COORDINATION CHEMISTRY AND COORDINATION COMPLEX WITH SCHIFF BASE DERIVES FROM DI-PICOLINIC ACID AND IT'S DERIVATIVES

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I hereby forward this review entitled **"COORDINATION CHEMISTRY AND COORDINATION COMPLEX WITH SCHIFF BASE DERIVES FROM DI-PICOLINIC ACID AND IT'S DERIVATIVES**" by **Sudipta Maity** in Partial fulfillment of the requirments for the degree of MASTER OF SCIENCE in chemistry of the Haldia Government College, debhog, haldia-721657.

This review has been completed under my guidance in the Department of Chemistry, Haldia Government College.

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CERTIFICATE OF APPROVAL

The foregoing project is hereby approved as a creditable study of a science subject carry out and presented in a manner satisfactory to warrant its acceptable as a prerequisite for which it has been submitted. It is understood that by this approval the undersign do not necessarily endorse of approve any statement mode , opinion expressed or conclusion drawn therein the thesis only for the purpose for which it is submitted.

Signature of Examiners

ACKNOWLEDGEMENT

A moment comes which but rarely in a student’s life, when with utmost pleasure and satisfaction, I myself, Sudipta Maity, Submit my review on “COORDINATION CHEMISTRY AND COORDINATION COMPLEX WITH SCHIFF BASE DERIVES FROM DI-PICOLINIC ACID AND IT’S DERIVATIVES_”.

I take this opportunity express my gratitude and sincere thanks to my project guide, Dr. SUDIPTA PATHAK whose motivating Personality, constant encouragement and sustained guidance has made this project to come true.

I am also thankful to all my teachers Dr. Dipankar pramanik, Dr. Khokon Samanta, Dr. Saikat Kumar Manna, Dr. Uday Sankar Midya, Dr. Monotosh Mondal & Dr. Barnali Jana for their continuous inspiration.

I am also thankful to my friends for their co-operation during my project period, Finally, I acknowledge all my friends.

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CONTENTS

COORDINATION CHEMISTRY AND COORDINATION COMPLEX WITH SCHIFF BASE DERIVES FROM DI-PICOLINIC ACID AND IT’S DERIVATIVES

INTRODUCTION:

Today coordination chemistry comprises a large body of inorganic chemistry research. It is mainly the chemistry of metal complexes and has fascinated and inspired the chemists all over the world. Coordination Chemistry involves the study of coordination compounds, their structures, properties and application. There is an ever increasing academic, commercial and biochemical interest on the metal complexes of organic chelating ligands. This has resulted in the emergence of associated fields like organometallic chemistry, homogeneous catalysis and bioinorganic chemistry. Among the chelating ligands, Schiff bases have attracted the attention of chemists due to the ease of preparation and complexation.

In 1864, German chemist Hugo Schiff developed a new class of organic compounds. These groups of compounds, imines, are often referred to as Schiff bases in his honour.[1]

Schiff bases contain the azomethine group (–RC=N–) and are usually formed by the condensation of a primary amine with an active carbonyl compound. Intensive research on the physicochemical properties and molecular structure of complexes with Schiff bases has provided interesting new results, which need to be surveyed and compared with earlier literature on these types of compounds.

The Schiff base plays significant role in the area of Co-ordination chemistry they have wide applications in industrial and biological application.[2]

In 1889, Alphonse Combes synthesized the first metal complex of a Schiff base. [3]

In 2014, Sharma M. and co-worker synthesized a new Schiff base compounds of hydrazine derivatives with different substitution group and all these derivatives were characterized by using physical and chemical analytical technique. These derivatives were used as antimalarial activity and there were compared with chloroquine, which is used as an antimalarial medication. These Schiff base derivatives exhibit a good antimalarial activity if it compared with chloroquine.[4]

In 2015, Anjali J. and co-worker prepared different triazole Schiff base ligands and there complexes with Co (II), Ni (II), Ag (I) ions, and characterized using physical and analytical technique,.

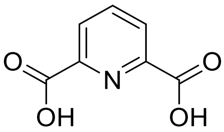
The Schiff base ligand was act as a chelate ligand. The octahedral structure was investigated in Ni (II) and Cu (II) complexes and the square planar structure was detected for the Ag (I) complex.[5]

In 2019, Sheida E. and co-workers studied the molecular properties of five Schiff base ligands with Sn (IV) ion. All these ligands and complexes were investigated by density functional theory . The theoretical calculation was shows the bond angles, bond distances and optimized structures of Sn (IV) complexes. The geometry of the complex was monomer type and it's coordinate with chelating ligand through deprotonated phenolic and imine group. Also, the calculation was included IR frequencies, HOMO, LUMO energy gap, dipole moment, Mulliken charges and Hartree–Fock energies.[6]

LITERATURE REVIEW ON DIPICOLIC ACID :

