Self-organized three dimensional architectures based on non-covalent interactions in square planar Cu(II) thiosemicarbazone: Solvent mediated crystallization and EPR based correlation study

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Abstract

A series of copper complexes of 2-acetylpyridine-N^4-methylthiosemicarbazone (HL4M) were synthesized and characterized by elemental analyses, UV–Vis, FT-IR, conductivity and EPR studies. The molecular structures of [Cu(L4M)Cl] (**1**), [Cu(L4M)I] (**2**), [Cu(L4M)OAc]·H_2O (**3**) and [Cu(μ-S-L4M)(NCS)]$_2$·DMSO (**4**) were confirmed by single crystal X-ray crystallography. Complexes **1**, **2** and **3** have square planar geometry constituted by NNS donor sites from deprotonated thiosemicarbazone ligand and the fourth site is occupied by anionic group/atom. Complex **4** is a centrosymmetric dimer. The XRD results revealed that the solvents play a decisive role in the crystallization of products. These four complexes exhibit strong hydrogen bonding interactions in the solid state and are self-assembled into infinite 3D supramolecular structure *via* π···π stacking interactions. The $g_{||}$ and $A_{||}$ of complexes were analyzed by Peisach–Blumberg plot which proves an inverse correlation among NNS and ONS thiosemicarbazone complexes.

Keywords: *Copper complexes, X-ray crystal structure, Solvent effect, Hydrogen bonding, Supramolecular structures,* $A_{||}$ *-* $g_{||}$ *correlation*

1. Introduction

Thiosemicarbazones, an important class of N–S donor ligands, have shown wide range of coordination modes, flexible coordination fashions, structural diversity and outstanding supramolecular binding with most of the transition or rare earth metal ions. Cu(II) thiosemicarbazone chemistry remains an area of unabated attention due to their catalytical, analytical and biological applications. [1-3] Among these, N-heterocyclic thiosemicarbazones have attracted more attention, because many of them displayed promising anticancer activity [4].

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Cu(II) complexes of the type [CuLX], where L is an anionic tridentate thiosemicarbazone and X is a monoanionic donor like Cl, I, OAc etc. and its binuclear complexes are especially attractive due to