

DFT Studies on the Mechanism of CO₂ Reduction Catalyzed by Diazapyridinophane Metal Complexes

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There is an increasing demand to reduce atmospheric CO₂ because of the recent threat of global warming and climate changes. To solve these problems, there has been a growing interest in light-driven reduction of CO₂ by molecular catalysts. Recently, an increasing number of studies focusing on the precious-metal-free systems for photocatalytic CO₂ reduction have been reported.¹ In this context, we previously demonstrated that the visible light-driven CO₂ reduction catalyzed by diazapyridinophane (dapp) derivatives of Fe and Co (Fig. 1) can be effectively promoted by combining them with a heteroleptic Cu(I) photosensitizer.²

In this study, the density functional theory (DFT) calculations were carried out in order to clarify the mechanisms of CO₂ reduction by these metal complexes. All the intermediates were fully optimized by the B3P86/6-31G* level of DFT with the effect of solvation in DMF taken into consideration using C-PCM. We also succeeded to optimize the transition states for the CO₂ binding processes, leading to determine the activation free energy of each catalysis. In addition, it has been shown that the SOMO together with the HOMO of M(I) center cooperatively provides the electron density at the less sterically hindered reactive metal center, offering the CO₂ binding site. This is the first example of a catalyst demonstrating the CO₂ binding with the high spin metal center. Moreover, we have found that an unusual side-on-(CO₂²⁻) M(II) intermediate can be given in these systems (Fig. 1).³

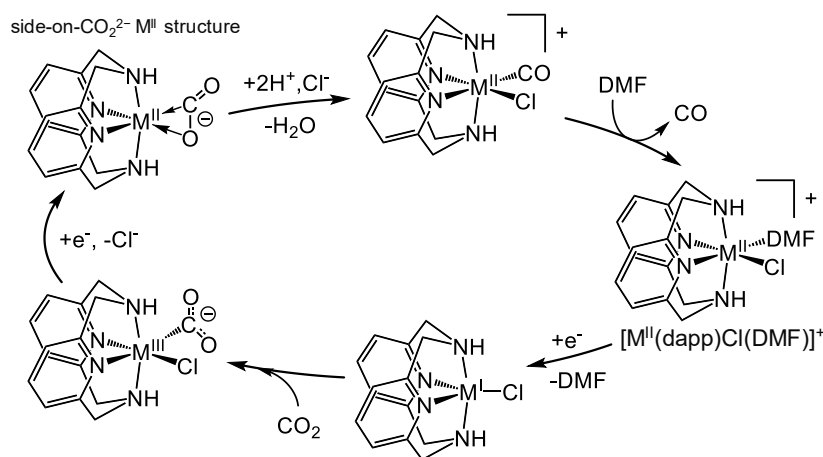


Fig. 1 Proposed mechanism of CO₂ reduction catalyzed by the M(dapp) complexes (M = Fe, Co).

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