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Vibration and DFT Comparative Study of Pyridine with Cu, Ni and Zn Metals

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***Abstract*:-Theoretical study of 3d transition metals Ni, Cu and Zn have been done. The comparasion of pyridine with 3d transition metals Ni Cu and Zn were optimized.. vibrational of spectra give fine changes at molecular levels because the vibration spectra results from the molecular vibration. The metal atoms Ni (II), Cu (II) and Zn (II) coordinated with pyridine through nitrogen atom of the ring. Raman and IR bands belongs to the vibrations of coordination. All studies will lead to better understanding of the effect of three different transition metals Ni, Cu and Zn with thebiological systems. Pyridine has C2V symmetry. The complexes have a symmetry.**

Keywords:- Comparative Study of Pyridine ,DFT, Transition metals Cu, Ni and Zn.

I. INTRODUCTION

Gas-phase studies of metal ion-molecule complexes have provided a wealth of valuable information on binding energies, geometries, and the microscopic behaviour of chemical and physical processes. Such information is critical to the understanding of heterogeneous catalysis, organ metallic reactions in condensed phase, and electron transfer involved in biological systems [1-4]. 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 [5-9]

Pyridine (C_5H_5N) is an aromatic molecule consisting of a π-electron ring and a nitrogen atom. Pyridines (C5H5N) 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. The only published results have been the formation of Ag+-$(pyridine)_n$ with $n = 1,2,3$, or 4 through gas-phase clustering reactions by Castle man [10] The binding energies of the third and fourth pyridines attached to Ag+ were deduced from the van't Hoff plot. However, the detailed interaction, geometry, and binding energy of bare Ag+ interacting with one pyridine molecule remain unknown. Mulliken noted that pyridine can be treated as a π-type complex or as a π-donor-type ligand because of the lone-pair electrons on its nitrogen atom.[11] 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 (2.19 D), [12] 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 ions 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 bound to Co atoms[9].

Recently, the charge transfer process of Ag+-pyridine have been observed experimentally [13] 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 [14].

Attractiveness of copper ions in these compounds results mainly from the magnetic properties of Cu_2^+ ion, mixed-valance oxidation-state pairs Cu_2^+/Cu^+ , photoluminescence, structural features and biological relevance involving the binuclear site in cytochrome oxidases and related model compounds [8]. Having one different donor atoms pyridine ions can coordinate to metals through the nitrogen, giving rise to linkage isomers, dimers or polynuclear species with different dimensionality and nuclearity. According to the HSAB (hard soft acid base) theory, SCN– ion coordinates to hard acids (Mn2+, Co2+ and Ni2+) through nitrogen atom, and the uncoordinated sulfur atom is involved in hydrogen bonds and sometimes involved in S. . .S interactions. If the transition metal center is soft acid (Cd2+, Cu+ and Hg2+) SCN– ligand binds to central ion through sulfur 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 [9-11]. A search in the CSD (The Cambridge Structural Database, Version 5.33) reveals 270 mononuclear copper(II) complexes containing N-coordinated thiocyanate groups and only 10 compounds with SCN– bound to Cu centre via the S end [12].

Another interesting feature of Cu(II) complexes is the coordination geometry around the metal ion. Cu (II) ions can be four- six- and five-coordinate. The last ones usually display intermediate stereochemical environment ranging between trigonal and bipyramidal.

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In the present work we have synthesized metal-ligand complexes of pyridine with three major d-block metals, viz. Ni, Cu and Zn 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 calculations **[3]** and experimental FT-IR and Raman spectra.

II. THEORETICAL

The optimized geometries of pure pyridine as well as of the complexes of pyridine with three different (3d) metals and the harmonic wavenumbers, Raman and IR intensities of different normal modes of pyridine and of all the complexes were calculated using the Gaussian 03 program package [15]. Theoretical DFT calculations were done using the hybrid functional that mixes the Lee, Yang and Parr functional for the correlation part and the Becke's three-parameter functional for the exchange part (B3LYP) [11,12]; employing the 6-31+G(d,p) and LANL2DZ basis sets and the geometries of the pure form of pyridine as well as of the pyridine-metal complexes were optimized. The vibrational wavenumbers of the pyridine were calculated at B3LYP/6-31+G(d,p) theoretical level. For optimizing the geometrical structures of the metal complexes of pyridine $M(py)_2Cl_2$ (where M = , Ni(II), Cu(II) and Zn(II)), we have used the B3LYP functional with LANL2DZ split-valence basis set.

