

Cooperative Dual Redox Sites in a Dinuclear Cobalt Complex Decrease the Overpotential of CO₂ Electroreduction

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Keywords: CO₂ electroreduction; dinuclear metal complex; redox; DFT calculation

Electrochemical CO₂ reduction (eCO₂R), which provides valuable chemicals from CO₂ using electric power, has attracted growing attentions as a solution to the environmental and energy problems.¹ As eCO₂R catalysts, metal complexes have been widely studied because of their high designability², although the overpotential for eCO₂R is still not satisfiable. In this study, we focused on dinuclear complexes, whose multiple redox sites would be advantageous for eCO₂R involving multiple electron reductions. Inspired by the cobalt tetraphenylporphyrin (**Co₁**, **Fig. 1 left**), which is a well-studied catalyst owing to its high selectivity for CO (Faradaic efficiency; >90%),³ we targeted a dinuclear complex, [Co^{II}₂(bpypz)₂]²⁺ (Hbpypz = 3,5-bis(2-pyridyl)pyrazole), which is referred to as **Co₂** (**Fig. 1 right**). Previously, we revealed that **Co₂** exhibits 250 mV more positive onset potential in *N,N*-dimethylformamide (DMF) solution compared to that of **Co₁**.⁴ In this study, we discuss their catalytic cycles based on the experimental and computational studies in order to reveal the reason for the superior catalytic performance of **Co₂**.

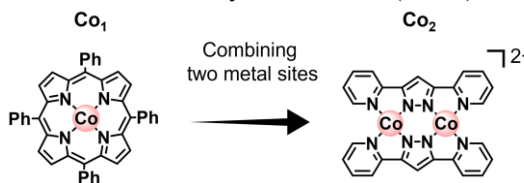


Fig. 1. Molecular structures of **Co₁** (left) and **Co₂** (right).

Chronoamperometry using a microelectrode revealed that **Co₂** exhibits the one-step two-electron reduction, i.e., (Co^{II}, Co^{II})→(Co^I, Co^I), which is absent in **Co₁**. This behavior affords the difference in the sequence of the electron-transfer steps and CO₂-binding step in the catalytic cycles of **Co₁** and **Co₂**, which was supported by the density functional theory (DFT) calculations. We found that the simultaneous two-electron reduction before the CO₂-binding on **Co₂** circumvents the electron transfer after the CO₂-binding which prevents the catalytic cycle of **Co₁**. Furthermore, DFT calculations suggested the cooperation of the two Co ions in catalytic cycle of **Co₂**, i.e., the metal-to-metal electron transfer and the intermediate with the COOH moiety bridging over the two Co sites (**Fig. 2**). We then concluded that the cooperative functions on the dinuclear complex are the key to the lower overpotential.

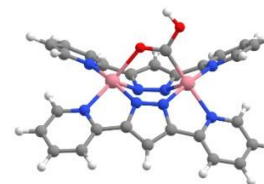


Fig. 2. DFT-optimized structure of an intermediate for eCO₂R on **Co₂**.

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