

Vibrational Analysis and DFT Calculation of Complexes Pyridine with Transition Metal Zn

Abstract

Theoretical study of interaction of pyridine with transition metal Zn have been done. The structure of pyridine with Zn were optimized. Pyridine has c_2 symmetry. The complex has c_1 symmetry. Vibrational spectra give fine changes at molecular levels because the vibrational spectra result from the molecular vibrations. Binding energies and structures also are presented and analyzed herein.

Keywords: Pyridine, Transition Metal Zn, Vibrational Studies and DFT.

Introduction

Gas phase studies of metal ion-molecule complexes have provided a wealth of valuable information on binding energies, geometries and microscopic behaviour of chemical and physical processes.

The continued development of metal catalysis have provided by studies in to co-ordination chemical and physical processes. 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, MP2 and DFT) were applied in an attempt to approach accurate values and to establish trends in the metal ion-ligand systems. [1].

Pyridine (C_5H_5N) is an aromatic molecule consisting of a π electron ring and a nitrogen atom pyridines and their derivatives have been widely used in fields ranging from medicinal to industrial applications. 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 systems. Very few studies containing gas phase interactions of pyridine with metal ions along with the experimental results have appeared so far[2]. The only published result have been the formation of $Ag^+(pyridine)_n$ with $n=1,2,3$, or 4 through gas-phase clustering reactions by castle man. [3].The binding energies of the third and fourth pyridines attached to Ag^+ were deduced from the van'tHoff plot. However, the detailed interaction, geometry and binding energy of bare Ag^+ interacting with one pyridine molecule remain unknown [4]. Mulliken noted that pyridine can be treated as a π -type complex or as a π -donor-type ligand because of the lone pair electron on its nitrogen atom. Because conjugation between a lone-pair and the π electrons of an aromatic ring has rendered nitrogen the favored basic site, it is reasonable to expect metal cations to orient themselves toward the N atom.The electrostatic model predicts that the metal ions are likely to align with pyridine dipole moment[5]which is along the C_2 axis. Because the lone-pair electrons and dipole moment coexist on the same plane and in the same direction, electron, donation from pyridine to metal ion may be important for the pyridine complexes as well. Henson has theoretically studied $Co(acacen)$ (Pyridine) and $Co(salen)$ (pyridine) complexes and shown that the nitrogen of the pyridine is bond to Co atoms.

Recently the charge transfer process of Ag^+ pyridine have been observed experimentally[6] and this report was later extended to experimental works to Zn^+ pyridine and theoretical studies of Zn^+ and Ag^+ metal pyridine complexes have been performed.[7].Attractiveness of Zn ions in these compounds results mainly from the magnetic properties of Zn_2^+ ions, mixed valance oxidation-state pair Zn_2^+/Zn^+ photoluminescence, structural features and biological relevance involving the binuclear site in cytochrome oxidases and related model compounds.[8]. Having one different doner atoms pyridine ions can coordinate to metal through the



Wakil Ray

Assistant Professor,
Deptt. of Physics,
DBSD Degree College,
Kadna, Saran, Bihar,
India

nitrogen giving rise to linkage isomers, dimers or polynuclear species with different dimensionality and nuclearity. According to the HSAB theory, SCN-ion coordinates to hard acids Zn_2 through nitrogen atom, and the uncoordinated sulfur atom is involved in hydrogen bonds and some times involved in $s\dots\dots s$ interaction. Another interesting feature of Zn(II) complexes is the coordination geometry around the metal ion.

Zn(II) ions can be four-six and five coordinate. The last ones usually display intermediate stereochemical environment ranging between trigonal and bipyramidal.

In the present work the formed the complex of pyridine with transition metal $Zn(Py)_2Cl_2$ have been investigated the FT-IR and micro-Raman spectroscopic in the frame work of coordination on the fundamental vibrational frequencies and molecular structure of mentioned ligand molecules using density function theory and characterized these with help of standard spectroscopic techniques. A comparative study of pure pyridine and its metal zn complexes have been done by theoretical DFT calculation[13] and experimental FT-IR and Raman Spectra[9].

Theoretical

The optimized geometries of pure pyridine as well as of the complexes of pyridine with transition metal Zn and the harmonic wave number Raman and IR intensities of different normal modes of pyridine and transition metal zn complex . was calculated using the Gausaian-03 Program package [10].

Theoretical DFT calculations were done using the hybrid functional that mixes the lee, yang and parr functional for the correlations part and the becke's three parameter functional for the exchange part (B3LYP) [11]employing the 6- 31+G(d,p) and LANL2DZ basic sets and the geometries of the pure form of pyridine as well as of the pyridine with transition metal complexes were optimized.The vibrational wavenumbers of pyridine were calculated at B3LYP/6-31 +G(d,p) theoretical level or optimizing the geometrical structures of the metal complexes of pyridine $M(Py)_2Cl_2$ (where $M=Zn(II)$). We have used the B3LYP functional with LANL2DZ splint-valence basic set.

