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Cadmium(II) organometallic complex with 4-chloro-N ((pyridine – 2 yl) methylene) benzene amine: synthesis, spectroscopy and antibacterial evaluation

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In the present paper, first the ligand Schiff base was synthesized by condensing the amine with an aldehyde. Then, it was identified by ^{13}C NMR, ^{1}H NMR and IR spectrometry. Next step was coordinating it with transition metal cadmium (II) chloride. Since the produced complex was of ML type, the weighed metal should be equal to 0.001 mol. This yielded 1 to 1 molar ratio. Then, ^{13}C NMR, ^{1}H NMR and IR spectrometry was used to prove its formation. Studies on antibacterial features were performed and the obtained results showed that the metal complexes are more active than the free ligands.

Keywords: Cadmium (II) complexes, Schiff base, Antibacterial activity, Metal complexes

INTRODUCTION

Metal Schiff base molecules provide potential sites for biochemically active compounds relevant to intermolecular hydrogen bonding and proton transfer equilibria [1]. Metal complexes of Schiff base ligands can afford several applications in biological, analytical, clinical and industrial fields [2]. Considering the biological activity and highly qualified physicochemical, stereochemical, electrochemical, structural and catalytic properties of Schiff base metal complexes, their values have been considered to be highly important and this is related to their application as facilities to analyze pharmacological constituents [3]. Necessary biological reactions in life processes mostly involve transition metals; these metals usually coordinate with O- or N- terminals from protein in several modes and play a dominant role in the conformation and function of biological macromolecules [4].

Regarding the metal coordination complexes, much has been studied so far. Specially, their antimicrobial and anticancer properties have been the focus of attention through studies [5].

Recently, metal-based antioxidants have been studied to a great deal due to their capacity to protect organisms and cells from damage caused by oxidative stress or scavenging free radicals [6].

These metal complex derivatives indicating noticeable biological activity, may pave the way for a novel trend in designing new antibacterial drugs. It is of great significance to note that there have been extensive studies on the preparation of many symmetrical tetradentate bis-diamines with O-hydroxyl aldehydes/ketones [7,8].

In the present study the synthesis, characterization and antibacterial activity of complex Schiff base with transition metals, particularly with cadmium, are worked out.

EXPERIMENTAL

Ligand synthesis

To synthesis 4-chloro-N ((pyridine-2-yl) methylene) benzene amine, 0.001 mol of 4-chloro aniline was solved in 15 cm^3 of ethanol solution and 0.001 mol of pyridine 2-carbaldehyde was solved in 15 cm^3 of ethanol. Then, the two compounds were mixed at room temperature for 30 min and let to react for 30 min.

The desired ligand was formed with 88 % efficiency.

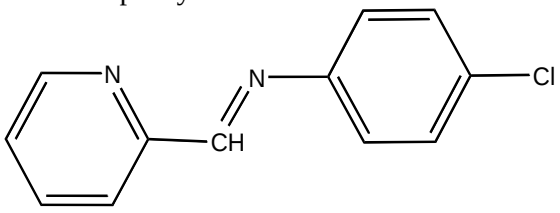

Fig. 1. Ligand structure.

