Synthesis and Reactivity of Doubly Oxido-Bridged Diruthenium Complex with Terminal Aqua/Hydroxido Ligands

([1]*Fac. of Sci. and Tech., Sophia University*) ○Tomoyo Misawa-Suzuki,[1] Nanako Asai,[1] Hirotaka Nagao[1]

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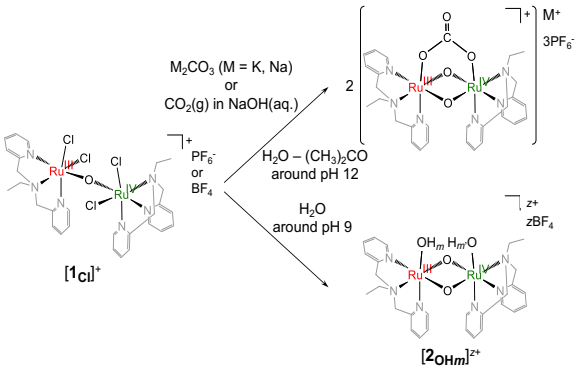
We have been studying syntheses, structures, electrochemical and spectroscopic properties of a series of diruthenium complexes having the $\{Ru_2(\mu\text{-}O(H))_n\}$ (n = 1, 2) core bearing ethylbis(2-pyridylmethyl)amine (ebpma),[1)] which could be the structural model compounds of metalloenzymes in nature. We have reported a carbonato-bridged complex having the $\{Ru_2(\mu\text{-}O)_2\}$ core, $M[\{Ru^{III,IV}(ebpma)\}_2(\mu\text{-}O)_2(\mu\text{-}O_2CO)]_2(PF_6)_3$, which was prepared through reactions of the singly oxido-bridged dirutheniumcomplex with chlorido ligands, $[\{Ru^{III,IV}Cl_2(ebpma)\}_2(\mu\text{-}O)]PF_6$ ($[\mathbf{1_{Cl}}]PF_6$),[1d)] with carbonate sources in aqueous solution of around pH 12[1a)] (Scheme 1 upper).

In aqueous solutions containing NaOH or KOH around pH 9 without any possible bidentate donor ligands, in this work, a doubly oxido-bridged Ru(III)-Ru(IV) complex with terminal aqua/hydroxido ligands, $[\{Ru^{III,IV}(OH_m)(ebpma)\}_2(\mu\text{-}O)_2](BF_4)_z$ ($[\mathbf{2_{OH}}_m](BF_4)_z$; m = 1 or 2), was synthesized from $[\mathbf{1_{Cl}}]^+$ (Scheme 1 lower). The reactivity of $[\mathbf{2_{OH}}_m]^{z+}$ in acetone and acetonitrile, and properties in aqueous solutions were investigated by electrochemical and spectroscopic methods. In a pH 9 aqueous solution at 60 ˚C within around 15 min., all the four chlorido ligands of $[\mathbf{1_{Cl}}]^+$ were dissociated, resulting in the framework conversion from $\{Ru_2\mathbf{(\mu\text{-}O)}\}$ to $\{Ru_2\mathbf{(\mu\text{-}O)_2}\}$ and the coordination of terminal OH_m ligands. The ESI MS supported the doubly bridged structure (m/z = 725.8).

$[\mathbf{2_{OH}}_m]^{z+}$ showed an MLCT band at 337 nm and an IVCT-like band at 1028 nm in a pH 9.2 water, which was attributed to the transitions on the $\{Ru_2(\mu\text{-}O)_2\}$ core and similar to those of our series of the Ru(III)-Ru(IV) system having the $\{Ru_2(\mu\text{-}O)_2\}$ core.[1a,c)] Upon dissolution of $[\mathbf{2_{OH}}_m]^{z+}$ into acetone or acetonitrile, the X-ray crystallography of the obtained crystalline samples revealed that two OH_m ligands were substituted or reacted with the solvent used. We will discuss the electrochemical and spectroscopic behaviors and reactivity of $[\mathbf{2_{OH}}_m]^{z+}$ in solution.



Scheme 1. Synthesis of $[\mathbf{2_{OH}}_m]^{z+}$.

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