## Electronic Supporting Information

# Fe, Ru, and Os Complexes with the Same Molecular Framework: Comparison of Structures, Properties and Catalytic Activities

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**Table of Contents**

**UV-visible Absorption Spectra**

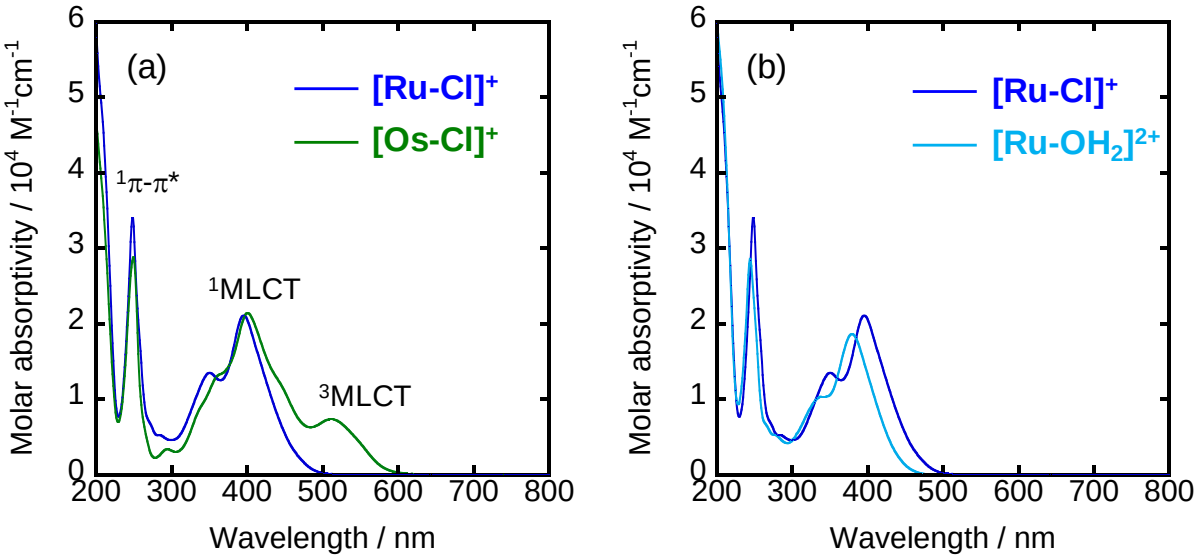


**Figure S1.** (a) UV-visible absorption spectra of **[Ru-Cl]**$^+$ (blue line) and **[Os-Cl]**$^+$ (green line) in an acetonitrile solution at 20 °C in air. (b) The comparison of UV-visible absorption spectra of **[Ru-Cl]**$^+$ in an acetonitrile solution (blue line) and **[Ru-OH$_2$]**$^{2+}$ in an aqueous solution (pale blue line) at 20 °C in air.