2,6-pyridine-dicarboxylic acid (Di-picolinic acid) is a versatile, strong, nitrogen-oxygen, multimodal donor ligand, which forms stable complexes with diverse metal ions, sometimes in unusual oxidation states.[7][8]

In 1973, Takusagawa et al. first solved the crystal structure of 2,6-pyridine-dicarboxylic acid (pic-1).[9]

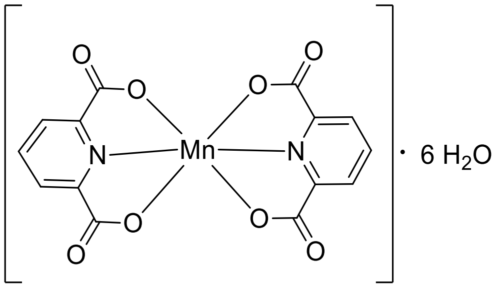


pic-1

d-block and f-block elements shows interesting properties when coordinated with 2,6-pyridine-dicarboxylic acid (di-picolinic acid) and its derivatives as ligands. 2,6-Pyridinedicarboxylic acid (di-picolinic acid) (pic 1), is a widely used building block in coordination and supramolecular chemistry.

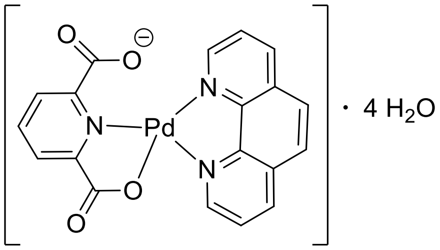
Di-picolinic acid and its derivatives are now being featured as ligands in coordination complexes that have medicinal uses.

A manganese complex, $[Mn(dipic)_2]\cdot 6H_2O$,(Pic-2) was prepared and characterized by element analyses, spectral analysis, thermal analysis and single X-ray diffraction techniques . In In-vitro antibacterial and antifungal activities of the complex were evaluated by the use of the agar well diffusion method by minimal inhibition concentration (MIC). It was concluded that the complex was very effective against Gram-positive bacteria and fungi but ineffective against Gram-negative bacteria.[10]

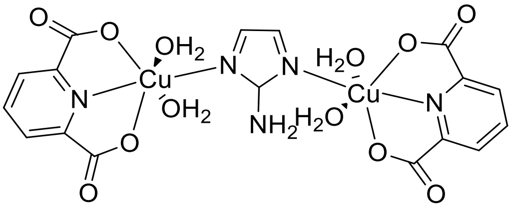


pic-2

The palladium(II) complexes have been highly sought after in the realm of therapeutic anticancer drug development because of the similarities in bioactivities and coordination behavior between palladium(II) and platinum(II) complexes. Although the principle mechanism of its antitumor property is not yet known, it is confirmed that some species of the aromatic heterocycles can stack with nucleobases and then enhance the complex formation with DNA, which is the target in the chemotherapy of tumor. An example of such a heterocyclic complex is [Pd(phen)(Hdipic-)]·4H_2O as reported by Wang and Okabe (2005).[11]



A copper complex, pic-4, was tested for their ability to bind to DNA, and it was seen that there was π-π stacking between the ligands of the complex and the base pairs of DNA (Tabatabaee et al. 2013).[12]



Pic- 4

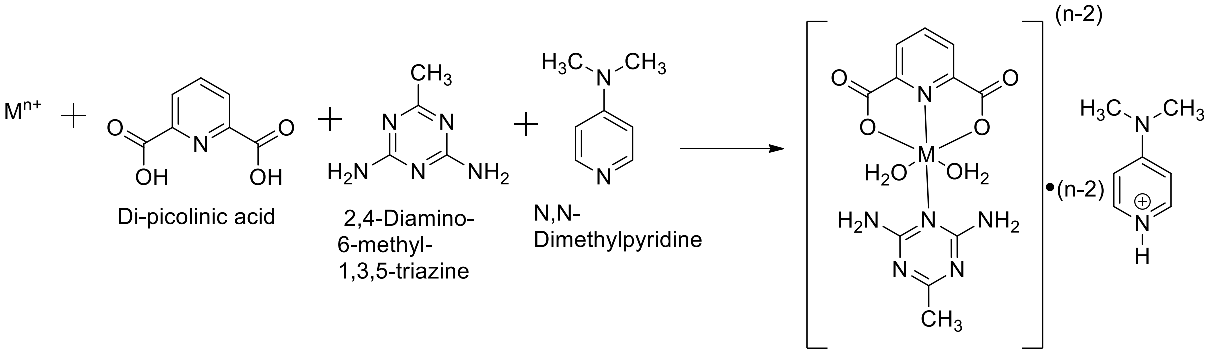
It is seen that the di-picolinic acid complexes show a varied resistance to bacterial growth. It was therefore the general conclusion from these results that showed the overall structure of the tested compounds to be the principal factor influencing the antimicrobial activity.

