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Structural and spectral characterization of Cu(II) complexes of N(4)-substituted thiosemicarbazones derived from 2-hydroxyacetophenone: Crystal structure of a dinuclear Cu(II) complex

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Abstract. Copper(II) complexes of 2-hydroxyacetophenone-N(4)-cyclohexylthiosemicarbazone (H_2L^1) and 2-hydroxyacetophenone-N(4)-phenylthiosemicarbazone (H_2L^2) have been synthesized and characterized by different physicochemical techniques like magnetic studies and electronic, infrared and EPR spectral studies. [(CuL¹)₂] (1) is a dinuclear complex having four coordination around copper(II) with distorted square planar geometry. The two individual dinuclear complexes are interconnected through two bifurcated classical hydrogen bond interactions producing a sheet-like structure along b axis. [(CuL²)₂]·¹/₂H₂O (2) also has a dimeric structure. The thiosemicarbazones bind to the metal as dianionic ONS donor ligand in all the complexes, except in the complexes [Cu(HL¹)Cl]·2H₂O (3), [Cu(HL¹)Br]·4H₂O (4) and [Cu(HL¹)NO₃]·C₂-H₅OH(H₂O) (5), where the ligand moieties are coordinated as monoanionic (HL) ones. Complexes [CuL¹-dmbipy] (6), [CuL²dmbipy]·3H₂O (7), [CuL²bipy]·H₂O (8) and [CuL²phen]·2C₂H₅OH (9) are heterocyclic base adducts.

Keywords. 2-Hydroxyacetophenone; thiosemicarbazone; X-ray crystallography; copper(II) complex; EPR spectrum.

1. Introduction

Thiosemicarbazones form a class of versatile nitrogen and sulfur (NS) donor chelating ligands and are known to exhibit diverse biological activities. The biological activities are dependent upon the chemical nature of the moiety attached to the C=S carbon atom. They can act as tridentate ligands if additional donor atoms are present near the thiosemicarbazone moiety. Thiosemicarbazones derived from 2-hydroxyace-tophenone can act as a dianionic tridentate ligand by deprotonation of both phenol and thiol functions.

They can also behave as monoanionic tridentate ligands coordinating with a metal centre through the deprotonated phenolic oxygen, thione sulfur and the azomethine nitrogen.² Thiosemicarbazones form complexes with copper(II) exhibiting interesting structures.³

Thiosemicarbazones and their copper complexes are of considerable interest because of their chemical and promising biological properties. ^{4,5} They can easily be modified by varying the parent aldehyde or ketone used for the synthesis, particularly with compounds having additional potential coordinating sites or by

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