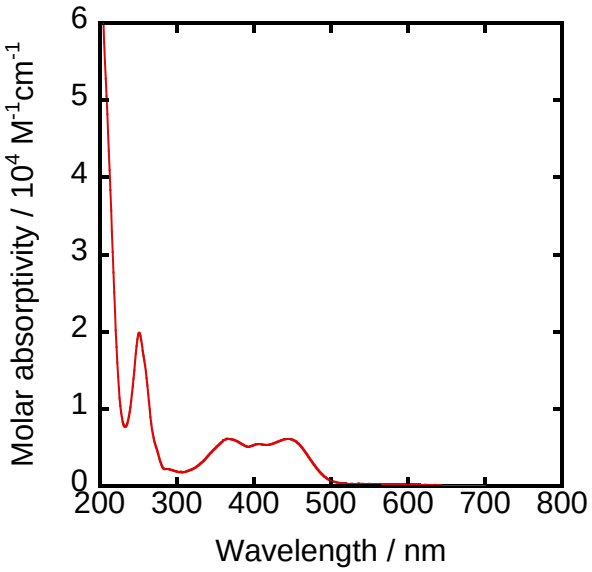


**Figure S2.** UV-visible absorption spectrum of **[Fe-OH$_2$]$^{2+}$** in an aqueous solution at 20 °C in air.

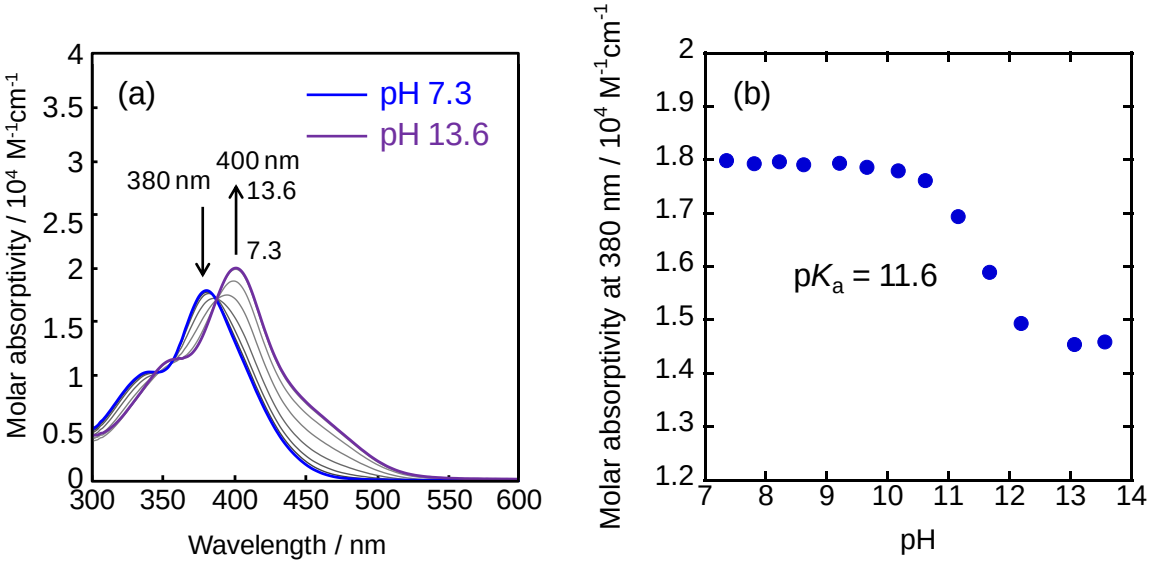


**Figure S3.** (a) UV-visible absorption spectra of an aqueous solution of **[Ru-OH$_2$]$^{2+}$** (28.3 μM) at 20 °C under Ar atmosphere (optical-path length: 1 cm) under various pH conditions (pH = 7.3-13.6, where pH values were adjusted with NaOH and $Na_3PO_4$). Well-anchored isosbestic points at 344, 356, and 387 nm are maintained throughout the pH range. (b) The dependence of the absorbance at 380 nm on pH. The p$K_a$ value of **[Ru-OH$_2$]$^{2+}$** was determined to be 11.6, which is higher than that of other ruthenium(II) pentapyridyl complex, such as [Ru(terpy)(bpy)(OH$_2$)]$^{2+}$ (p$K_a$ = 9.7).[1] This p$K_a$ value is similar to that of ruthenium(II) complex bearing strongly σ-donating ligand, such as [Ru(tmtacn)(bpy)(OH$_2$)]$^{2+}$ (p$K_a$ = 11.8).[2]

**Electrochemical Measurements**

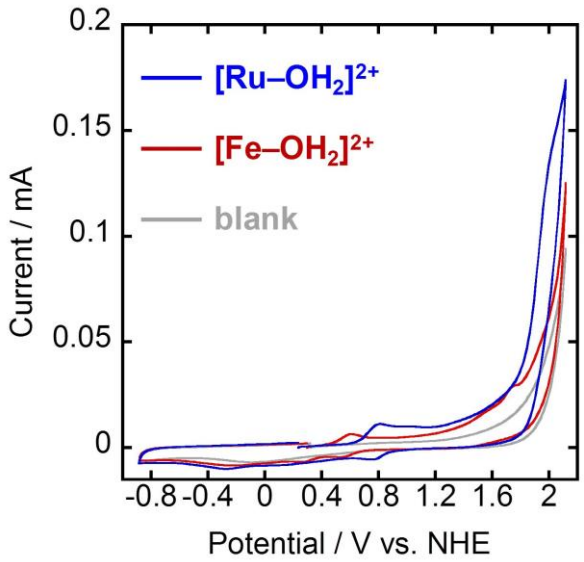


**Figure S4.** The cyclic voltammograms of **[Fe–$OH_2$]$^{2+}$** and **[Ru–$OH_2$]$^{2+}$** (0.5 mM) in an aqueous solution containing 0.5 M $Na_2SO_4$ (pH 5.31) under Ar atmosphere, recorded at a scan rate of 10 mV/s (working electrode, glassy carbon; counter electrode, Pt wire; reference electrode, $Hg/Hg_2SO_4$).

## References


1. K. J. Takeuchi, M. S. Thompson, D. W. Pipes and T. J. Meyer, *Inorg. Chem.*, 1984, **23**, 1845.
2. M. Yoshida, S. Masaoka and K. Sakai, *Chem. Lett.*, 2009, **38**, 702.