

Control over Catalytic Activity of a Multinuclear Metal Complex Using an Encapsulated Hydrogen Ion

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Proton transfer reaction plays important roles both in biological and artificial systems for acquiring their unique functions. Therefore, the development of molecules which can control the behavior of protons is an attractive research target for obtaining novel functional materials. In this work, we discovered that a heterometallic pentanuclear complex, which composed of 3,5-bis(pyridyl)pyrazole (Hbpp) and ruthenium and cobalt ions, can encapsulate a proton in its structure. We also found that the encapsulated proton greatly affects catalytic activity for hydrogen production.

Synthesis of heterometallic pentanuclear complexes was performed by the step-wise complexation of metal ions with Hbpp. Initially, $[\text{Ru}(\text{Hbpp})_3](\text{ClO}_4)_2$ was synthesized as a precursor. The obtained complex was further reacted with 5 eq. of $\text{Co}(\text{OAc})_2 \cdot 4\text{H}_2\text{O}$ and $[\text{Ru}_2\text{Co}_3\text{OH}(\text{bpp})_6](\text{ClO}_4)_3$ (**Ru₂Co₃OH**, Figure 1 (left)) was obtained. The deprotonated form of the complex, $[\text{Ru}_2\text{Co}_3\text{O}(\text{bpp})_6](\text{ClO}_4)_2$ (**Ru₂Co₃O**, Figure 1 (right)), was also obtained by treating **Ru₂Co₃OH** with a base.

Subsequently, we investigated electrochemical properties of **Ru₂Co₃OH** and **Ru₂Co₃O** (Figure 2). In cyclic voltammograms (CVs) of **Ru₂Co₃OH**, two reversible oxidation and three reversible reduction waves were observed. On the other hand, CVs of **Ru₂Co₃O** exhibited four reversible oxidation and two reversible reduction waves. In addition, we explored the catalytic activity of **Ru₂Co₃OH** and **Ru₂Co₃O**. As a result, it was suggested that the encapsulated hydrogen ion can largely influence the catalytic activity of **Ru₂Co₃** complexes.

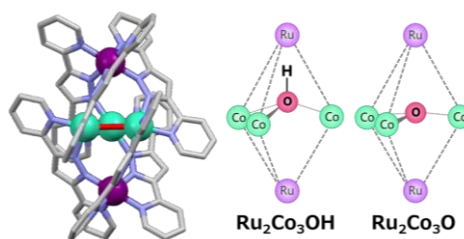


Fig. 1. The structures of heterometallic pentanuclear complexes, **Ru₂Co₃OH** (left) and **Ru₂Co₃O** (right).

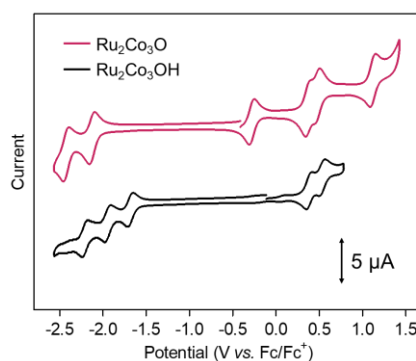


Fig. 2. CVs of **Ru₂Co₃** complexes.