AIM OF THE RESEARCH WORK :

Our work is formation of complex with di-picolinic acid and 2,4-Diamino-6-methyl-1,3,5-triazine as ligand. And synthesis of 2,6-Pyridinedicarboxylic acid derivatives. Then synthesis of complex with various metal {Fe(II), Mn(II), Co(II), Ni(II) ..etc.} using the Schiff base derived from di-picolinic acid. And investigate the chemosensor and pharmaceutical activity of the new form complex.

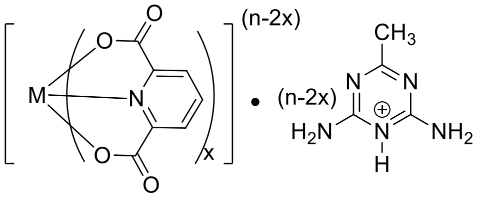
SCHEME OF THE PROBABLE REACTION AND PROBABLE COMPLEXES :

- **SCHEME 1 :**



COMPLEX 1

Or,



COMPLEX 2

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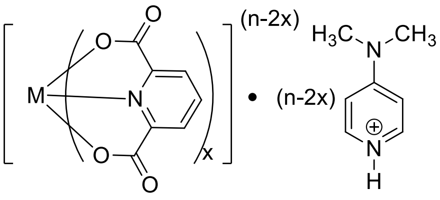
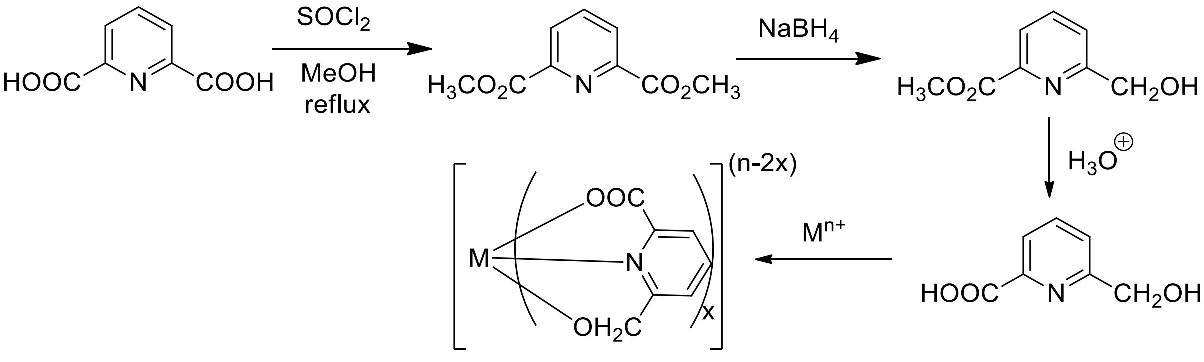


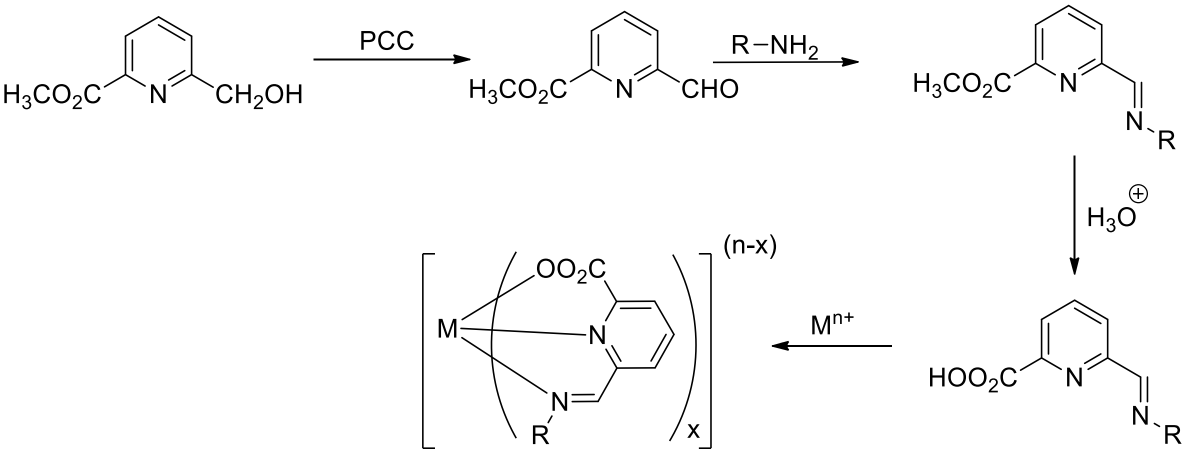
COMPLEX 3

- **SCHEME 2:**



COMPLEX 4

- **SCHEME 3:**



COMPLEX 5

Where , M = Fe, Cr, Mn, Co….etc.