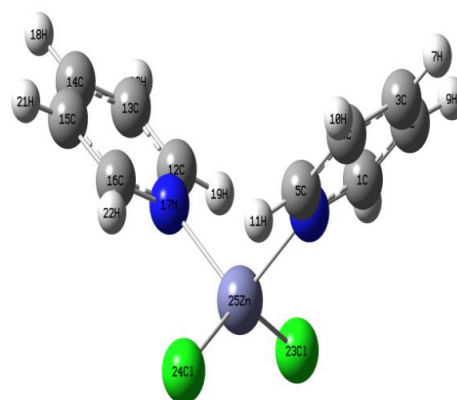
Experimental

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 Zn complexes were obtained . The FT-IR spectrometer used was the PerkinElmer spectrum 65 FT-IR spectrometer. The FT-IR spectra were recorded in the range 400-4000 cm^{-1} with the sample Kept in the form of KBrpellets.

The laser Raman set-up consists of a 14.5 nm Ar^{-1} laser delivering about 5 mw.Intensity as an excitation source an Olympus 50x objective microscope for proper focussing of laser beam on desired portion of the sample and the Raman spectrometer (Renishaw RM 1000) having spectral resolution of $1cm^{-1}$. The Raman spectra were recorded in the rang 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 a dedicated computer using Gram wire software. The origin 6.1 software was used for further analysis of band shape.

Result & Discussion

In the present work the theoretical study of interaction of pyridine with transition metal have been done. The structure of pyridine with transition metal Zn were optimized .The optimization were done using density function theory (DFT) and at B3LYP functional, employing the LANL2DZ and 6-311+G(d,p) basic sets. The optimized structures are given in figure.1



The binding energy for PY+Zn are given in table.-(1).

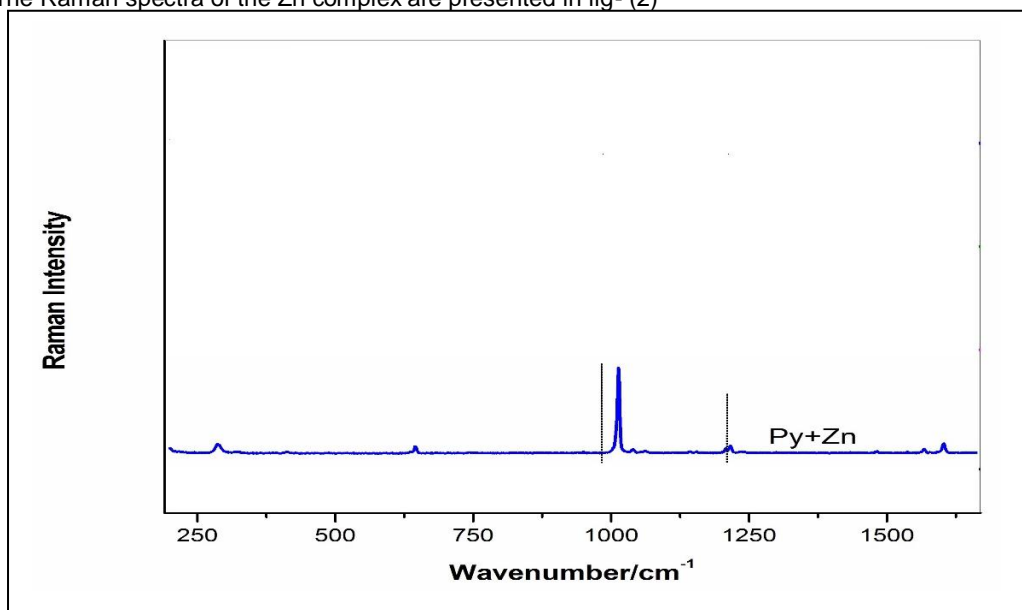
Complex/molecule	Dipole moment (Debye)
Py + Zn	10.55