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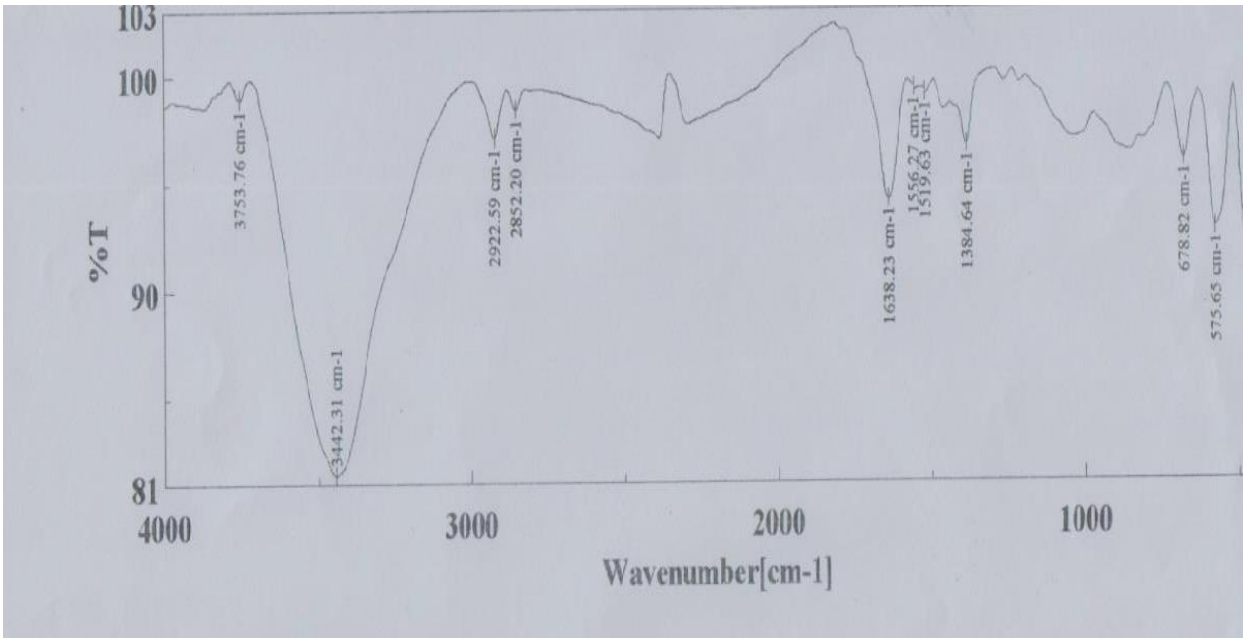

Fig. 2. IR spectrum of ligand

1- According to the graph, the strong band seen in the area of 3442 cm^{-1} is that of aromatic C-H stretching frequency.

2- The average band seen in the area of 1638 cm^{-1} is that of C=N bond. This proves the formation of the aimed product.

3- Average band between 1384 and 1533 cm^{-1} is relevant to benzene C=C bond.

4. Weak band between 870 and 1039 cm^{-1} is that of aromatic C-H bending vibration.

There are some identified signals related to various carbons. Methylene chlorides are seen at 21 ppm. Aimin carbon is seen in 148/59 ppm and aromatic carbons are seen in the range between 122 ppm and 130 ppm.

Proton aimin 7.98 ppm and aromatic protons are observed between 7.31 ppm and 7.36 ppm as multiple groups. In ligand's ^{1}H NMR spectrum appears a clear sign at 2.11 ppm representing methylene protons

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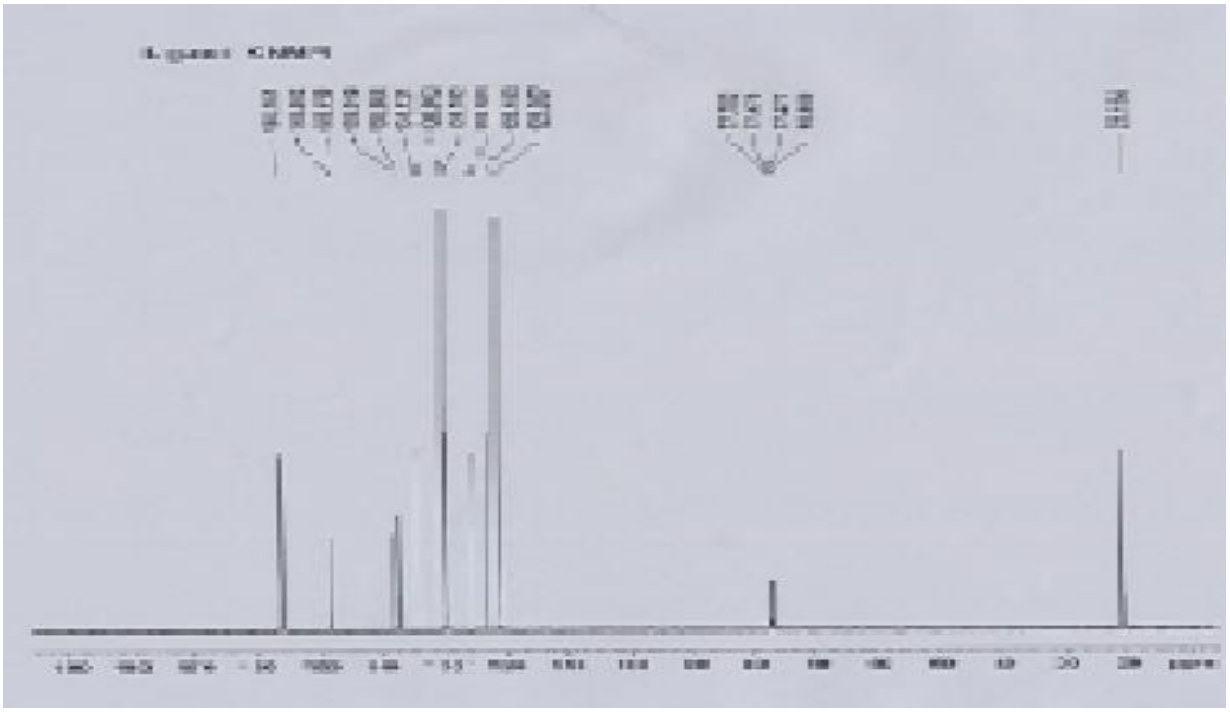

