Synthesis, Characterization, and Structures of Copper (I) Complexes with N,N′-bis[(-chlorophenyl)ethylidene]ethane- -diamine and N,N′-bis[(-nitrophenyl)ethylidene]ethane -diamine

Ali Mahmoudi* mahmoudi.ali@yahoo.com and Saeed Sadeh, Department of Chemistry, Islamic Azad University, Karaj Branch, P.O.Box: - , Karaj, Iran.; Saeed Dehghanpour, Department of Chemistry, Alzahra University, Tehran, Iran.

Abstract:
Two ligands, N,N′-bis[(-chlorophenyl)ethylidene]ethane- -diamine (L) and N,N′-bis[(-nitrophenyl)ethylidene]ethane -diamine (L) and their corresponding copper (I) complexes, [Cu(L)]ClO₄ (1), and [Cu(L)]ClO₄ (2), have been synthesized and characterized by CHN analyses, H-NMR, IR, and UVVis spectroscopy. The crystal structures of L and [Cu(L)]ClO₄ (1) were determined from single crystal X-ray diffraction. L lies across a crystallographic inversion center and the C=N is approximately coplanar with the benzene ring and adopts E configuration. The coordination polyhedron about copper (I) is best described as a distorted tetrahedron. Quasireversible redox behavior is observed for the complexes.

Keywords: Acetophenone derivatives; Diimine ligands; Copper (I) complexes; Distorted tetrahedral structure.

. Introduction
Copper(I) complexes containing bidentate diimine ligands have been the focus of much investigation. It has been pointed out and confirmed that four-electron donor diimines are or very efficient bidentate ligands and many copper(I) complexes containing diimine ligands are known with a variety of stereochemistry [– ]. A key feature in the chemistry of Cu(NN)₂ complexes is the relatively flexible framework and metal-ligand charge transfer transitions in the visible region. These features are the reasons for the reactivity and catalytic properties of such complexes that make them applicable for catalytic processes [ , ], photosensitization of isomerization reactions [ , ], light harvesting studies [– ], and the design of supramolecular arrays [–14]. Steric, electronic, and conformational effects of the coordinated diimines play important roles in modifying the properties of metal complexes. Diimine ligands derived from acetophenone derivatives seem to be good candidates, however, there are few reports on structural data and properties of copper(I) complexes of such ligands [ , ]. In our ongoing study of copper(I) complexes [– ], here we report the synthesis and characterization of two ligands with different electronic effects, N,N₀-bis[(-chlorophenyl)ethylidene]ethane- -diamine (L₁), and N,N₀-bis[(-nitrophenyl)ethylidene]ethane -diamine (L₂), and the corresponding copper(I) complexes, [Cu(L₁)]ClO₄ (1) and [Cu(L₂)]ClO₄ (2) (figure ). The structures of N,N₀-bis[1-(4-chlorophenyl)ethylidene]ethane -diamine (L₁) and [Cu(L₁)]ClO₄ (1) and spectral properties and redox chemistry of these complexes are discussed.

. Experimental

2.1. General
Elemental analyses were performed using a Heraeus CHN-O-RAPID elemental analyzer. Infrared spectra were recorded on a Bruker Tensor 27 instrument. Electronic absorption spectra were recorded on a JASCO V- spectrophotometer and reported as ƛmax (log e). NMR spectra were obtained on a Bruker Avance DRX 500 MHz spectrometer. Proton chemical shifts are reported (ppm) relative to an internal standard of MeSi. All voltammograms were recorded with a three electrode system consisting of an Ag/AgCl reference electrode, a platinum wire counter electrode, and glassy carbon as a working electrode. A Metrohm multipurpose instrument model VA stand was used. In all electrochemical experiments the test solution was purged with argon for at least 15 min. All chemicals used were reagent grade and used as received. Solvents were purified by the methods given in [ ]. [Cu(CH₃CN)₄]ClO₄ was freshly prepared according to the procedure provided in [ ].

2.2. Synthesis of N,N₀-bis[(-chlorophenyl)ethylidene]ethane- -diamine (L₁)