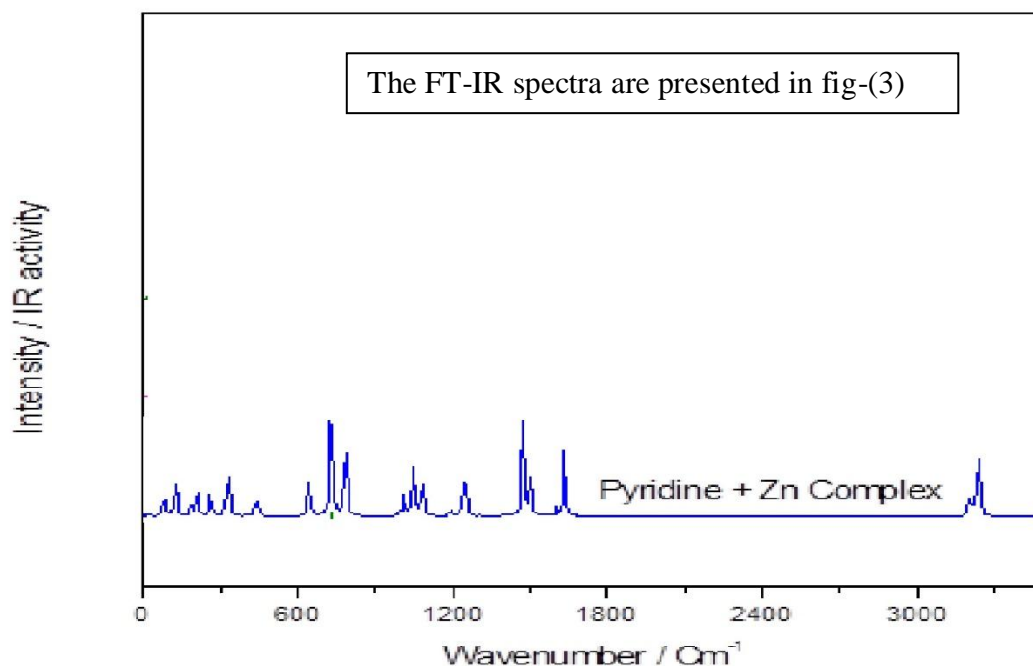
The dipole moments for Py+Zn are also calculated and presented in table -2

S.N.	Atoms	Charge Distribution
		PY + Zn
1	C1	-0.202
2	C2	-0.182
3	C3	-0.155
4	C4	-0.183
5	C5	-0.202
6	N6	-0.260
7	H7	0.245
8	H8	0.292
9	H9	0.242
10	H10	0.242
11	H11	0.291
12	C12	-0.202
13	C13	-0.182
14	C14	-0.155
15	C15	-0.183
16	C16	-0.202
17	N17	-0.260
18	H18	0.245
19	H19	0.292
20	H20	0.242
21	H21	0.242
22	H22	0.291
23	C123	-0.485
24	C124	-0.485
25	Ni25	0.714

Pyridine has C_2 symmetry. The complexes have c_1 symmetry. In vibrational spectra give fine changes at molecular levels because the vibrational spectra results from the molecular vibrations. In order to observed the fine changes, we have calculated the vibrational Raman and IR spectra pyridine with transition metal Zn Complex.

The Raman spectra of the Zn complex are presented in fig- (2)





The vibration of harmonic wave number along with infrared and Raman activity depolar P and depolar U factors are tabulated in table (-3)

S.N.	PY + Zn		
	Atom1	Atom2	Bond Length
1	C1	C2	1.4036
2	C1	N6	1.3616
3	C1	H8	1.0856
4	C2	C3	1.4077
5	C2	H9	1.0852
6	C3	C4	1.4077
7	C3	H7	1.0868
8	C4	C5	1.4035
9	C4	H10	1.0852
10	C5	N6	1.3616
11	C5	H11	1.0857
12	N6	Zn25	2.1359
13	C12	C13	1.4035
14	C12	N17	1.3616
15	C12	H19	1.0857
16	C13	C14	1.4078
17	C13	H20	1.0852
18	C14	C15	1.4077
19	C14	H18	1.0866
20	C15	C16	1.4034
21	C15	H21	1.0852
22	C16	N17	1.3616
23	C16	H22	1.0856
24	N17	Zn25	2.1361
25	Cl23	Zn25	2.3271
26	Cl24	Zn25	2.3281

Binding energies and structures also are presented and analyzed here in. The metal ligand binding modes of the theoretically calculated as well as experimentally observed spectra of the complexes. Confirmed that the metal (II) atom

coordinated with pyridine through the endocyclic nitrogen atom. This observation was further verified by observing the Raman and IR wave number shifts corresponding the C-H stretching and ring stretching bending vibrations.

Conclusion

Theoretical study of interaction of pyridine with transition metal have been done. The structure of pyridine with transition metal Zn were optimized pyridine has c_2 symmetry and complexes have c_1 symmetry. The metal atoms of Zn(II) coordinated with pyridine through nitrogen atom of the ring. The band belong to the ring and C-H group appearing in the higher wave number region also shifted in the experimental and IR spectra. This study and further similar study will lead to better understanding of the effect of coordination of the metal with the biological system.

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