

Catalytic promiscuity of mononuclear copper(II) complexes in mild conditions: catechol and cyclohexane oxidations

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The high performance of enzymatic catalysis is usually associated to the precise optimization of the enzyme's active site for a specific reaction. Nevertheless, enzymatic flexibility in performing multiple functions, known as enzyme promiscuity, is currently perceived as a useful feature. Promiscuity allows for application in biocatalysis and biotechnology. While the general term is valid, multiple mechanisms have been established where (i) catalysis of the same chemical reaction can be performed using different substrates; (ii) catalysis of chemically distinct reactions involve different transition states, and (iii) different media conditions lead to distinct reactions [1]. Two Cu²⁺ mononuclear complexes have been synthesized and investigated as promiscuous oxidative catalysts: [Cu(pymimi)Cl₂]: [(2-(pyridyl-2-yl)ethyl)((1-methylimidazol-2-yl)methyl)imine](bischlorido)copper(II), **C1**, previously reported [2], and [Cu(pymima)Cl₂]: [(2-(pyridyl-2-yl)ethyl)((1-methylimidazol-2-yl)methyl)amine](bischlorido) copper(II), **C2**, which is novel. Both complexes were characterized by several techniques including X-ray crystallography, decomposition point, elemental analysis, IR, UV-Vis and EPR spectroscopies, conductimetric analysis and electrochemistry. Theoretical calculations at DFT level were carried out to corroborate structural, vibrational information and spin Hamiltonian parameters (g_x , g_y and g_z). Electronic spectra were also calculated at TDDFT level. Cyclohexane peroxidation promoted by **C1** and **C2** yielded the following overall conversions / turnover numbers: 48 % / 531 s⁻¹ and 46% / 508 s⁻¹, respectively. Both complexes also catalyze the conversion of 3,5-DTBC to its o-quinone (3,5-DTBQ), with turnover numbers of 6.0 and 11.0 x 10⁻² s⁻¹ for **C1** and **C2**, respectively. Their ability to promote catecholase and cyclohexane peroxidation qualifies them as substrate promiscuous catalysts.

[1] Dey, S. K.; Mukherjee, A.; Coordination Chemistry Reviews 310, 2016, 80–115.

[2] De, S.; et al.; Inorganica Chimica Acta, 362, 2009, 2879-2883.

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