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Research paper

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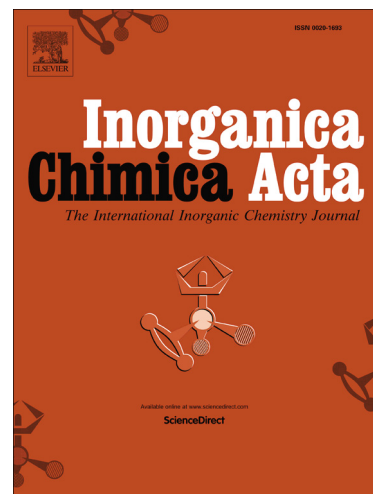
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# Influence of induced steric on the switchover reactivity of mononuclear Cu(II)-alkylperoxo complexes

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## Abstract

Coordination and steric environment around a metal center plays an indispensable role in its reactivity. In this report we have synthesized two bispidine based Cu(II)-OOR (R = 'Bu) complexes  $[\text{Cu}(\text{L1})(\text{OO}'\text{Bu})]^+$  and  $[\text{Cu}(\text{L2})(\text{OO}'\text{Bu})]^+$  having different steric environment around the metal center and characterized by various spectroscopic techniques. These Cu(II)-OOR species show reactivity towards oxygen atom transfer and aldehyde deformylation reactions. In contrast to the previously reported nucleophilic oxidation, aldehyde deformylation reaction by these complexes proceed via an initial H-atom abstraction with KIE of 12 and 8 respectively. It has been observed that more steric bulk at N3 and N7 position of bispidine ligand prefers the oxygen atom transfer reaction while it hinders the H-atom abstraction for Cu(II)-alkylperoxo complexes.

Keywords: Cu(II)-alkylperoxo, Electrophilic deformylation, Steric effect, Kinetics, Biomimetic chemistry

## 1. Introduction

The aerobic life on earth is highly dependent on the activation of O-O bond of  $\text{O}_2$  by various metabolic and biosynthetic pathways. Fe, Mn and Cu containing metalloenzymes are mainly responsible for majority of these biological reactions. Although the activation of molecular oxygen is a crucial process but it is thermodynamically favoured, it is spin forbidden and hence kinetically not feasible unless accelerated by some transition metal ions.

The vital steps involved in activation of dioxygen is the formation/cleavage of O-O and O-H bonds, which leads to the formation of high valent metal-oxygen intermediates. High valent metal-oxygen intermediates are frequently involved in the catalytic cycles involved in the metabolically important oxidative transformations [1-9]. Metalloenzymes catalyzed oxidative reactions of organic molecules are often substrate specific, sometimes regioselectivity and stereoselectivity are also observed. The biological reactions are an enigma for synthetic chemists to fit

into normal condition (e.g. methanol from methane). The protein environment around the metal center plays a decisive factor for this kind of unusual reactions. In synthetic model chemistry, several examples have been reported in past few years, which shows how ligand architecture plays a vital role in the reactivity of the metal-oxygen intermediates [10-18]. Herein, we have demonstrated how changing steric bulk in the ligand architecture changes the reactivity of bispidine based Cu intermediates. Mononuclear transition metal alkylperoxo complexes are imperative in assorted biological and catalytic oxidation reaction [19-20]. In biology the direct formation of Fe(III)-alkylperoxo intermediate was observed in Homoprotocatechuate 2,3-dioxygenase and purple lipoxygenase like enzymes [21-22]. In past few years various Cu(II)-oxygen intermediates have been characterized and served as models of lipid peroxidation [23-25].

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