

# MODELLING CO DEHYDROGENASES: DINICKEL(II) $\mu$ -OH PLATFORM FOR CO OXIDATION TO CO<sub>2</sub>

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In industry, the water-gas shift is a crucial reaction that exploits the reducing power of CO to produce CO<sub>2</sub> and hydrogen from water. Hydrogen is subsequently used, for example, as a reductant in the Haber-Bosch process under harsh conditions [1]. On the other hand, anaerobic bacteria and archaea utilize CO dehydrogenases (CODHs) to perform the CO/CO<sub>2</sub> conversion under physiological conditions, producing two protons and two electrons [1]. The active site of the [NiFe] CODHs consists of a Fe<sub>3</sub>S<sub>4</sub> cluster connecting a Ni and an Fe center in close proximity [2]. The redox active and coordinatively unsaturated Ni center binds CO, while the nearby Fe center bears a hydroxide group. After nucleophilic attack of the Fe-bound hydroxide on the adjacent Ni-CO, CO<sub>2</sub> is released together with a proton and the Fe/S cluster is reduced [3].

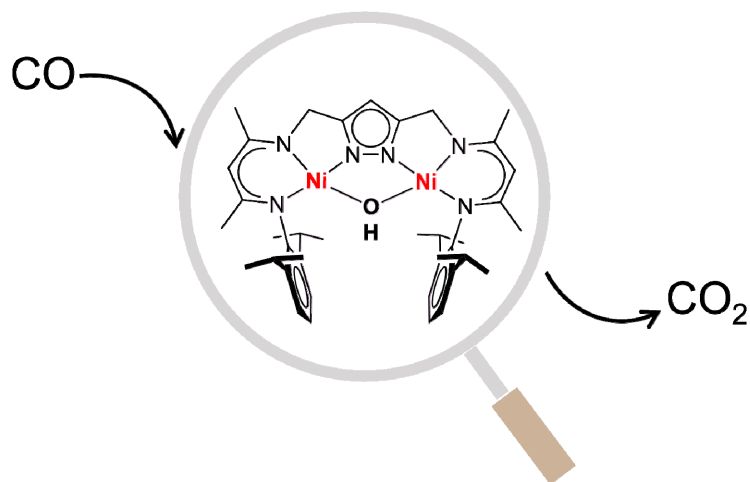


Figure 1. Schematic representation of the reactivity of the  $\mu$ -OH bridged dinickel complex.

Our group has developed pyrazolate-based bis( $\beta$ -diketiminato) dinickel complexes that are able to activate a wide range of small molecules via metal-metal cooperativity [4]. We now found that the  $\mu$ -OH bridged dinickel complex (Figure 1) is able to oxidize CO to CO<sub>2</sub> in the presence of an excess of CO via a bimetallic mechanism, suggesting its functionality relevant to the active center of the Ni,Fe-CODH. Herein, we report the synthesis, structural and spectroscopic characterization of a series of dinickel complexes related to the above CO/CO<sub>2</sub> conversion. Mechanistic investigations supporting the ability of the  $\mu$ -OH complex to mimic the CODH activity will be also presented.

[1] Evans, *Coordination Chemistry Reviews*, **2005**, 249, 1582–1595.

[2] Appel et al., *Chem. Rev.* **2013**, 113, 8, 6621–6658.

[3] Can et al., *Chem. Rev.* **2014**, 114, 8, 4149–4174.

[4] (a) Duan et al., *J. Am. Chem. Soc.*, **2017**, 139, 16720–16731. (b) Duan et al., *J. Am. Chem. Soc.*, **2018**, 140, 4929–4939. (c) Ferretti et al., *Angew. Chem. Int. Ed.*, **2019**, 58, 1705–1709. (d) Ferretti et al., *Inorg. Chem.*, **2019**, 58, 5154–5162.