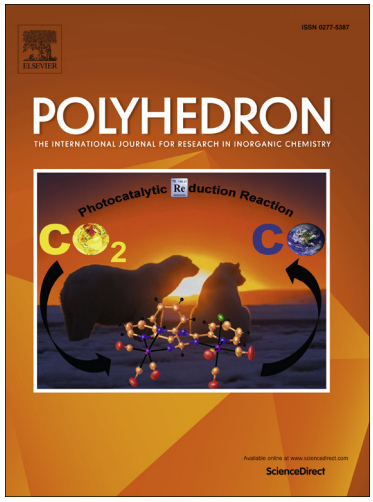

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Structure and antioxidant superoxide dismutase activity of copper(II) hydrazone complexes

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ABSTRACT : Three new mixed ligand hydrazone complexes viz., $[Cu(L)(neocuprin)]NO_3.H_2O$ **1**, $[Cu(L)(HL)]ClO_4$ **2** and $[Cu_2(2\text{-}(2\text{-pyridyl})benzimidazole)_2(L)_2]ClO_4$ **3** (L = *N*'-[(*E*)-phenyl(pyridin-2-yl)methylidene]furan-2-carbohydrazide) have been synthesized by the biomimetic synthesis strategy and their structures were determined by single crystals X-ray analysis. The effect of differing contagious, as well as the rotational conformational versatility of HL, was demonstrated by the difference in structures of complexes **1-3**. These complexes exhibited the antioxidant superoxide dismutase enzymatic activity. The geometry of copper(II) atom in complex **1** is distorted square pyramidal while in complexes **2** and **3** the geometries around copper(II) atoms are distorted octahedral. Magnetic measurements and epr spectroscopy of binuclear complex **3** have shown antiferromagnetic exchange interaction with a coupling constant (*J*) = -10.87 cm^{-1}. Electronic and spectral properties of these newly synthesized hydrazone complexes (**1-3**) are interpreted by DFT and TDDFT calculations. The results reveal that molecular structures have significant effect on antioxidant superoxide activity. Such biological experimental values (antioxidant SOD activity data) are indicative of the promising application of these complexes into the bioinorganic chemistry of superoxide dismutase.

1. Introduction

Antioxidant superoxide dismutases (SOD) are endogenous and first line defense enzymes that contain either Cu-Zn, Fe, Mn or Ni at the active site of these metalloenzymes. A large number of mononuclear Cu^{II}, dinuclear Cu^{II}-Cu^{II} or Cu^{II}-Zn^{II} low molecular weight complexes have been synthesized as superoxide dismutase mimics to emulate the structure and function of metal binding sites[1-15]. The synthesis of low molecular weight model compounds to mimic the active site of metalloenzyme has been an active area of research in the last few decades. However, these model complexes in homogeneous solution are still somewhat sensitive to the environments and they show lower activity and selectivity than the corresponding natural metalloenzymes. The main function of the metalloprotein backbone plays important roles in site-isolation, nanoconfinement and substrate duct to facilitate a specific catalytic function. Therefore, further integration of a scaffold with a model metal complex catalytic system would be most desirable to better mimic the structure and reactivity of metalloenzyme. For the ongoing integration of appropriate ligation with metal complex, site-isolation and confinement can be