n = 1,2,3……

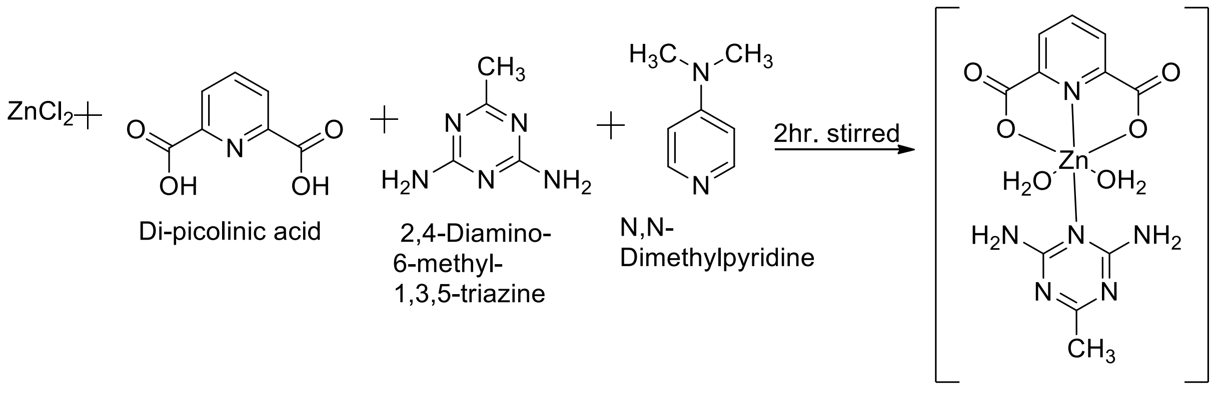
x = 1,2,3……

WORK DONE :

Preparation of Zn(II) complex:

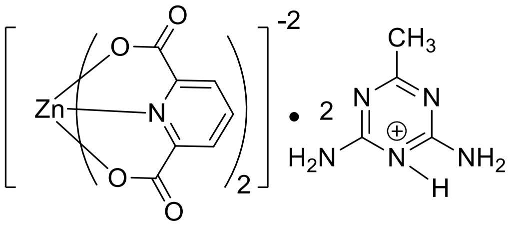
Procedure: At first a 100 ml cleaned beaker was taken and 40 ml of distilled water was added to it. Then 0.139 g (1mmol) of $ZnCl_2$ salt was added to this water and the solution was placed on a magnetic stirrer. After that 0.336 g (2mmol) of 2,6-Pyridinedicarboxylic acid and 0.127 g (1mmol) of 2,4-Diamino-6-methyl-1,3,5-triazine and 0.123 g (1mmol) of N,N-Dimethylpyridine were added to this solution and stirred for 2hours. Then the solution was heated and the solution became transparent. Then the solution cooled at room temperature and then filtered and kept the solution undisturbed. After 14 days a crystal was obtained.

Reaction:



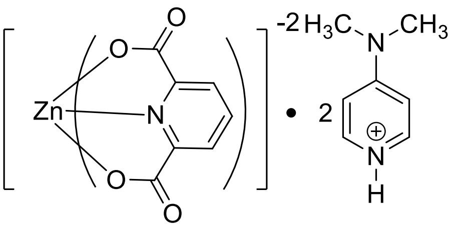
COMPLEX 1.1

Or,



COMPLEX 2.1

Or,



COMPLEX 3.1

SPECTRUM ANALYSIS :

