Characterization and Vibrational Studies of The Complexes Pyridine With Transition Metal Copper

Abstract

Theoretical study of interaction of pyridine with transition metal copper (Cu) have been done. The structure of pyridine with transition metal Cu and Pure Pyridine were optimized. In vibrational spectra give fine changes at molecular levels because the vibrational spectra results from the molecular vibrations. The metal atom of Cu(11) Coordinated with pyridine through nitrogen atom of the ring. Raman and IR bands belonging to vibrations of coordination All study and similar study will lead to better understanding of the effect of transition metal copper with the biological systems. Pyridine has c_{2v} symmetry. The complexes have c_1 symmetry.

Keywords: Pyridine, Transition Metal Copper, Vibration Spectroscopy and DFT.

Introduction

The continued development of metal catalysis have provided by studies in to coordination chemical and physical processes. These studies are particularly important when complex ligands are employed that may them selves because the focus of chemical transformation in direct competition with the catalytic substances. In addition to experimental investigations, theoretical studies have characterized detailed interactions between metal ions and molecules as well as provided binding energies. .

For calibration of experimental measurements, several theoretical methods (namely HF, MP_2, and DFT) were applied in an attempt to approach accurate values and to establish trends in the metal ion- ligand and system.

Pyridine (C_5H_5N) is an aromatic molecule consisting of a π electron ring and a nitrogen atom. The Pyridine ring Provides a potential binding site for metals and the information on their coordinating properties is important in understanding the role of metal ions in biological system. Very few studies containing gas-phase infractions of pyridine with metal ions along with the experimental results have appeared so far. Recently, the charge transfer process of Ag^{+} pyridine have been observed experimentally and this report was later extended to experimental work to cu[+]pyridine and theoretical studies of Cu+ and Ag+ metal pyridine complexes have been performed.

Attractiveness of copper ions in these compounds result mainly from the magnetic properties of Cu_2^+ ion mixed valance oxidation- stale – pair Cu_2^+/Cu^+ photoluminescence, structural features and biological relevance involving the binuclear site in cytochrome oxidases and related model compounds. According to the HSAB (hard soft acid base) theory, SCN-ion coordinates to hard acids (CO2+) Through nitrogen atom, and the uncoordinated sulfer atom is involved in hydrogen bonds and sometimes involved in s-----s interactions. If the transition metals center is soft acid (cu+) SCN-ligand binds to central ion through sulfer atom. Cu2+ ion behaves as an intermediate Lewis acid and it is expected to bind the two sides of the SCN-ligand, but with higher tendency to coordinate to the nitrogen. A search is the CSD (The Cambridge structural database, version 5.33) reveals 270 mononuclear copper (11) Complexes containing N-Coordinated thiocyanate groups and only to compounds with SCN-bond to cu centre via the S end.

Another interesting feature of cu (11) Complexes is the coordination geometry around the metal ion. Cu (11) ions can be four-six and five coordinates.

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The last onces usually display intermediate sterochemical environment ranging between trigonal and bipyramidal.

Aim of the Study

In the present work we have synthesized metal ligand complexes of pyridine with transition metal cu and characterized these with the help of standard spectroscopic techniques. A comparative study of pure pyridine and its metal complexes have been done by theoretical DFT calculation and experimental FT-IR and Raman spectra.

DFT Calculations

The Optimized geometries of pure pyridine with transition metal copper and the harmonic wavenumbers, Raman and IR intensities of different normal modes of pyridine with cu complex were calculated using the Gaussian 03 program package. Theoretical DFT calculation were done using the hybrid function that mixes the lee, yang and par functional for the correlation part and the Beck's three parameter functional for the exchange part (B3LYP) employing the 6-31+ (d,p) and LANL2DZ basic sets. The vibrational wavenumbers of the pyridine were calculated at B3LYP/6-31+G(d,p) theoretical level polarizability optimizing the geometrical structures of the metal complexes Pyridine (11) we have used the B3LYP functional with LANL2DZ split-valence basic set.

Experimental

The pyridine liquid was purchased from merck (Darmstadt Germany) and directly used without further purification. FT-IR and laser Raman spectra for pure pyridine with transition metal Cu(11) Complex was obtained. The FT-IR spectrometer used was the perkin Elmer spectrum 65 FI-IR spectrometer. The FI-IR spectra were recorded in range 400-4000 cm$^-$ 1 with the simples kept in the form of Kβr pellects. The Raman spectra were recorded in the range 200-3500 cm$^-$ 1.

The dispersion element of the spectrometer is a grating whose grating constant is 2400 grooves/mm . spectrometer scanning data collection and processing were done by dedicated computer using gram wire software.The origin 6.1 software was used for further analysis of band shape.

Result and Discussion

In the present work the theoretical study of important of pyridine with transition metal cu have been done. The structure of pyridine with transition metal cu were optimized. The optimization were done using density functional theory (DFT) at B3LYP functional employing the LANL2DZ and 6-31 + G (d,p) basic sets. The optimized structures are given in figure 1.
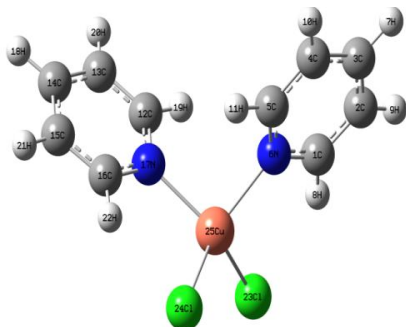
The binding energy polarizability py+cuare in given in table 1.

