

Unraveling the catalytic mechanism of proton reduction by a copper(I) diimine catalyst

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Due to the abundance, price and diverse redox activity of copper, Cu-based catalysts for proton reduction have recently gained special attention in facilitating solar and electrochemical energy storage via the formation of hydrogen fuel. [1] In the past few years, molecular Cu(II) complexes bearing polypyridine chelates have been extensively explored as proton reduction electrocatalysts and photocatalysts. [2],[3]

Herein, we examined the photocatalytic H₂ production behavior of [Cu^I(pq)₂](BF₄), a homoleptic tetrahedral Cu(I) diimine complex bearing the bidentate 2-pyridin-2-yl-quinoxaline (pq) ligand. Evaluation of the H₂ evolution mechanism by electrochemical and density functional theory (DFT) methods indicates that the quinoxaline nitrogen atoms are primarily protonated and subsequent metal centered proton coupled electron transfer leads to the formation of a Cu(II)-hydride, that can evolve H₂ via a low energy transition state. [4]

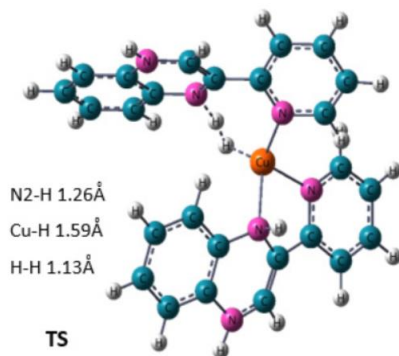


Figure 1: Transition state structure of the Cu(II)-hydride that evolves H₂ via intramolecular coupling between the hydride and the proton of a pendant pyridine nitrogen.

The research work was supported by the Hellenic Foundation for Research and Innovation (HFRI) under the HFRI PhD Fellowship grant 16199.

References:

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