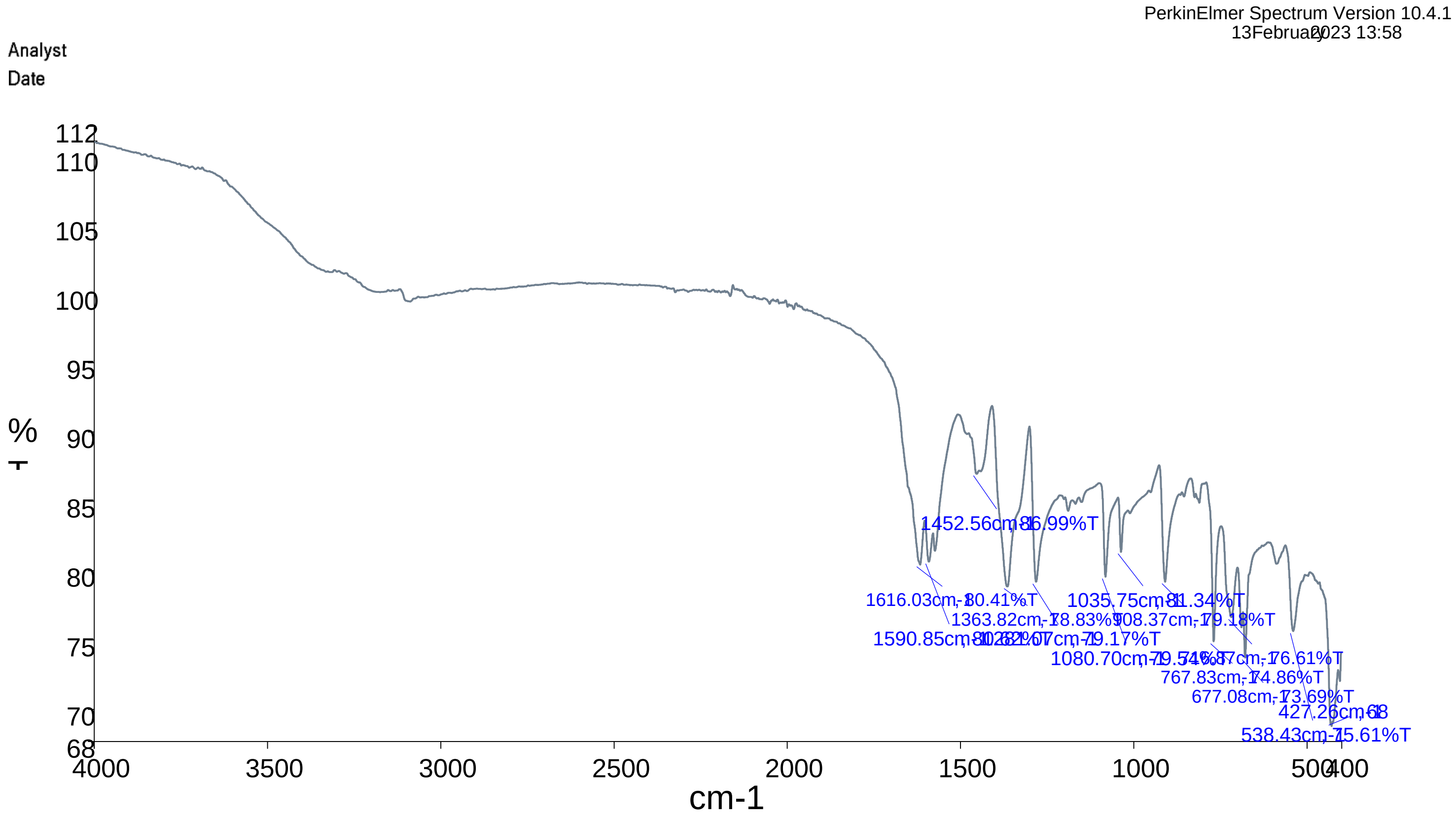
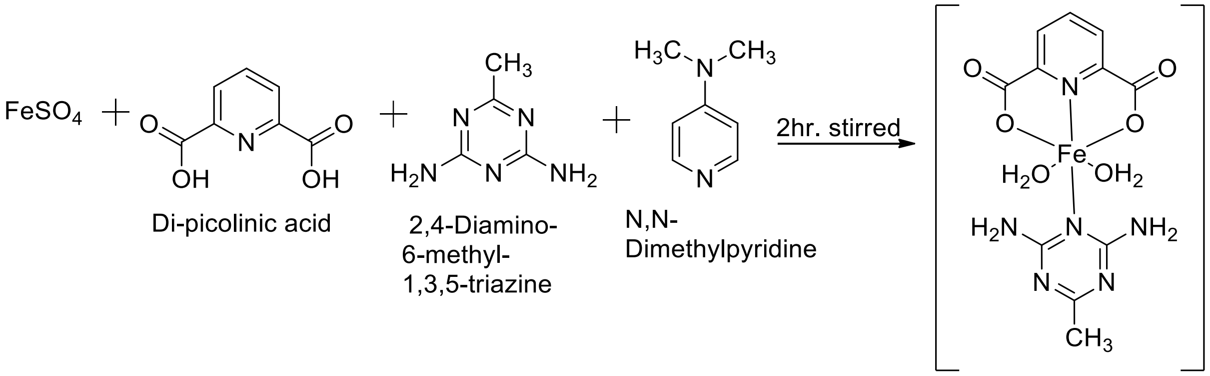


Figure 1: IR spectra for Zn(II) complex : 3090 cm^{-1}(aromatic C-H stretch);1616-1452 cm^{-1}(C=C, C=N pyridine ring stretch).

❖ Preparation of Fe(II) complex:

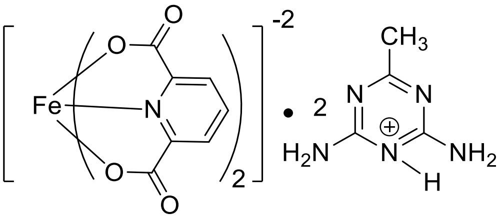
Procedure: At first a 100 ml cleaned beaker was taken and 40 ml of distilled water was added to it. Then 0.155 g (1mmol) $FeSO_4$ salt was added to this water and the solution was placed on a magnetic stirrer. After that 0.337 g (2mmol) of 2,6-Pyridinedicarboxylic acid and 0.128 g (1mmol) of 2,4-Diamino-6-methyl-1,3,5-triazine and 0.123 g (1mmol) of N,N-Dimethylpyridine were added to this solution and stirred for 2hours and the solution became greenish yellow coloured. Then the solution was heated and it's became transparent. Then the solution cooled at room temperature and then filtered and kept the solution undisturbed. After 14 days a crystal was obtained.

