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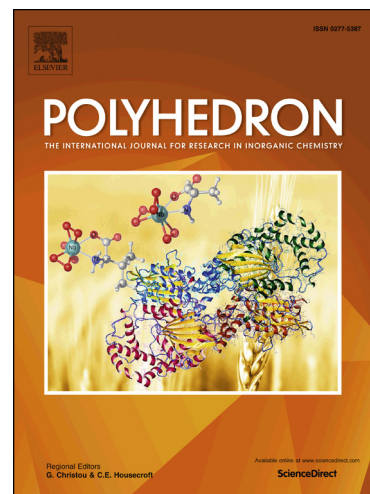
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Bioinspired Co(II) and Zn(II) complexes with an imidazole derived tripodal ligand. Structural models for astacins and MnSOD.

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Abstract

The syntheses of a new imidazole based tripodal ligand, namely *N,N*-bis(2-ethyl-4-methyl-imidazo-5-yl-methylen)-glycine (HemiGly) and its complexes with Co(II) and Zn(II) are described. HemiGly was prepared by a modification of the Mannich reaction giving a tripodal tetradentate ligand with a N₃O donor set that may model the coordinative environment of some metal ions in biological systems, such as astacin-type enzymes or metal-specific SODs. This article presents the syntheses and characterization of metal complexes with general formula [M(emiGly)X]ⁿ⁺, where n = 0,1 depending on X, which may be either an oxygen donor (from a water molecule or an adjacent carboxylate in the solid state) or an halide or pseudohalide. Cobalt and zinc systems resulted to be isostructural and the geometries of the complexes are driven by the nature of the X ligand: trigonal bipyramidal when X is an halide or pseudohalide and octahedral when X is an oxygen donor. Solution studies also indicate parallel behavior and speciation for Zn(II) and Co(II) complexes. Structural comparison of the pentacoordinated zinc complexes shows a considerable resemblance with the metal site in astacins.

Introduction

The synthesis of inorganic compounds that may mimic the active sites of different metalloenzymes is a significant subject of current research. While some Zn(II) containing enzymes, such as carbonic anhydrase and carboxypeptidase, have been known for more than eighty years [1,2], the *astacin* group of zinc metalloenzymes was not described until the 1990s.

Physiological activities of the astacin family include digestion, regulation of embryonic development, and peptide processing [3-8]. Astacin isolated from the crayfish *Astacus astacus* L., is the first peptidase of the metzincin superfamily for which the three-dimensional structure has been determined [9]. From

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