Fig. 3. ^{13}C NMR spectrum of ligand

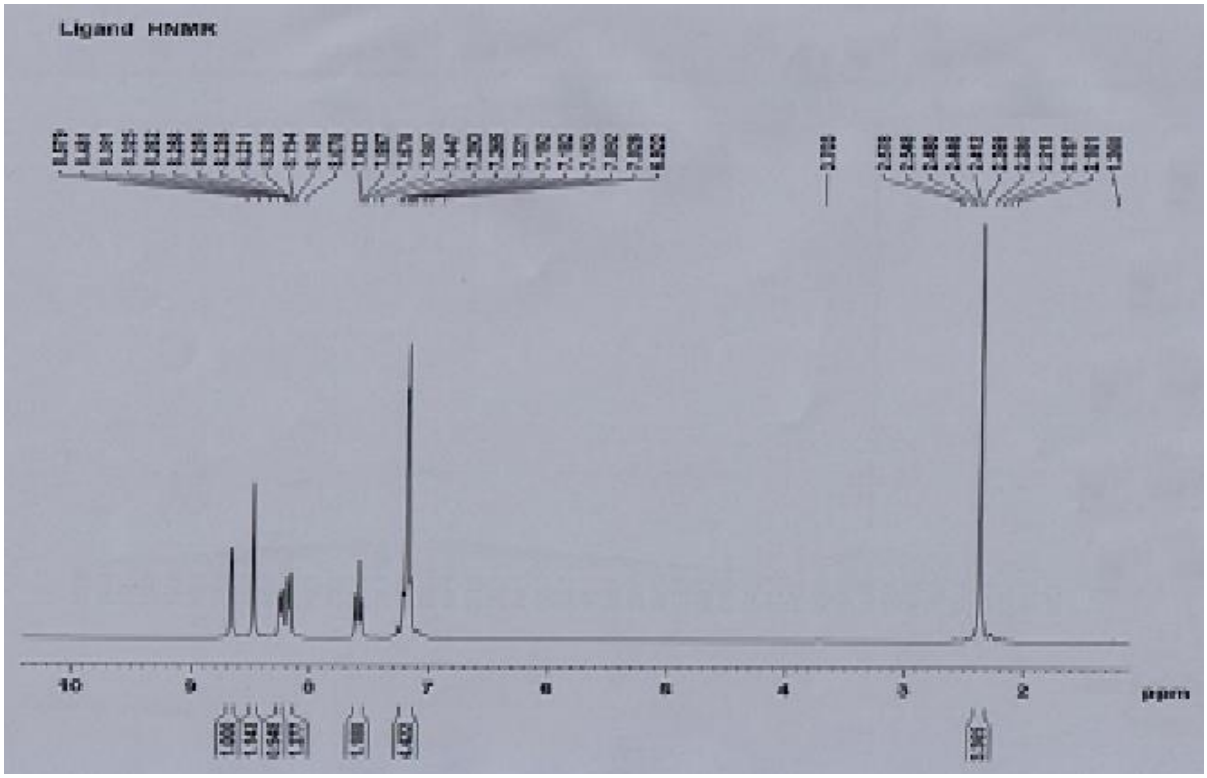

Fig. 4. ^{1}H NMR spectrum of ligand

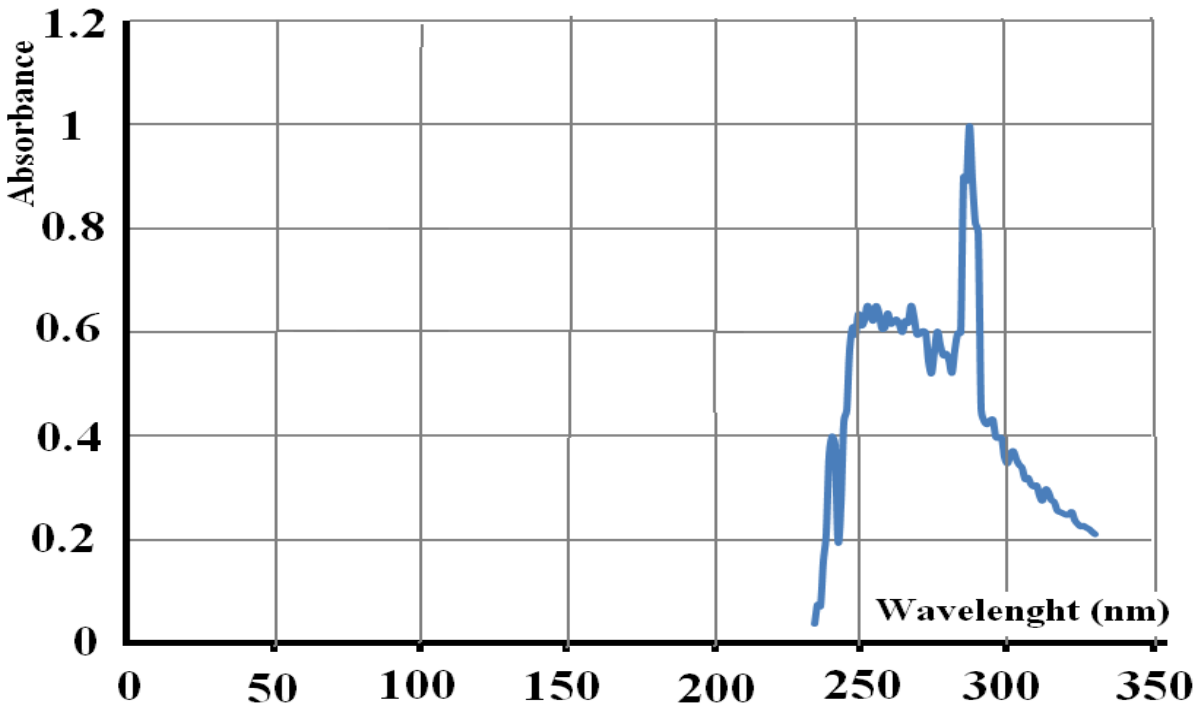

Fig. 5. UV spectrum of ligand

Two graphs are specified in the above spectrum showing electron transport: the one - transport of π to π* and the other - transport of n to π*. The first transport is of higher energy and accordingly of shorter wavelength.

Synthesis of 4-chloro-n ((pyridine-2 yl) methylene) benzene amine cadmium (ii) chloride complex

To synthesize 4-chloro-N ((pyridine-2 yl) methylene) benzene amine cadmium(II) chloride

complex, 0.001 ml of the above mentioned ligand

Then the solution was placed in a stirrer for 5 min at room temperature. Then, 0.001 ml of cadmium salt (II) was added (the least possible amount to be solvable by ethanol). This was done in 5 min like the addition of ligand. It is of great significance to consider that all stages of ligand and complex synthesis were done in absence of heat. This is because Schiff bases are sensitive to heat and decompose when exposed to heat.

