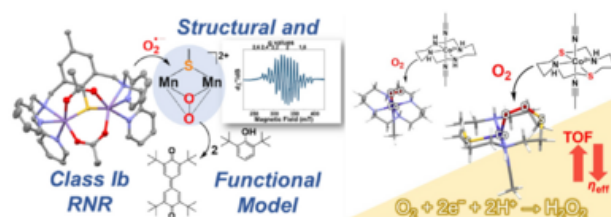


## Jointly achieved insights in different roles of thiolates in bioinorganic chemistry

Start Time: Thursday, February 2, 2023

End Time:



The three Unisyscat Groups ([Hildebrandt](#), [Dau](#) and [Ray](#)) reveal in two joint publications the vital role of sulfur as non-innocent ligand in the catalytic reduction of dioxygen to hydrogen peroxide and in mimicking the reactivity of class Ib ribonucleotide reductases (RNRs).

**Evidence of Sulfur Non-Innocence in [Co (dithiacyclam)] -Mediated Catalytic Oxygen Reduction Reactions**, B. Battistella, L. Iffland-Mühlhaus, M. Schütze, B. Cula, U. Kuhlmann, H. Dau, P. Hildebrandt, T. Lohmiller, S. Mebs, U. Apfel, K. Ray, *Angewandte Chemie International Edition* 2022, 62, [10.1002/anie.2022140](https://doi.org/10.1002/anie.2022140)

In many metalloenzymes, sulfur-containing ligands participate in catalytic processes, mainly via the involvement in electron transfer reactions. In a biomimetic approach, the implication of S-ligation in cobalt mediated oxygen reduction reactions (ORR) was demonstrated. A comparative study between the catalytic ORR capabilities of the four-nitrogen bound [Co(cyclam)]<sup>2+</sup> (**1**, cyclam=1,5,8,11-tetraaza-cyclotetradecane) and the S-containing analog [Co(S<sub>2</sub>N<sub>2</sub>-cyclam)]<sup>2+</sup> (**2**, S<sub>2</sub>N<sub>2</sub>-cyclam=1,8-dithia-5,11-diaza-cyclotetradecane) reveals improved catalytic performance once the chalcogen is introduced in the Co coordination sphere. Trapping and characterization of the intermediates formed upon dioxygen activation at the Co<sup>II</sup> centers in **1** and **2** point to the involvement of sulfur in the O<sub>2</sub> reduction process as the key for the improved catalytic ORR capabilities of **2**.

**A New Thiolate-Bound Dimanganese Cluster as a Structural and Functional Model for Class Ib Ribonucleotide Reductases**, B. Battistella, T. Lohmiller, B. Cula, P. Hildebrandt, U. Kuhlmann, H. Dau, S. Mebs, K. Ray, *Angewandte Chemie International Edition* 2023, [10.1002/anie.202217076](https://doi.org/10.1002/anie.202217076)

In class Ib ribonucleotide reductases (RNRs) a dimanganese(II) cluster activates superoxide ( $\text{O}_2^{\bullet-}$ ) rather than dioxygen ( $\text{O}_2$ ), to access a high valent  $\text{Mn}^{\text{III}}\text{--O}_2\text{--Mn}^{\text{IV}}$  species, responsible for the oxidation of tyrosine to tyrosyl radical. In a biomimetic approach, we report the synthesis of a thiolate-bound dimanganese complex  $[\text{Mn}^{\text{II}}_2(\text{BPMT})(\text{OAc})_2](\text{ClO})_4$  (BPMT=(2,6-bis{[bis(2-pyridylmethyl)amino]methyl}-4-methylthiophenolate) (**1**) and its reaction with  $\text{O}_2^{\bullet-}$  to form a  $[(\text{BPMT})\text{MnO}_2\text{Mn}]^{2+}$  complex **2**. Unlike all other previously reported  $\text{Mn--O}_2\text{--Mn}$  complexes, generated by  $\text{O}_2^{\bullet-}$  activation at  $\text{Mn}_2$  centers, **2** proved to be a capable electrophilic oxidant in aldehyde deformylation and phenol oxidation reactions, rendering it one of the best structural and functional models for class Ib RNRs