III. EXPERIMENTAL

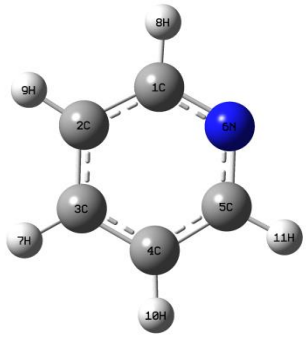
The pyridine liquid was purchased from Merck (Darmstadt, Germany) and directly used without further purification. FT-IR and laser Raman spectra for pure pyridine and three transition metals were obtained. The FT-IR spectrometer used was the PerkinElmer Spectrum 65 FT-IR spectrometer. The FT-IR spectra were recorded in the range 400-4000 cm^{-1} with the samples kept in the form of KBr pellets.

The laser Raman set-up consists of a 514.5 nm Ar^+ 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 ~1 cm^{-1}. 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 a dedicated computer using Gram Wire software. The Origin 6.1 software was used for further analysis of band shape.

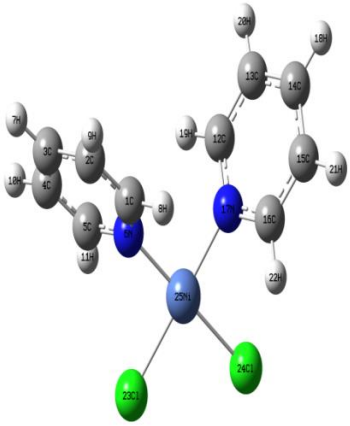
IV. RESULTS AND DISCUSSION

In the present work the theoretical study of interaction of Pyridine with transition metal have been done. The structure of Pyridine with Zn Cu, Ni, and pure Pyridine were optimized. The optimization were done using density functional theory (DFT) at B3LYP functional, employing the LANL2DZ and 6-31+G(d,p) basis sets.The optimized structures are given in Figure 1.

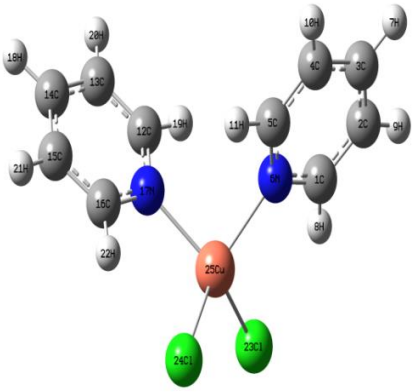
Figure 1 : Optimized structures of (a) Pyridine(Py) (b) Py+Ni (c) Py+Cu (d) PY+Zn .



(a)



(b)



(c)

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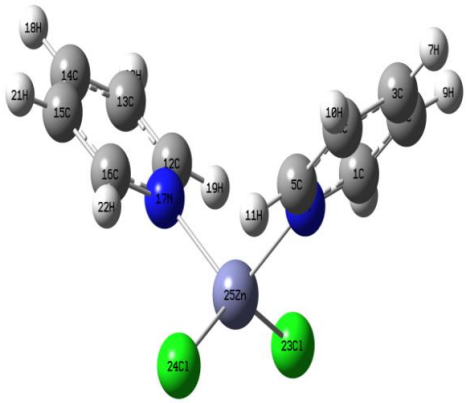

(d)

The binding energy for Py+Zn, Py+Cu, Py+Ni, and Py pure are given in table 1.

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

Complex/molecule	Dipole moment (Debye)
Pyridine	02.38
Py + Ni	14.09
Py + Cu	13.20
Py + Zn	10.55

The Dipole Moments for Py+Zn, Py+Cu, Py+Ni, and Py pure are are also calculated and presented in table 2.

Table: 2 Theoretical calculated Charge Distribution of Pyridine and the Complex with Ni, Cu and Zn.

S.N.	Atoms	Charge Distribution			
		PY Pure	PY + Ni	PY + Cu	PY + Zn
1	C1	-0.260	-0.105	-0.150	-0.202
2	C2	0.180	-0.203	-0.191	-0.182
3	C3	-0.323	-0.163	-0.158	-0.155
4	C4	0.180	-0.201	-0.204	-0.183
5	C5	-0.260	-0.129	-0.117	-0.202
6	N6	-174	-0.220	-0.248	-0.260
7	H7	0.136	0.246	0.246	0.245
8	H8	0.129	0.253	0.296	0.292
9	H9	0.132	0.240	0.244	0.242
10	H10	0.132	0.244	0.240	0.242
11	H11	0.129	0.296	0.258	0.291
12	C12		-0.106	-0.117	-0.202
13	C13		-0.203	-0.204	-0.182
14	C14		-0.163	-0.158	-0.155
15	C15		-0.201	-0.191	-0.183
16	C16		-0.129	-0.150	-0.202
17	N17		-0.221	-0.248	-0.260
18	H18		0.246	0.246	0.245
19	H19		0.253	0.258	0.292
20	H20		0.240	0.240	0.242
21	H21		0.244	0.244	0.242
22	H22		0.296	0.296	0.291
23	Cl23		-0.298	-0.335	-0.485
24	Cl24		-0.298	-0.335	-0.485
25	Ni25		0.081	0.235	0.714