Reaction :



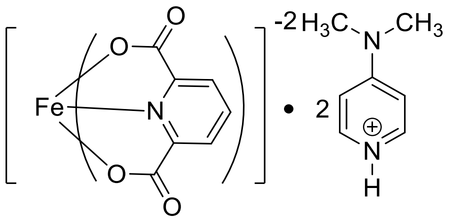
COMPLEX 1.2

Or,



COMPLEX 2.2

Or,



COMPLEX 3.2

Spectrum analysis :

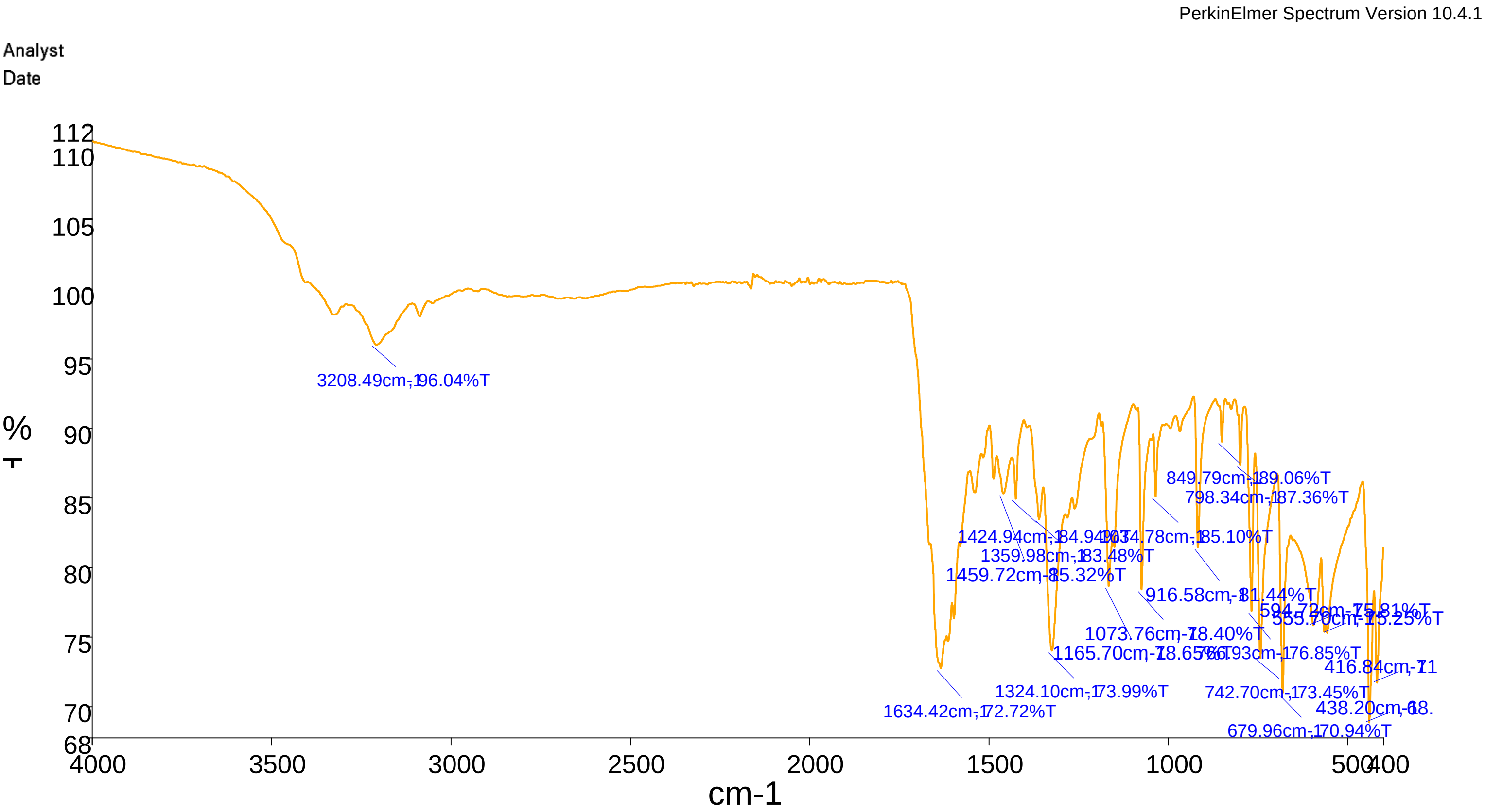
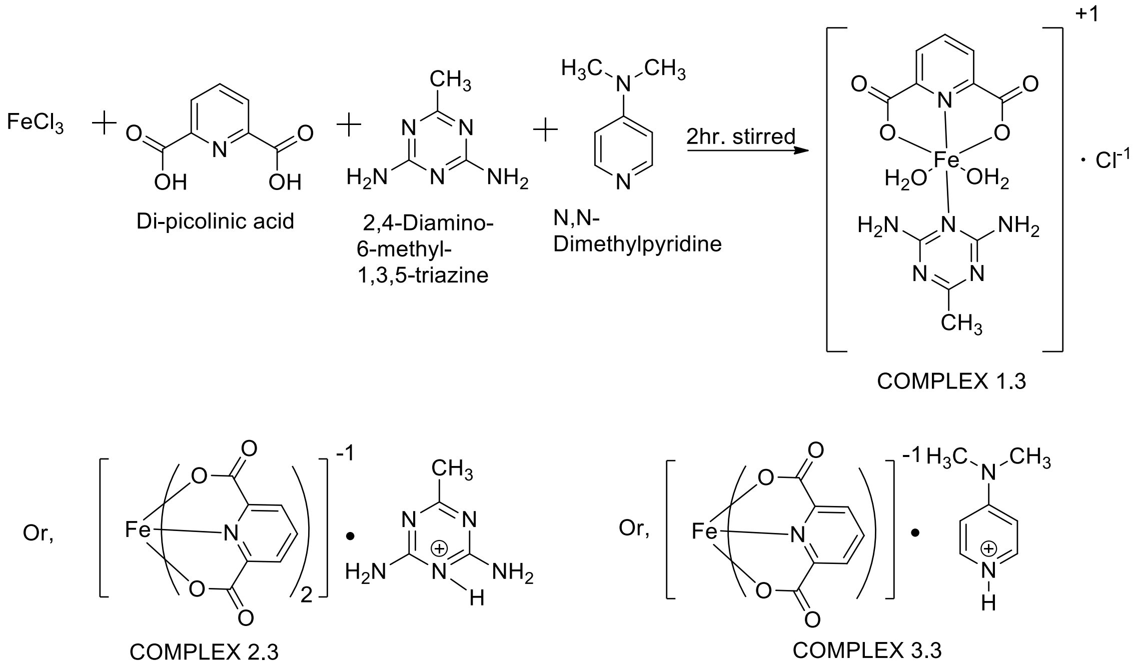


