The Unexpected Role of Ligand Moieties on the Catalytic Activity of Cobalt-Tetrapyridyl Complexes

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Photocatalytic hydrogen production is currently an intensively explored subject. The improvement of molecular, photocatalytic systems in terms of stability and efficiency is a common goal of a great variety of researchers but proved itself as a challenging matter. Limiting steps of 2-electron-2-proton transferring cycles often depend on more factors than immediately obvious. Nevertheless, the understanding of reaction mechanisms in every detail is of crucial importance to drive the system toward a sustainably applicable energy source.

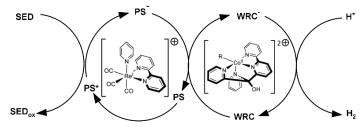


Figure 1: General mechanism of a molecular photocatalytic system including photosensitizer (PS), water reduction catalyst (WRC) and sacrificial electron donor (SED). R = H₂O

In this context, we have studied the catalytic mechanism of a cobalt(II)-tetra-pyridyl complex in a photocatalytic system including a rhenium(I)-based photosensitizer (PS) and triethanolamine as sacrificial electron donor (SED, see Fig.1). Laser flash photolysis experiments imply successive reduction-protonation-reduction-protonation steps, leading to

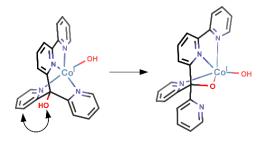


Figure 2: Ligand switch reaction from the pyridine-coordinated to the active, oxygencoordinated form of Co(II)-tetra- pyridine WRC

the release of H₂ and back to the initial Co(II) state of the catalyst.^[1] However, recently performed time resolved NEXAFS measurements in a new experimental setup have brought up so far not recognized mechanistic steps, specifically, an irreversible initial reaction leading to the actual catalytic cycle. More precisely, irreversible changes of X-ray absorption spectra upon photoexcitation combined with the remaining catalytic activity of the solution imply that the initial catalyst undergoes a ligand-switch reaction, stabilizing the low-spin state of the reduced Co(I)-intermediate, which is required for the following protonation (Fig.2). Thereby, a new,

stable and catalytically active form of the cobalt complex is formed *in situ*, remaining in this configuration even after switching off the light source. This mechanistic approach has not been considered so far and might have a large influence on the development of new, more active and stable WRCs.

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References:

[1] A. Rodenberg, M. Orazietti, B. Probst, C. Bachmann, R. Alberto, K. K. Baldridge, P. Hamm, *Inorg. Chem.*, **2015**, 54, 646 – 657