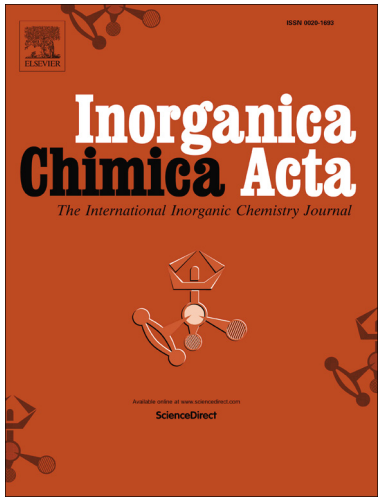

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Methylation as an Effective Way to Generate SOD-Activity in Copper Complexes of Scorpiand-Like Azamacrocyclic Receptors. ‡

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‡ This article is dedicated to Prof. Imre Sovago

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Abstract

Methylation of the secondary amine groups of a scorpiand-type ligand consisting of a pyridine spacer connected through methylene groups to a tris(2-aminomethyl) unit with the pendant arm further functionalised with a 3-pyridine unit leads to a ligand whose Cu(II) complex exhibits three-fold enhanced SOD activity with respect to the non-methylated ligand. Potentiometric studies indicate the formation of $[CuL]^{2+}$ species with a stability three orders of magnitude lower than that formed with the related non-methylated ligand. Kinetic studies indicate that methylation of the secondary nitrogens causes a deceleration of both the complex formation and the acid-induced dissociation of the metal ion. The reduction in stability associated to the poorer σ-donor ability of the tertiary amino groups shifts the Cu(II)/Cu(I) redox potentials towards more positive values permitting a better cycling between both states needed for the dismutation of superoxide radicals.

Keywords: SOD activity, scorpiand-like azamacrocycles, kinetics, copper complexes

1.- Introduction

Aerobic living systems need molecular dioxygen to generate all the energy required for their metabolic processes. Higher organisms have such a high O_2 consumption that they need a continuous supply of this element for their survival. Paradoxically, dioxygen has enough