

## The Unexpected Role of Ligand Moieties on the Catalytic Activity of Cobalt-Tetra-pyridyl Complexes

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The catalytic properties of Co(II)-tetra-pyridyl (CoTPY) complexes for hydrogen production have been examined for a long time. Despite the fact that more effective WRCs are known, CoTPY and its derivatives offer ideal subjects to study mechanistic aspects of water reduction. The understanding of this 2-electron-2-proton transfer is of crucial importance to improve catalytic systems in terms of efficiency and stability and finally to drive photo catalysis towards being a sustainably applicable energy source.

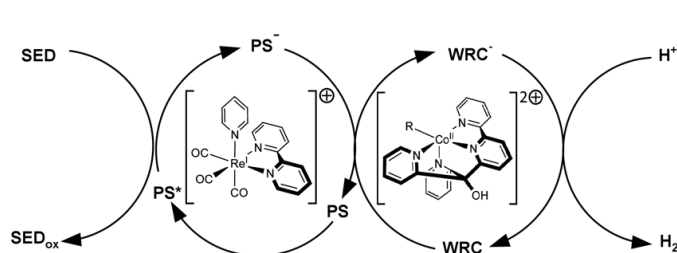


Figure 1: General mechanism of a molecular photocatalytic system including photosensitizer (PS), water reduction catalyst (WRC) and sacrificial electron donor (SED). R = H<sub>2</sub>O

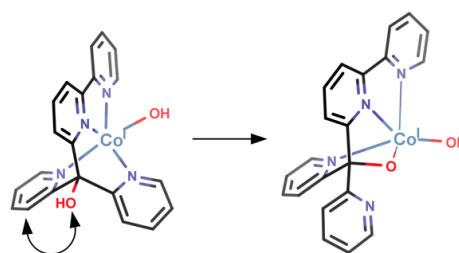


Figure 2: Ligand switch reaction from the pyridine-coordinated to the active, oxygen-coordinated form of Co(II)-tetra-pyridyl WRC

Following on the work of P. Hamm et al.<sup>[1]</sup>, we investigated the catalytic mechanism of a cobalt(II)-tetra-pyridyl complex at pH 8.5. For a photocatalytic system including a rhenium(I)-based photosensitizer (PS) and triethanolamine as sacrificial electron donor (SED, see Fig.1), P. Hamm suggested successive reduction-protonation-reduction-protonation steps, leading to the release of H<sub>2</sub> and back to the initial Co(II) state of the catalyst. However, our time resolved NEXAFS measurements in a new experimental setup on the very same system brought up so far not observed mechanistic steps, precisely, an irreversible initial reaction, leading to the actual catalytic cycle. More specifically, irreversible changes of the X-ray fluorescence spectra of the cobalt upon illumination of the sample, combined with the unchanged catalytic activity of the solution implied that the catalyst undergoes an irreversible structural change during the initial phase. Most probably, the low-spin configuration of the reduced Co(I) intermediate, which is required for the following protonation (see Fig. 2) is stabilized by a “ligand-switch”, upon which the oxygen at the bridge-position coordinates the cobalt center instead of one pyridine moiety. This in situ formed cobalt complex is catalytically active and retains its configuration even after switching of the light source. Such a mechanistic approach has not been considered so far and might have a large influence on the development of new, more active and stable WRCs.

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