XAFS Measurements for the reaction intermediate in carbon dioxide reduction catalyzed by [Ru(bpy)$_2$(CO)$_2$]$^{2+}$

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1 Introduction

Ruthenium bipyridyl carbonyl complexes such as [Ru(bpy)$_2$(CO)$_2$]$^{2+}$ (bpy: 2,2'-bipyridine) act as the catalysts for CO$_2$ reduction in the artificial photosynthetic system$^1$ as well as the homogeneous catalyses.$^2$ The reaction mechanisms are elucidated as follows$^3$: [Ru(bpy)$_2$(CO)$_2$]$^{2+}$ is reduced with two electrons to yield a five-coordinated species [Ru(bpy)$_2$(CO)] and CO. The reduced ruthenium complex reacts with CO$_2$ to afford the $\eta^1$-CO$_2$ adduct [Ru(bpy)$_2$(CO)(CO$_2$)]. In an aqueous solution, [Ru(bpy)$_2$(CO)(CO$_2$)] exists as an equilibrium mixture of [Ru(bpy)$_2$(CO)(C(O)OH)]$^+$ and [Ru(bpy)$_2$-(CO)$_2$]$^{2+}$. The catalytic cycle can also be traced from [Ru(bpy)$_2$(CO)$_2$]$^{2+}$ by reacting OH$^-$ ions: the dicarbonyl complex reacts with OH$^-$ to yield [Ru(bpy)$_2$(CO)-(C(O)OH)]$^+$, which further reacts with OH$^-$ to give [Ru(bpy)$_2$(CO)(CO$_2$)].$^4$ The crystal structure of the $\eta^2$-CO$_2$ complex has been determined,$^5$ however the difference on the electronic states between [Ru(bpy)$_2$-(CO)(C(O)OH)]$^+$ and [Ru(bpy)$_2$(CO)(CO$_2$)] still remains unclear. It is because there are hydrogen bonding networks between the CO$_2$ complex and a couple of water molecules even in the crystals. In this work, we examined the XAFS spectrum of [Ru(bpy)$_2$(CO)$_2$]$^{2+}$ in an organic solution and compared it to the spectra of $in situ$ generated [Ru(bpy)$_2$(CO)(C(O)OH)]$^+$ and [Ru(bpy)$_2$-(CO)(CO$_2$)] by adding $n$-Bu$_4$NOH.

2 Experiment

The DMF solution of [Ru(bpy)$_2$(CO)$_2$](PF$_6$)$_2$ (3.0 or 30.0 mM) was placed in a polypropylene tube under Ar. To the solution, 1, 2, 3 and 6 equiv. of $n$-Bu$_4$NOH in methanol to the ruthenium complex was added to yield [Ru(bpy)$_2$(CO)(C(O)OH)]$^+$ and [Ru(bpy)$_2$-(CO)$_2$]. The XAFS experiments were conducted at the undulator beamline NW10A of the Photon Factory Advanced Ring (PF-AR) in Tsukuba.

3 Results and Discussion

The XAFS spectrum of [Ru(bpy)$_2$(CO)$_2$]$^{2+}$ in DMF is shown in Fig. 1(a). The spectrum was fitted based on the DFT calculation result. Addition of an equivalent $n$-Bu$_4$NOH caused a nucleophilic attack of OH$^-$ to the carbonyl group to yield [Ru(bpy)$_2$(CO)(C(O)OH)]$^+$ in solution. The XAFS spectrum was dramatically changed (Fig. 1(b)). Further addition of OH$^-$ made the solution color change from yellow to dark red, however the XAFS spectrum was unchanged. It suggests that there is little difference in the metal valence and the structures around the metal center between [Ru(bpy)$_2$(CO)(C(O)OH)]$^+$ and [Ru(bpy)$_2$(CO)(CO$_2$)].

![Figure 1: XAFS spectra of (a) [Ru(bpy)$_2$(CO)$_2$]$^{2+}$ and (b) [Ru(bpy)$_2$(CO)(C(O)OH)]$^+$ in DMF.](image)

Acknowledgement

We acknowledge the PRESTO Program of JST for the financial support.

References


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