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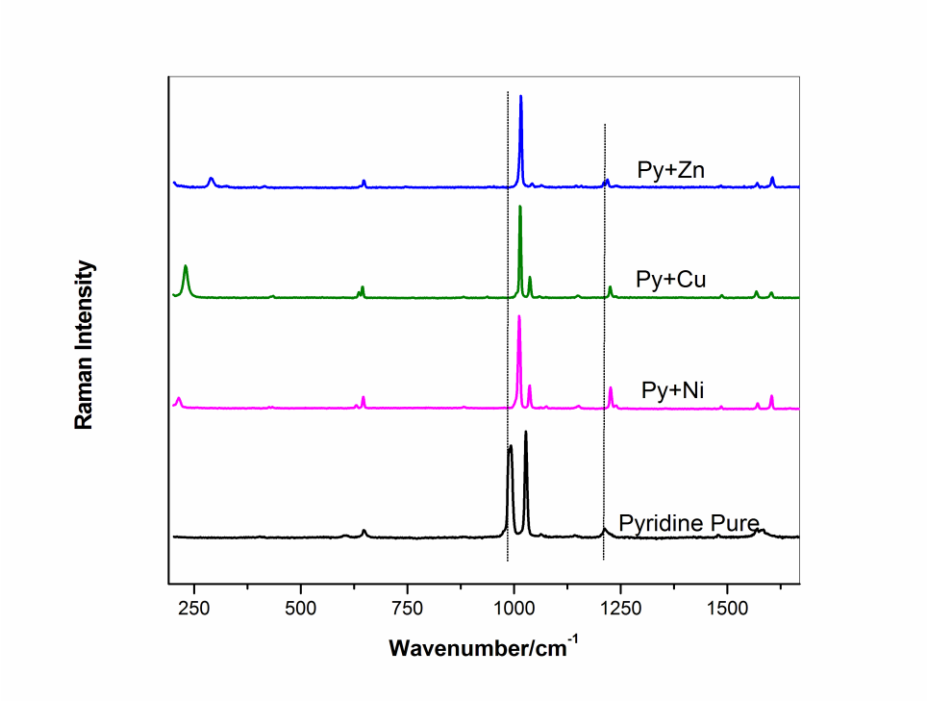
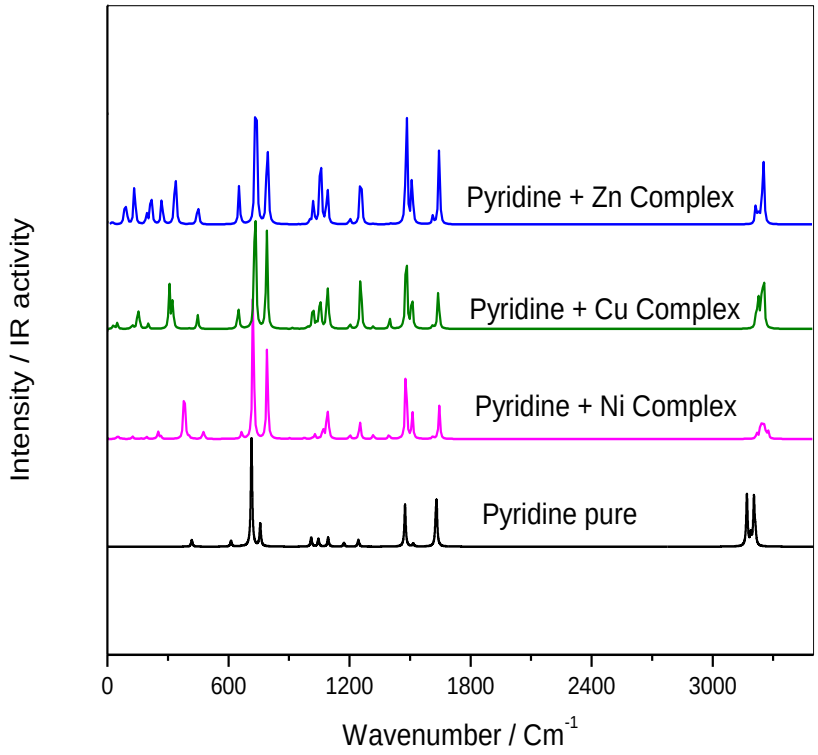
Pyridine has C_{2v} symmetry. All the complexes have C_1 symmetry. In vibrational spectra give fine changes at molecular levels because the vibrational spectra results from the molecular vibrations. In order to observe the fine charges, we have calculated the vibrational Raman and IR spectra of pure Pyridine and all the complexes of Pyridine. The Raman spectra of all the complexes and they are presented in Figure 2.

