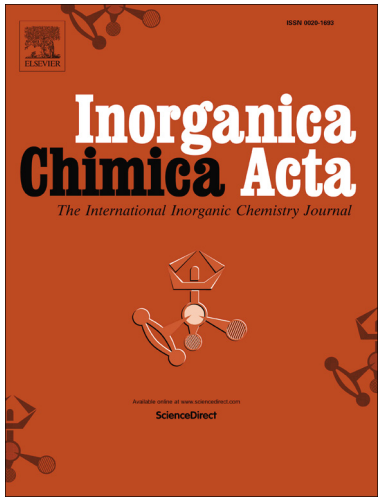

Research paper

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PII: S0020-1693(17)31880-7
DOI: https://doi.org/10.1016/j.ica.2018.04.042
Reference: ICA 18233

To appear in: *Inorganica Chimica Acta*

Received Date: 12 December 2017
Revised Date: 17 April 2018
Accepted Date: 20 April 2018

Please cite this article as: J.L. Pratihar, P. Mandal, P. Brandão, D. Mal, V. Felix, Synthesis, characterization, spectral and catalytic activity of tetradentate (NNNO) azo-imine Schiff base copper(II) complexes, *Inorganica Chimica Acta* (2018), doi: https://doi.org/10.1016/j.ica.2018.04.042

Revised Manuscript
Ms. Ref. No.: ICA-2017-1641R1

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

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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) & $[Cu(HL)]ClO_4$ respectively [where H_2L 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) & $[Cu(HL)]ClO_4$ were determined by X-ray diffraction analysis. The diffraction analysis revealed that the ligand (H_2L) binds Cu(II) centers in (N,N,N,O) tetra dentate fashion in distorted square planer geometry. In complex $[Cu(HL)]ClO_4$ the apical position of copper center is weakly coordinated with one perchlorate ion. The dimeric structure of the molecule $[Cu(HL)]ClO_4$ is stabilized through $NH_2\cdots O$ hydrogen bonds. The fluorescence and redox property of ligand 1 and complexes Cu(L) & $[Cu(HL)]ClO_4$ 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 benzaldeyhde (under solvent-free condition) and organic thioethers to sulfoxide and sulfones using H_2O_2 as the oxidant.

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

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