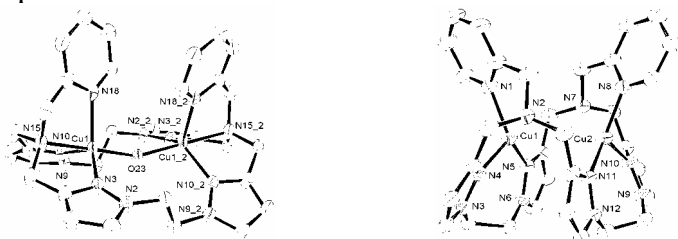


## Catechol oxidase models: kinetic studies and reaction mechanism

Iryna A. Koval,<sup>1</sup> Catherine Belle,<sup>2</sup> Katalin Selmeczi,<sup>2</sup> Eric Saint-Aman,<sup>3</sup> Patrick Gamez,<sup>1</sup> Jean-Louis Pierre<sup>2</sup> and Jan Reedijk<sup>1</sup>

<sup>1</sup>Leiden Institute of Chemistry, Leiden University, The Netherlands, <sup>2</sup>LEDSS, Equipe de Chimie Biomimétique Université J. Fourier, Grenoble Cedex, France, <sup>3</sup>Laboratoire d'Electrochimie Organique et de Photochimie Redox, Université J. Fourier, Grenoble Cedex, France

We report the mechanism of catechol oxidation by the copper(II) complex with macrocyclic pyrazole-based ligand [Cu<sub>2</sub>([22]py4pz)(μ-OH)](ClO<sub>4</sub>)<sub>3</sub>·H<sub>2</sub>O<sup>1</sup> (Figure 1, left). Catechol oxidase is an enzyme encountered in plants that oxidizes a wide range of catechols (*o*-diphenols) to the respective quinones, a first step in melanin production.<sup>2</sup> The complex catalyzes the catechol oxidation by a “classic” biphasic mechanism. The reaction shows a Michaelis-Menten type of behavior ( $K_M = 4.9$  mM,  $V_{max} = 1.3 \times 10^{-6}$  Ms<sup>-1</sup>). In anaerobic conditions one equivalent of DTBC is oxidized stoichiometrically, while the copper(II) ions are reduced to the Cu(I) oxidation state. The respective dicopper(I) complex [Cu<sub>2</sub>([22]py4pz)](ClO<sub>4</sub>)<sub>2</sub>·2CH<sub>3</sub>OH, which was isolated and structurally characterized (Figure 1, right), reacts with dioxygen, forming trans-μ-1,2-peroxydicopper(II) complex, which oxidizes the 2<sup>nd</sup> equivalent of catechol in the absence of dioxygen, thus completing the catalytic cycle. The electrochemical properties of all three complexes are also reported.



### References:

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