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Research paper

Synthesis, characterization, spectral and catalytic activity of tetradentate (NNNO) azo-imine Schiff base copper(II) complexes

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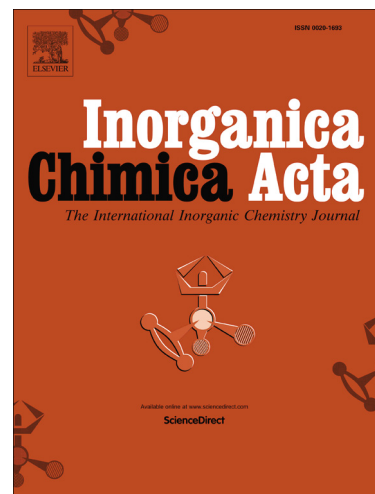
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Revised Manuscript

Ms. Ref. No.: ICA-2017-1641R1**Synthesis, characterization, spectral and catalytic activity of tetradentate (NNNO) azo-imine Schiff base copper(II) complexes****Jahar Lal Pratihara^{a*}, Paritosh Mandal^a, Paula Brandão^b, Dasarath Mal^b, Vitor Felix^b**^aDepartment of Chemistry, Kandi Raj College, Murshidabad 742137, India^bDepartamento de Química, CICECO, Universidade de Aveiro, 3810-193 Aveiro, Portugal

Abstract

The hexadentate ligand, 2,2'-bis(salicylideneamino)azobenzene, **1** has been synthesized from 2,2'-diaminoazobenzene and salicylaldehyde in refluxing diethyl ether. Reaction of ligand **1** with Cu(II) acetate and Cu(II) perchlorate separately in methanol afforded tetradentate (N,N,N,O) Cu(II) complexes, Cu(L) & [Cu(HL)]ClO₄ respectively [where H₂L represent the one imine moiety cleavage product of ligand **1** (H represents the dissociable amino and phenolic protons)]. These were characterized by microanalytical data and spectroscopic studies. In addition, the crystal structures of the ligand **1** and complexes Cu(L) & [Cu(HL)]ClO₄ were determined by X-ray diffraction analysis. The diffraction analysis revealed that the ligand (H₂L) binds Cu(II) centers in (N,N,N,O) tetra dentate fashion in distorted square planer geometry. In complex [Cu(HL)]ClO₄ the apical position of copper center is weakly coordinated with one perchlorate ion. The dimeric structure of the molecule [Cu(HL)]ClO₄ is stabilized through NH₂...O hydrogen bonds. The fluorescence and redox property of ligand **1** and complexes Cu(L) & [Cu(HL)]ClO₄ were studied. Preliminary DFT calculations were carried out using crystallographic coordinates to understand the electronic spectra and redox properties of the ligand and complexes. The complex Cu(L) shows very good catalytic activities towards oxidation of benzyl alcohol to benzaldehyde (under solvent-free condition) and organic thioethers to sulfoxide and sulfones using H₂O₂ as the oxidant.

Keywords: Copper(II); C=N bond cleavage; Crystal structures; Redox; Emission; Oxidation reactions

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