



Mixed ligand copper(II) chelates derived from an O, N, S- donor tridentate thiosemicarbazone: Synthesis, spectral aspects, FMO, and NBO analysis

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ABSTRACT

Five new copper(II) chelates [(Cu(bmct))₂] (**1**), [Cu(bmct)(phen)] (**2**), [Cu(bmct)(bipy)] (**3**), [Cu(bmct)(4,4'-dmbipy)] (**4**) and [Cu(bmct)(5,5'-dmbipy)] (**5**) with 5-bromo-3-methoxysalicylaldehyde-N(4)-cyclohexylthiosemicarbazone (H₂bmct) as the chelating ligand and 1,10-phenanthroline, 2,2'-bipyridine, 4,4'-dimethylbipyridine, 5,5'-dimethylbipyridine as coligands have been synthesized and characterized by different physicochemical techniques like CHNS analysis, molar conductivity and magnetic studies, IR, UV/Vis and EPR spectral studies. In all the complexes, the thiosemicarbazone exists in thioiminolate form and coordinates to the metal through azomethine nitrogen, thioiminolate sulfur, and phenolate oxygen. EPR spectra in polycrystalline state at 298 K showed that compounds **1**, **4**, and **5** are isotropic, **2** is axial and **3** is rhombic in nature. In DMF at 77 K, compound **1** showed hyperfine lines in the parallel and perpendicular regions as well as superhyperfine lines due to the interaction of copper center with azomethine nitrogen of the ligand. Complex **2**, in which $g_{\parallel} > g_{\perp} > 2.0023$ suggests a distorted square pyramidal structure. To analyze the stability of the complexes, quantum chemical parameters like hardness, softness, polarizability, electrophilicity, electronegativity, and dipole moment were calculated and discussed within the framework of electronic structure principles known as Maximum Hardness, Minimum Polarizability and Minimum Electrophilicity Principles. Besides, the intramolecular donor-acceptor interactions for all complexes were evaluated by using NBO analysis. All calculations proved that Compound **3** is the most stable chelate among them.

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1. Introduction

Thiosemicarbazones, having the general formula R¹R²C = N-NH-C(=S)-NR³R⁴, can coordinate with various metal ions as neutral molecules (thioamido form) or after deprotonation, as anionic ligands (thioiminol form) and can adopt a variety of coordination modes. The thiosemicarbazones of *o*-hydroxy aromatic aldehydes and ketones are envisaged as an important class of O, N, S donor chelating ligands for their coordinating versatility and diverse range of biological activities [1-7]. Copper(II) metal ion, an essential and the most abundant trace element in biological systems [8,9] has been extensively studied and forms a wide variety of

complexes with neutral or anionic thiosemicarbazones of nuclearity ranging from mono- to poly-nuclear with distorted tetrahedral, square planar, square pyramidal or octahedral geometry [10-12]. The copper complexes with planar heterocyclic ligands are efficient DNA-binders and display a stronger affinity with DNA than the corresponding free ligands [13].

Our interest in the study of the structure of copper chelates of thiosemicarbazones lies in the fact that transition metal complexes with planar aromatic side groups, can bind with DNA by both metal ion coordination and intercalation of the aromatic moiety [14]. The focus of our present study is to provide an experimental and theoretical study of a new set of copper chelates of a thiosemicarbazone with a future perspective to pursue their biological and analytical applications. Our group has already reported the chelating behavior, spectral aspects, and biological and catalytic activity of a variety of metal complexes of thiosemicarbazones [15-18].

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