

An XAFS Study of Electrochemically-induced Linkage Isomerization of Ruthenium Complexes in Solution

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Introduction

Model compounds for molecular memory devices have recently drawn much attention. So far, we have made electrochemical and UV/visible measurements on $[\text{Ru}^{\text{II}}(\text{bpy})(\text{tpy})(2\text{-pySH})](\text{PF}_6)_2$ complex (bpy = 2,2'-bipyridine, tpy = 2,2':6',2''-terpyridine, 2-pySH = 2-mercaptopyridine) in solution and revealed that the complex undertakes electrochemically-induced linkage isomerization, i.e. a change of the coordination atom of 2-pyS⁻ between Ru(II)-S(2-pyS⁻) and Ru(III)-N(2-pyS⁻) only in a basic solution [1]. In this study, we aimed at confirming the change of the coordination atom with the oxidation state of ruthenium within the complexes by XAFS that can characterize the coordination environment around the metal center.

Experimental

Acetonitrile solutions of $10 \times 10^{-3} \text{ mol dm}^{-3}$ $[\text{Ru}(\text{bpy})(\text{tpy})(2\text{-pySH})](\text{PF}_6)_2$ with $10 \times 10^{-3} \text{ mol dm}^{-3}$ $(\text{CH}_3\text{CH}_2)_3\text{N}$ and 0.5 mol dm^{-3} $(n\text{-C}_4\text{H}_9)_4\text{NPF}_6$ were prepared. The XAFS measurements were carried out using a home-made *in-situ* electrochemical XAFS cell (Fig. 1). The cell was made of Macor (Ishihara Chemical) with boron nitride windows; A 50-mm long porous carbon and Pt coil were used as working and counter electrodes, respectively, with a home-made Ag⁺/Ag reference electrode. The oxidation from Ru(II) to Ru(III) was checked by measuring oxidation currents with time.

XAFS spectra at the Ru K-edge were taken in the transmission mode at station NW10A of KEK-PF. Energy calibration was made against a pre-edge peak of a copper foil.

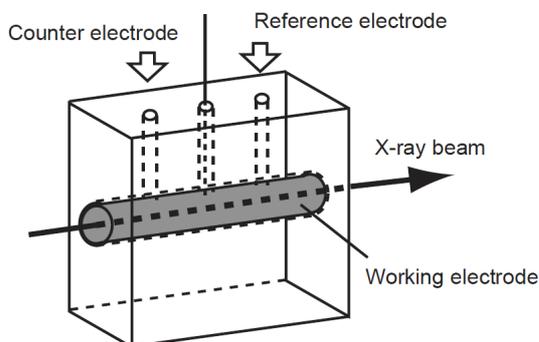


Fig. 1. *In-situ* electrochemical XAFS cell

Results and Discussion

Ru K-edge XANES spectra of deprotonated complexes of Ru(II) and Ru(III) are shown in Fig. 2. The absorption

edge shifted to a higher energy side with oxidation from Ru(II) (blue line) to Ru(III) state (red line), which is consistent with a general tendency on oxidation. Figure 3(a) and (b) shows the k^2 -weighted Ru K EXAFS oscillations and their Fourier transforms (FT) without the phase shift correction, respectively. The FT spectra showed different signatures for both oxidation states of Ru. Detailed data analysis is in progress.

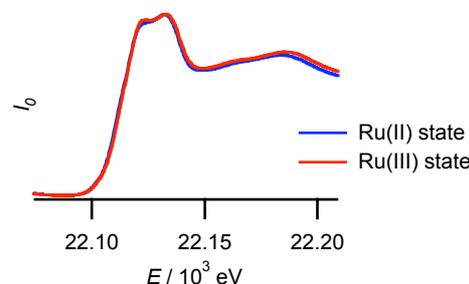


Fig. 2. Ru K XAFS spectra of the Ru(II) and Ru(III) complexes.

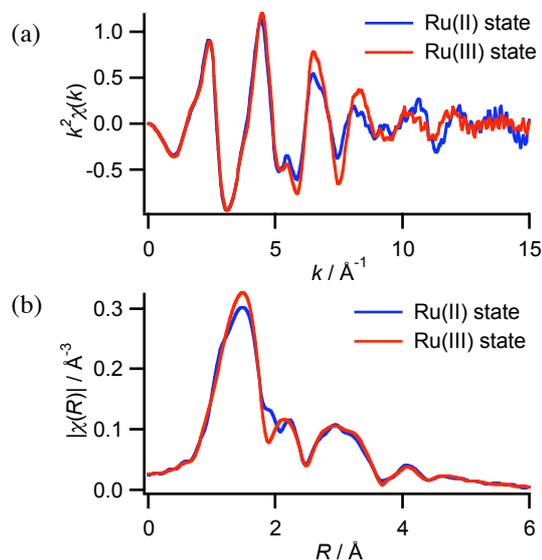


Fig. 3. Ru K EXAFS spectra of the Ru(II) and Ru(III) complexes.

Reference

[1] T. Hamaguchi et al., *Inorg. Chem.* **2007**, *46*, 10455-10457.

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