The addition of the corresponding halide ion to the $[\text{Cu}^{\text{II}}(\text{tptm})\text{X}]$ complex solution affects greatly the redox properties in CV. Figure 3 shows the example of X = Cl. The formal potential shifts negatively and the peak potential separation decreases on the addition of chloride ion in the reduction process, indicating the progress via a square ECEC mechanism involving the dissociation of Cl ligand on the reduction to Cu(I) and the uptake of Cl^- on the reoxidation to Cu(II). The oxidation process changes from the reversible one-electron oxidation to the quasi-reversible two-electron oxidation on the addition of 0.1 M Cl^- . Spectroelectrochemical measurements shown in Fig. 4 and thin-layer cyclic voltammetric measurements suggest that the oxidation

proceeds *via* an EEC mechanism involving the uptake reaction of concerning halide ions. The details of the oxidation process are under examination now.

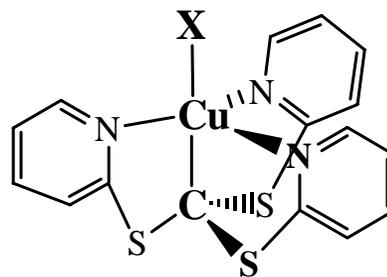


Fig. 1. Structure of the complex $[\text{Cu}^{\text{II}}(\text{tptm})\text{X}]$.

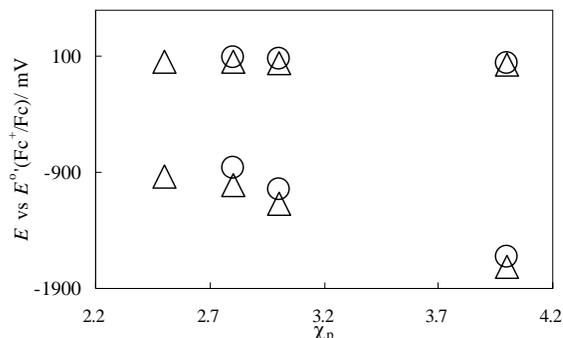


Fig. 2. Dependence of the axial halogen ligand on the formal potential in acetonitrile (circle) and dichloromethane (triangle).

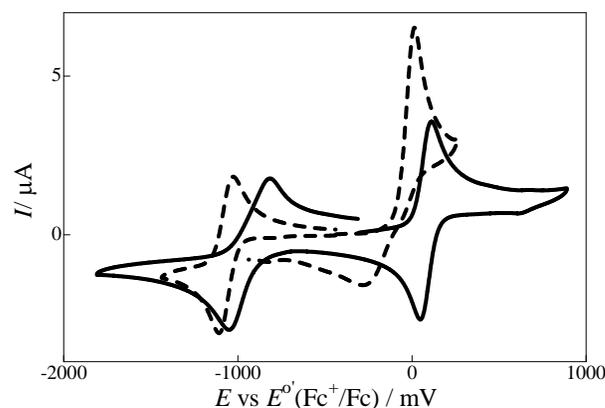


Fig. 3. Cyclic voltammograms of $[\text{Cu}(\text{tptm})\text{Cl}]$ in the absence (solid line) and the presence (broken line) of 0.1 M chloride ion in acetonitrile with a scan rate of 0.1 V/s.

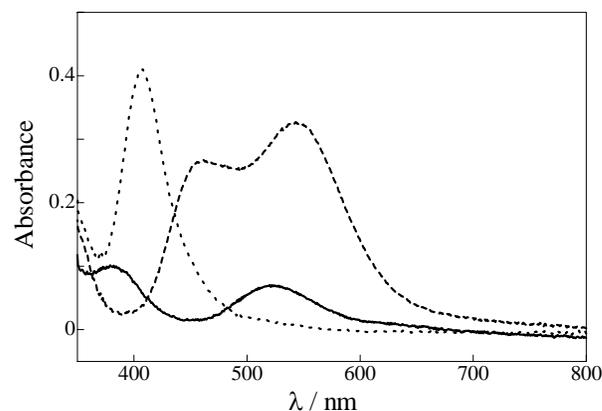


Fig. 4. Visible spectra of $[\text{Cu}(\text{tptm})\text{Cl}]$ (solid line), one-electron oxidation product $[\text{Cu}^{\text{III}}(\text{tptm})\text{Cl}]^+$ (broken line) and two-electron oxidation product $[\text{Cu}^{\text{III}}(\text{tptm})\text{Cl}_2]^+$ (dotted line).