

# SMALL MOLECULE ACTIVATION AT TRANSITION METAL CENTERS STUDIED BY EPR: OXYGEN ACTIVATION AT BIOMIMETIC DINUCLEAR SITES AND CO<sub>2</sub> REDUCTION BY A Co COMPLEX

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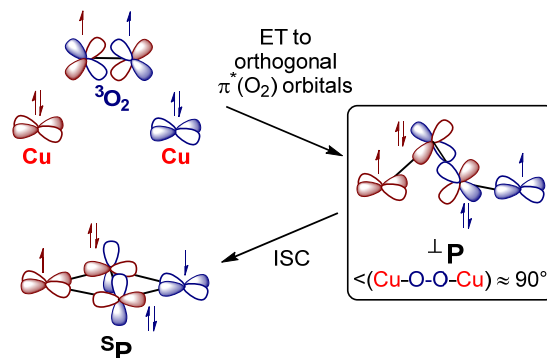
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Small molecules are key substrates in processes that are central for sustainable energy scenarios, such as the reductive conversion of CO<sub>2</sub> into fuels or the reduction of O<sub>2</sub> in fuel cells. A major challenge due to their relative stability is their binding and activation by efficient, stable catalysts, ideally based on cheap materials, such as abundant transition metals. Rational design of improved catalysts requires profound understanding of the structural and electronic aspects that facilitate these steps. EPR spectroscopy provides a versatile toolbox for obtaining essential information on the catalysts and reactive intermediate states.

Here, we present recent examples of the application of a variety of EPR experiments to understand the functioning of novel catalysts and biomimetic model complexes for oxygen activation [1, 2] and CO<sub>2</sub> reduction. This includes a series of stable  $\mu\text{-}\eta^1\text{:}\eta^1\text{-peroxodicopper(II)}$  intermediate models for the O<sub>2</sub> binding process in type III Cu proteins, for which the type and strength of the Cu<sup>II</sup>-Cu<sup>II</sup> spin exchange interaction plays a decisive role. We used frequency-domain THz-EPR to directly probe magnetic transitions over a broad energy range up to several hundred cm<sup>-1</sup>, which allowed us to study and quantify the intricate spin couplings in detail [1]. On this basis, we could develop robust magneto-structural correlations, and we propose a functional role of antisymmetric (Dzyaloshinskii-Moriya) exchange to overcome the spin-forbiddenness of O<sub>2</sub> activation at dicopper sites.



**Scheme 1.** Mechanism for O<sub>2</sub> binding at type III dicopper sites.

Furthermore, we present a novel Co-based electrocatalyst that very selectively and efficiently reduces CO<sub>2</sub> to CO. Isolation and EPR-spectroscopic investigation of 1- and 2-electron-reduced forms of the complex indicate redox-non-innocence of the Hbbpya ligand, the functional relevance of which will be discussed.

[1] Lohmiller, T.; Spyra, C.-J.; Dechert, S.; Demeshko, S.; Bill, E.; Schnegg, A.; Meyer, F. *JACS Au* **2022**, *2*, 1134-11443.

[2] Battistella, B.; Lohmiller, T.; Cula, B.; Hildebrandt, P.; Kuhlmann, U.; Dau, H.; Mebs, S.; Ray, K. *Angew. Chem. Int. Ed.* **2023**, *62*, e202217076.