In the next step, the metal was added to the ligand and the desired complex was formed. After

was solved in 10 cm^{-3} of ethanol. solvent evaporation, the produced sediment, brown in color, is separated and washed by ether. The formed complex is brown in color. The synthesis efficiency of this complex is 88 %.

The coordination number of the final product is 4 and it has *cis* isomer.

The color of the complex's points to the presence of cadmium (II) in it. Since cadmium has orbital d^{10}, it is of diamagnetic type.

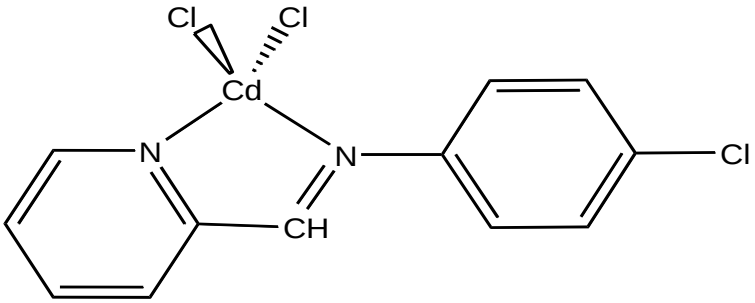

Fig. 6. Structure of the Cd(II) complex.

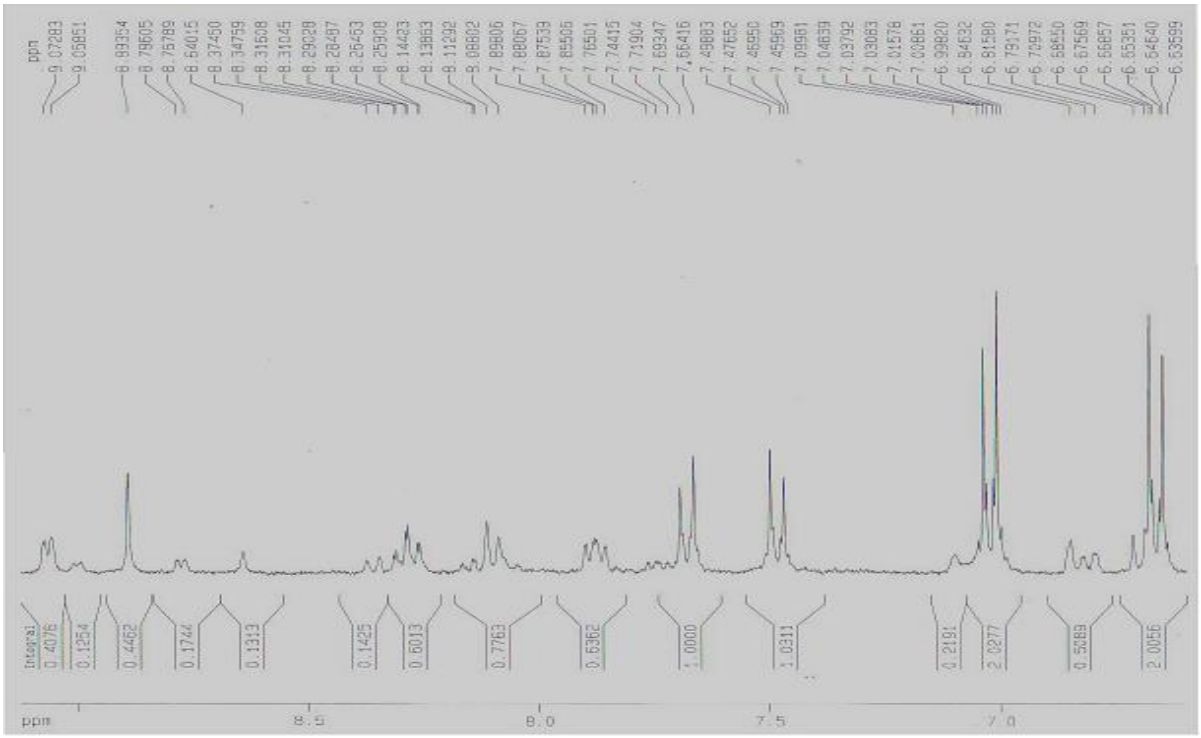

Fig. 7. ^{1}H NMR spectrum of the complex

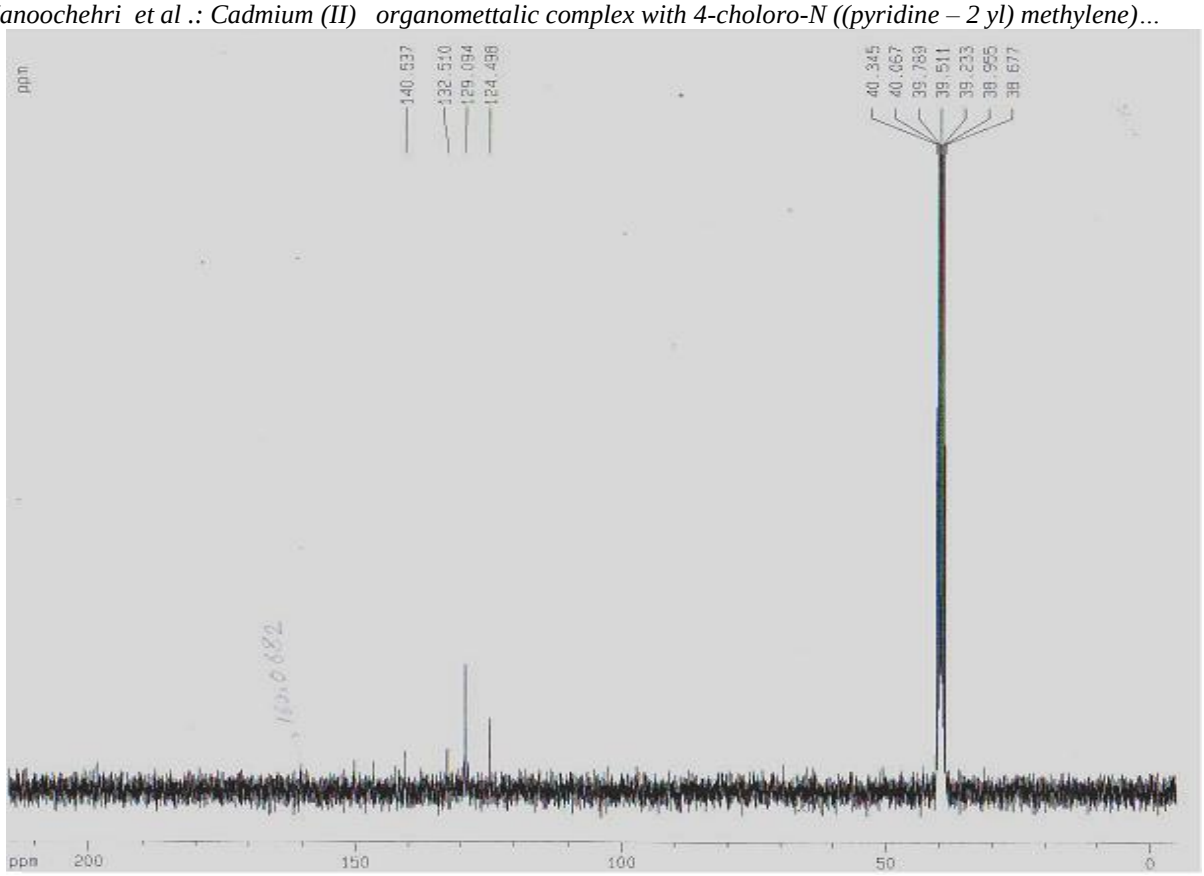

Fig. 8. ^{13}C NMR spectrum of the complex

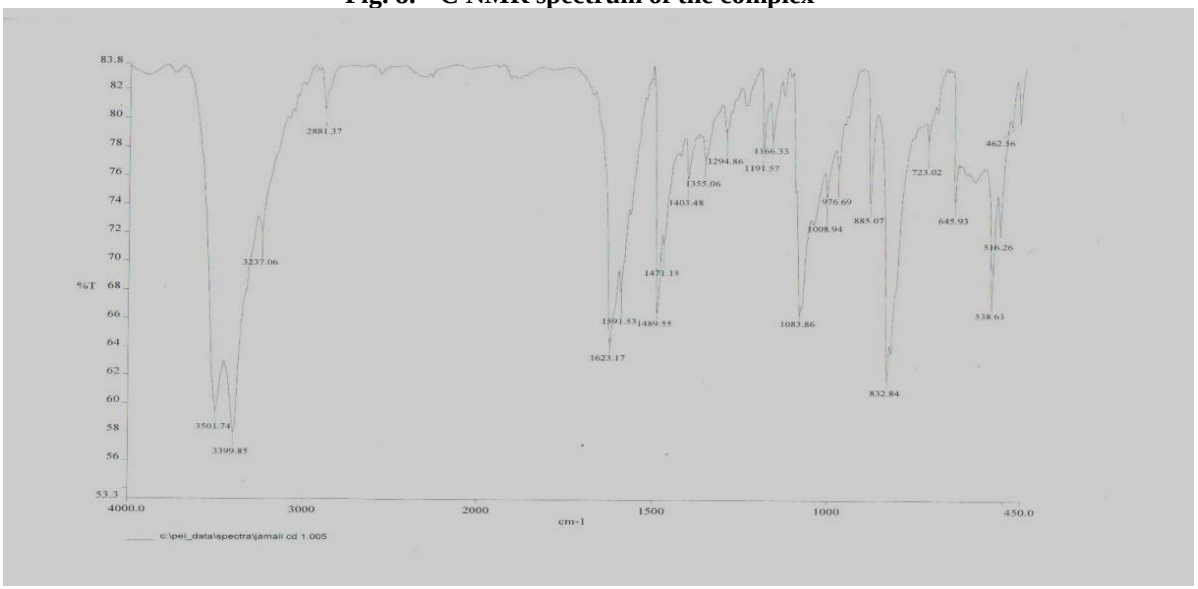

Fig. 9. IR spectrum of the complex.

Aimin proton 7.8 ppm and aromatic protons are also seen between 7.14 ppm and 7.23 ppm. In ligand's HNMR spectrum, an obvious band appears in 2.6 pmm showing methylene protons.

