BIOINORGANIC CHEMISTRY IN ENDO-FUNCTIONALIZED CAGES

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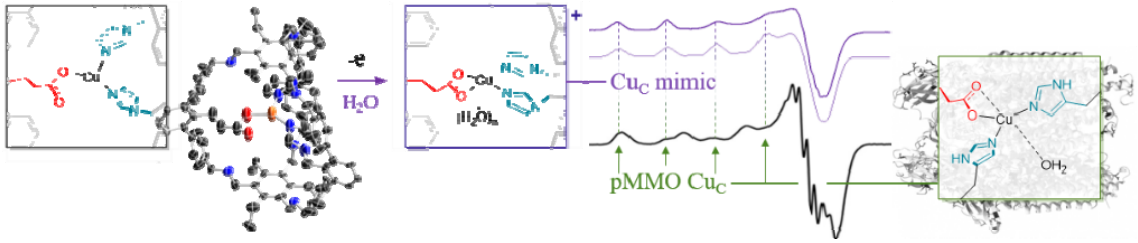
Imidazole units are a reoccurring motif in the active sites of enzymes. An example can be seen in tyrosinase (Tyr). Other functional groups, such as carboxylates, are also observed as ligands, leading to heteroleptic coordination environments. This can be seen, for instance, at the particulate methane monooxygenase (pMMO) and naphthalene dioxygenase (NDO). The active site of pMMO and its mechanism of action are not yet fully understood.

Our group has developed synthetic approaches to mimic the active sites of iron and copper enzymes, employing endohedral-functionalized cage compounds. We have reported cages that offer three imidazole units which can coordinate to copper in a T-shaped manner [1]. This coordination mode is reminiscent to the one that occurs in copper enzymes such as Tyr.

We could extend this strategy to coordinate iron centers in a bio-inspired manner, mimicking 2-His-1-carboxylate heteroleptic ligation [2]. Such cages can also be used to mimic the coordination in the CuC site of pMMO (see the graphical abstract) [3]. The copper cage complexes can catalyze the aerobic oxidation of various hydroquinones. EPR data obtained from our complexes matches well with those reported for pMMO. Recently, we have extended our modular approach to mimic the newly proposed CuD active site of pMMO [4].



[1] S. C. Bete, C. Würtele, M. Otte, *Chem. Commun.* **2019**, *55*, 4427-4430.

[2] S. C. Bete, M. Otte, *Angew. Chem. Int. Ed.* **2021**, *60*, 18582-18586.

[3] S. C. Bete, L. K. May, P. Woite, M. Roemelt, M. Otte, *Angew. Chem. Int. Ed.* **2022**, *61*, e202206120.

[4] S. Miao, L. Gerndt, M. Roemelt, M. Otte, *Chem. Eur. J.* **2025**, *31*, e202500533.