Journal of Molecular Structure 1277 (2023) 134866

Contents lists available at ScienceDirect

Journal of Molecular Structure

journal homepage: www.elsevier.com/locate/molstr

Copper(II) chelates derived from an N,N,O-tridentate 2-pyridinecarboxaldehyde-N^4-phenylsemicarbazone: Synthesis, spectral aspects, crystal structure, FMO and NBO analysis

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ARTICLE INFO

Article history:
Received 8 September 2022
Revised 6 December 2022
Accepted 24 December 2022
Available online 25 December 2022

Keywords:
2-Pyridinecarboxaldehyde
Semicarbazone
Copper(II) chelate
EPR spectrum
Quantum chemical parameters
NBO analysis

ABSTRACT

Seven novel Cu(II) complexes [Cu(HPySc)Cl_2] (**1**), [Cu_2(PySc)$_2$(NO_3)$_2$]·H_2O (**2**), [Cu(HPySc)(SO_4)]·½H_2O (**3**), [Cu_2(PySc)$_2$(OAc)$_2$]·CH_3OH (**4**), [Cu_2(PySc)$_2Br_2$]·H_2O (**5**), [Cu(PySc)(NCS)]·2H_2O (**6**) and [Cu_2(PySc)$_2$(N_3)$_2$] (**7**) with 2-pyridinecarboxaldehyde-N^4-phenylsemicarbazone (HPySc) have been prepared and characterized using different analytical and spectroscopic techniques. The complex **6** is expected to be square planar while the other complexes are expected to be square pyramidal arrangement, among these, the geometry of complex **4** has been conformed by single crystal XRD study that it is a dimer and adopts distorted square pyramidal geometry around copper(II) centre. All the complexes are found to be paramagnetic and non-conductive in nature. The semicarbazone ligand is coordinated in neutral form in two of the complexes and in ionic form in others. DFT/B3LYP/6-311g**/LANL2DZ computations of the ligand HpySc (PyCHNNCONHPh) and seven Cu(II) complexes were performed to analyze the FMOs and important electron delocalizations that existed in each compound. Molecular stability and bond strengths have been investigated by applying natural bond orbital (NBO) analysis. All the complexes are more stable than the semicarbazone and the complex **2** is the most electronically stable (-5.160 eV) among the complexes. Furthermore, the semicarbazone is the hardest and complex **5** is the softest than all complexes due to the η values. The calculated energy gap between HOMO and LUMO energies show the variations of nucleophilic and electrophilic reactivity regions in the semicarbazone and in complexes **1-7**.

1. Introduction

The metal complexes of semicarbazones have received much attention from researchers and scientists because of their widespread biological and interesting structural properties [1–4]. They are the subject of considerable interest for the number of chemists due to the formation of transition metal complexes having different chemical, physical and structural properties [3]. The structure of the complex depends upon the type and the nature of the ligand and nature refers to the number of donor atoms, the flexibility between them and the ability to combine with metal ions. Interestingly, copper(II) complexes of pyridine based semicarbazones have interesting crystal structures involving diverse noncovalent interactions [5].

Semicarbazones are also found to have anti-Trypanosoma cruzi activity [6]. Moreover, the biological activities of their complexes could be due to metal ion coordination. Semicarbazones are also used as inhibitors in different biological processes. 2-Hydroxy-1-naphthaldehyde semicarbazone was employed as a new Jack bean urease inhibitor [7]. Semicarbazone derived from di-2-pyridyl ketone is found to have gelation properties [8].

Considering the above facts, we have prepared seven Cu(II) chelates with *2*-pyridinecarboxaldehyde-N^4-phenylsemicarbazone (HpySc, PyCHNNCONHPh) and different copper(II) salts. The magnetic parameters measured in EPR study are related to the structure of the paramagnetic complex, the number of ligands, nature of bonding and spatial arrangements of the ligands around the central metal ion. EPR spectroscopy is used as a powerful tool to deduce valuable information about the electronic environment of the paramagnetic Cu(II) center [9]. Electronic spectroscopy, IR spectroscopy and thermogravimetric analysis have been carried out to confirm the coordination of ligands and the presence of water molecules in

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https://doi.org/10.1016/j.molstruc.2022.134866
0022-2860/