Table 1: Dipole moments of pyridine and Different Transition metal copper complexes calculated by DFT method at B3LYP/ 6-31+G(d,p) and LANL2DZ level.

Complex/molecule (Debye)	Dipole moment
Py+ Cu	13.20

The Dipole moments for given in py+cuare also calculated and presented in table 2.

S.N.	Atoms	Charge Distribution PY + Cu
1	C1	-0.150
2	C2	-0.191
3	C3	-0.158
4	C4	-0.204
5	C5	-0.117
6	N6	-0.248
7	H7	0.246
8	H8	0.296
9	H9	0.244
10	H10	0.240
11	H11	0.258
12	C12	-0.117
13	C13	-0.204
14	C14	-0.158
15	C15	-0.191
16	C16	-0.150
17	N17	-0.248
18	H18	0.246
19	H19	0.258
20	H20	0.240
21	H21	0.244
22	H22	0.296
23	Cl23	-0.335
24	Cl24	-0.335
25	Ni25	0.235

Pyridine has c_{2v} symmetry. The complex has C_1 symmetry. In vibrational spectra give fine changes at molecular levels because the vibrational spectra results from the molecular vibrational spectra. In order to observe the fine charges. We have calculated the vibrational as Raman and IR spectra of pyridine with copper metal (p y + cu). The Raman spectra and they are presentedfigure (2).
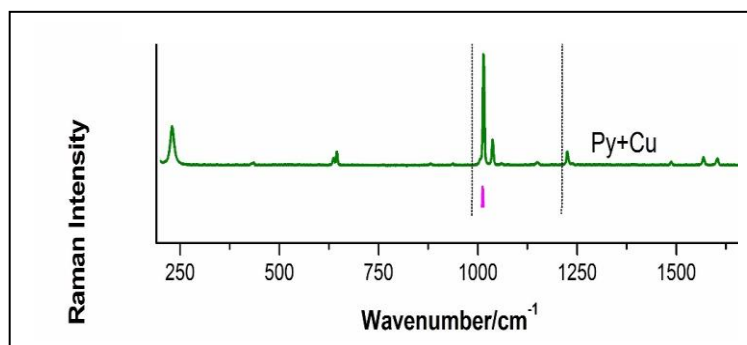
The FT – IR spectra are presented in figure (3).
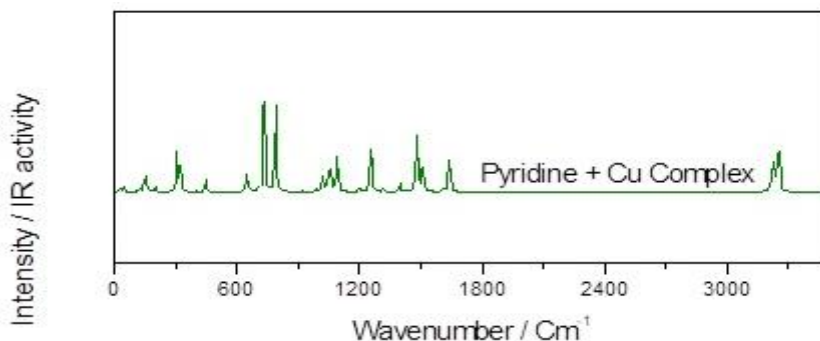
The vibration harmonic wave number along along with Infrared and Raman activity Dipolar p and dipolar U factors are tabulated in table (3).

S.N.	PY + Cu		
	Atom1	Atom2	Bond Length
1	C1	C2	1.4049
2	C1	N6	1.3607
3	C1	H8	1.0852
4	C2	C3	1.4067
5	C2	H9	1.0852
6	C3	C4	1.4085
7	C3	H7	1.0866
8	C4	C5	1.4022
9	C4	H10	1.0853
10	C5	N6	1.3617
11	C5	H11	1.0853
12	N6	Cu25	2.0889
13	C12	C13	1.4022
14	C12	N17	1.3616
15	C12	H19	1.0854
16	C13	C14	1.4085
17	C13	H20	1.0852
18	C14	C15	1.4068
19	C14	H18	1.0866
20	C15	C16	1.4049
21	C15	H21	1.0851
22	C16	N17	1.3607
23	C16	H22	1.0853
24	N17	Cu25	2.0891
25	Cl23	Cu25	2.2927
26	Cl24	Cu25	2.2928

Binding energies and structures also are presented and analyzed herein dipole moments of pyridine with transition metal copper complex calculated by DFT method at B3LYP/6- 31 +G(d,p) and LANL2DZ is optimized the dipole moments 13.1945 Debye and (UB3LYP) -722656844825 a,u .

Conclusion

Theoretical study of interaction of pyridine with transition metal copper have been done. The structure of pyridine with transition metal cu were optimized. pyridine has c_{2v} symmetry. The complex has c_1 symmetry. In vibrational spectra give fine changes at molecular level because the vibrational spectra results from the molecular vibration.The metal atoms of cu(11) coordination with pyridine through nitrogen atoms of the ring on coordination Raman and IR band belonging to vibrations of coordination region were observed in the DFT derived spectra

The bands belong to the ring and C-H group appearing in the higher wave number region also shifted is the experimental Raman and IR spectra. This study will and further similar study lead is better under standing of the effect of coordination of metals swith the biological systems.

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