1. The strong band seen at 3438 cm^{-1} is due to C-H stretching frequency.
2. The average band seen at 1631 cm^{-1} is due to C=N bond which proves the formation of aimin.
3. The average bands between 1394- 1591 cm^{-1} are due to C=C benzene.
4. The weak bands between 835 and 1097are of aromatic C-H bending vibration.

Antibacterial activity

The antibacterial activity of 4-chloro-N ((pyridine-2 yl) methylene) benzene amine cadmium (II) chloride complex and 4-chloro-N ((pyridine-2-yl) methylene) benzene amine ligand were achieved by macrodilution broth susceptibility

method. For this experiment *E. coli* no: 25922 from Azad university of Karaj was used.

E. coli is an indicator of water and sewage pollution and is the cause of the most prevalent urinary tract infection. In this method MIC of the complex was determined to be 19×10^2 μg/ml, MBC 33×10^2 μg/ml, MIC for ligand 12×10^3 μg/ml and MBC was 21×10^3 μg/ml.

CONCLUSION

(C-H) 34425 cm^{-1}, (C=N)1637 $cm^{-1}$and (C=C) 1535 $cm^{-1}$are the results of ligand IR spectrum showing the formation of the desired ligand.

(C-H) 2433 $cm^{-1}$and (C=N)1632 cm^{-1} in the IR spectrum of the complex show the formation of the desired complex.

Comparison of the IR spectra shows that due to a decrease in frequency, resulted from the formation of returned π bond, it may be concluded that the complex is formed.

The shifts to lower positions in ^{1}H NMR, UV and ^{13}C NMR are an evience that the complex is formed.

Ligand, due to having two nitrogens in its structure, as a donor, incorporates well the coordinated metal and the complex. As it is clear from complex structure, the produced complex has a coordination number 4 and is a *cis* isomer. It is connected to nitrogen at two heads and to chlorine at the other two heads. The produced complex is diamagnetic due to the lack of electron-electron pairs. The obtained results for Schiff base ligand antibacterial properties are too low, but when it forms a complex, its antibacterial activity increases.

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