Figure 2: Raman Spectra for Pyridine with different transition metal complexes



The FT-IR spectra are presented in Figure 3.

Figure 3: FTIR Spectra for Pyridine with different transition metal complexes



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The vibration of harmonic wavenumbers along with Infrared and Raman activity depolar P and dpolar U factors are tabulated in Table 3.

Table: 3 Theoretical calculated Bond Length of Pyridine and the Complex with Ni, Cu and Zn.

	Pyridine(PY)			PY + Ni			PY + Cu			PY + Zn		
	Atom1	Atom2	Bond Length	Atom1	Atom2	Bond Length	Atom1	Atom2	Bond Length	Atom1	Atom2	Bond Length
1	C1	C2	1.3976	C1	C2	1.4022	C1	C2	1.4049	C1	C2	1.4036
2	C1	N6	1.3405	C1	N6	1.3605	C1	N6	1.3607	C1	N6	1.3616
3	C1	H8	1.0881	C1	H8	1.084	C1	H8	1.0852	C1	H8	1.0856
4	C2	C3	1.3958	C2	C3	1.4071	C2	C3	1.4067	C2	C3	1.4077
5	C2	H9	1.0856	C2	H9	1.0852	C2	H9	1.0852	C2	H9	1.0852
6	C3	C4	1.3957	C3	C4	1.4071	C3	C4	1.4085	C3	C4	1.4077
7	C3	H7	1.0863	C3	H7	1.0865	C3	H7	1.0866	C3	H7	1.0868
8	C4	C5	1.3976	C4	C5	1.4026	C4	C5	1.4022	C4	C5	1.4035
9	C4	H10	1.0856	C4	H10	1.085	C4	H10	1.0853	C4	H10	1.0852
10	C5	N6	1.3405	C5	N6	1.3622	C5	N6	1.3617	C5	N6	1.3616
11	C5	H11	1.0882	C5	H11	1.0824	C5	H11	1.0853	C5	H11	1.0857
12				N6	Ni25	1.9563	N6	Cu25	2.0889	N6	Zn25	2.1359
13				C12	C13	1.4021	C12	C13	1.4022	C12	C13	1.4035
14				C12	N17	1.3606	C12	N17	1.3616	C12	N17	1.3616
15				C12	H19	1.0839	C12	H19	1.0854	C12	H19	1.0857
16				C13	C14	1.4072	C13	C14	1.4085	C13	C14	1.4078
17				C13	H20	1.0851	C13	H20	1.0852	C13	H20	1.0852
18				C14	C15	1.407	C14	C15	1.4068	C14	C15	1.4077
19				C14	H18	1.0865	C14	H18	1.0866	C14	H18	1.0866
20				C15	C16	1.4028	C15	C16	1.4049	C15	C16	1.4034
21				C15	H21	1.085	C15	H21	1.0851	C15	H21	1.0852
22				C16	N17	1.3624	C16	N17	1.3607	C16	N17	1.3616
23				C16	H22	1.0824	C16	H22	1.0853	C16	H22	1.0856
24				N17	Ni25	1.9557	N17	Cu25	2.0891	N17	Zn25	2.1361
25				Cl23	Ni25	2.2346	Cl23	Cu25	2.2927	Cl23	Zn25	2.3271
26				Cl24	Ni25	2.2324	Cl24	Cu25	2.2928	Cl24	Zn25	2.3281

Binding energies and structures also are presented and analyzed herein.

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 wavenumber shifts corresponding to C-H stretching and ring stretching, bending and out of plane bending vibrations.

CONCLUSION

Theoretical study of interaction of Pyridine with transition metal have been done. The structure of Pyridine with Zn Cu, Ni, and pure Pyridine were optimized. Pyridine has C_{2v} symmetry. All the complexes have C_1 symmetry. In vibrational spectra give fine changes at molecular levels because the vibrational spectra results from the molecular vibrations. Binding energies and structures also are presented and analyzed herein. The metal atoms of Ni(II), Cu(II) and Zn(II) coordinated with pyridine through nitrogen atom of the ring. On coordination Raman and IR bands 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 wavenumber region also shifted in the experimental Raman and IR spectra. This study and further similar study will lead to better understanding of the effect of coordination of metals with the biological systems.

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