



Diversities in the chelation of aroylhydrazones towards cobalt(II) salts: Synthesis, spectral characterization, crystal structure and some theoretical studies

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ABSTRACT

Five cobalt complexes synthesized from two aroylhydrazones were characterized by elemental analyses, thermogravimetric analysis, molar conductivity, magnetic susceptibility measurements, IR and electronic spectra. Single crystal X-ray structure of one of the complex is also reported and it got crystallized in triclinic space group $P\bar{1}$ and the crystal structure shows a distorted octahedral geometry around the metal center. Spectral data reveal that both the aroylhydrazones are tridentate and coordinate through the azomethine nitrogen, hydrazone oxygen, and pyridyl nitrogen. Magnetic susceptibility measurements confirm the paramagnetic nature of the Co(II) complexes and one of the complex was found to be diamagnetic in nature. Additionally, HF/6-311G(d,p)/LANL2DZ calculations were performed to predict the possible intramolecular interactions contributing to the lowering of the stabilization energy. Accordingly, $\pi \rightarrow \pi^*$ transitions were found to be responsible for the stabilization energy for the ligands and their cobalt complexes. To describe and discuss the chemical reactivity and stability of synthesized complexes, quantum chemical parameters like frontier orbital energies, hardness, softness, energy gap, electronegativity, chemical potential, electrophilicity, polarizability and dipole moment were calculated. Also, the main electronic structure principles such as maximum hardness, minimum polarizability, and minimum electrophilicity principles were considered to evaluate the stability of the complexes.

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1. Introduction

The architectural beauty of coordination complexes arises due to the interesting ligand systems containing different donor sites. In aroylhydrazones, it is well known that a proton transfer can occur between the hydrazinic-N and keto group of hydrazone part. Therefore, tautomerization equilibrium exists between amido form and iminol form through intramolecular proton transfer. The available donor sites in aroylhydrazone compounds are amide oxygen and azomethine nitrogen [1]. By suitable substitution on the hydra-

zone framework, the number of coordination sites can be increased thereby increasing the denticity. The hydrazone ligands act mostly as tridentate moieties though they have the potential to behave as bridging tetradentate ligands [2]. Among the ligand systems, hydrazone and hydrazone occupy a special place because of their straightforward synthesis, high purity and wide range of applications [3–5]. The presence of azomethine nitrogen in hydrazones is responsible for their biological importance. Metal complexes of aroylhydrazones have been studied for many years as they exhibit antimicrobial and anticancer activities [6,7]. Reported studies claim that the cadmium complex of pyridine-2-carbaldehyde isonicotinoylhydrazone could contribute alternatives as a drug candidate for the treatment of microbial diseases. Studies on cytotoxicity of cadmium complexes of hydrazones have reported that they have shown a greater effect than cis-platin [8]. It was reported recently

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