Figure 2: IR spectra for Fe(II) complex : 3208 cm^{-1}(NH$_2$ stretch); 3090 cm^{-1}(aromatic C-H stretch);1634-1424 cm^{-1}(C=C, C=N pyridine ring stretch);

❖ Preparation of Fe(III) complex :

Procedure : At first a 100 ml cleaned beaker was taken and 40 ml of distilled water was added to it. Then 0.275 g (1mmol) of FeCl$_3$ salt was added to this water and the solution was placed on a magnetic stirrer. After that 0.337 g (2mmol) of 2,6-Pyridinedicarboxylic acid and 0.130 g (1mmol) of 2,4-Diamino-6-methyl-1,3,5-triazine and 0.122 g (1mmol) of N,N-Dimethylpyridine was added to this solution. Then the solution was stirred for 2hours and the solution became green coloured. after the solution was heated and it's became transparent . After cooling, the solution was filtered and kept undisturbed. After 14 days a green coloured crystal was obtained.

Reaction:



Spectrum analysis :

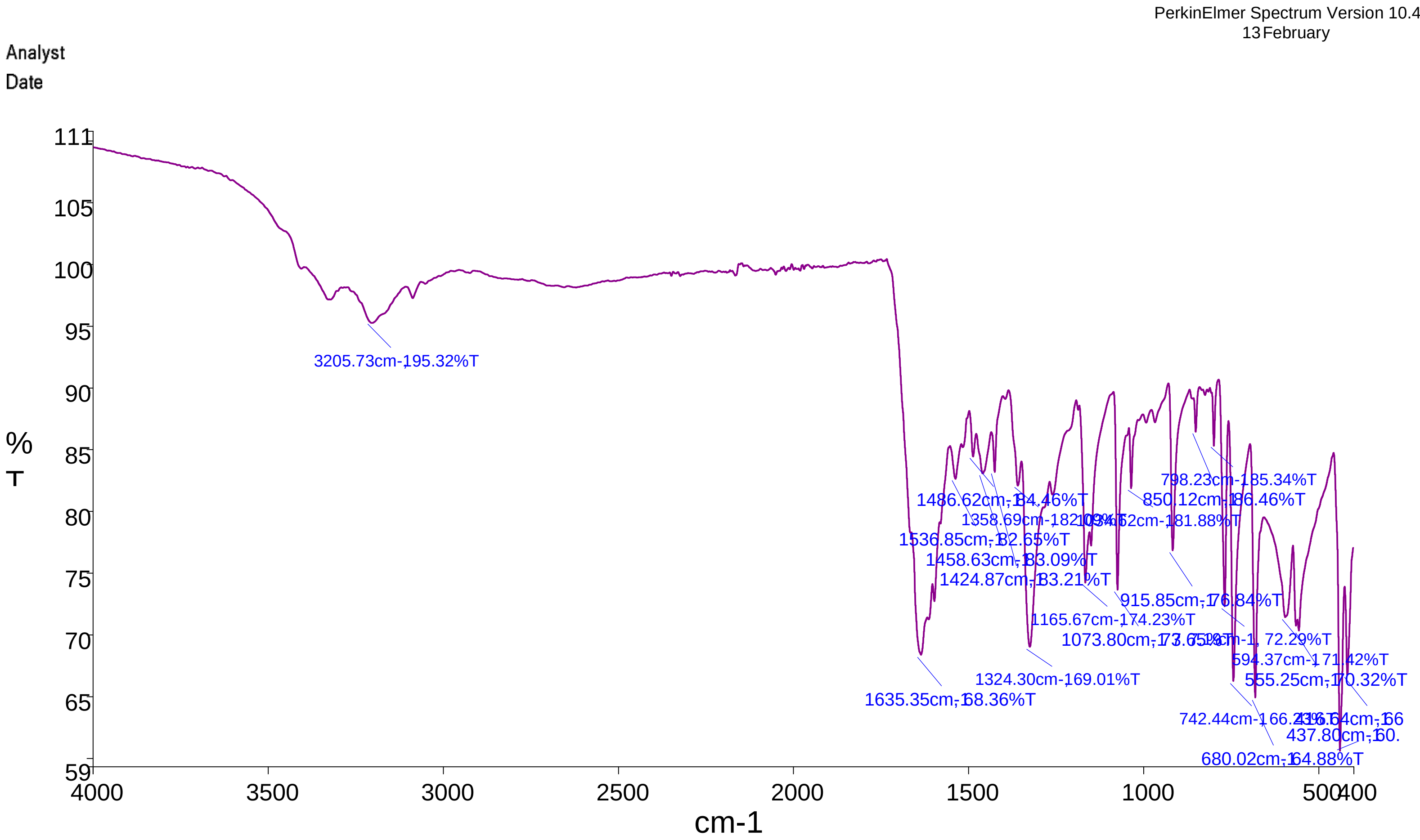
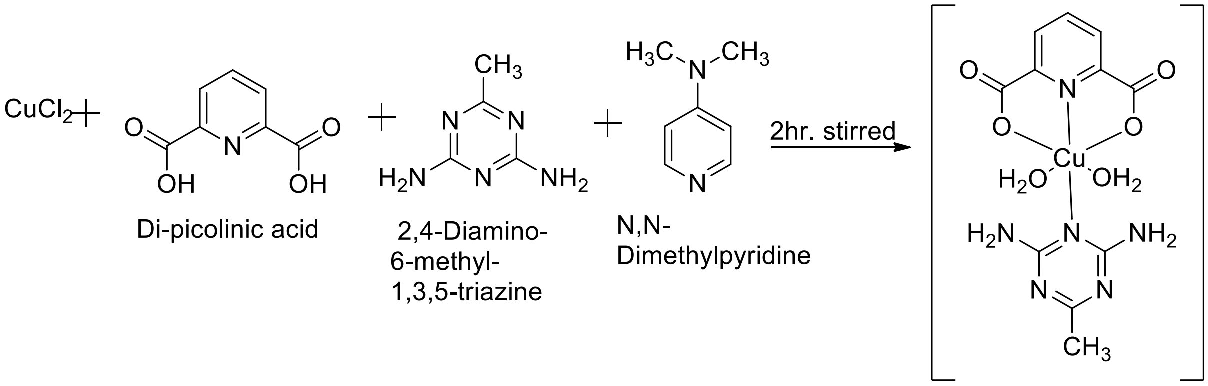


Figure 3: IR spectra for Fe(III) complex : 3205 cm^{-1}(NH$_2$ stretch); 3090 cm^{-1}(aromatic C-H stretch);1635-1424 cm^{-1}(C=C, C=N pyridine ring stretch);

❖ Preparation of Cu(II) complex :

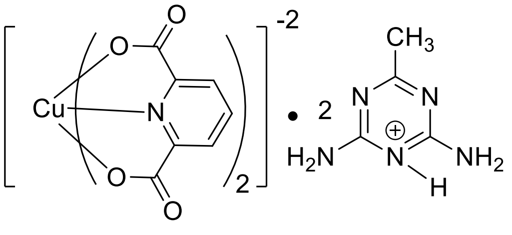
Procedure : At first a 100 ml cleaned beaker was taken and 40 ml of distilled water was added to it. Then 0.176 g (1mmol) of $CuCl_2$ salt was added to this water and the solution was placed on a magnetic stirrer. After that 0.337 g (2mmol) of 2,6-Pyridinedicarboxylic acid and 0.126 g (1mmol) of 2,4-Diamino-6-methyl-1,3,5-triazine and 0.123 g (1mmol) of N,N-Dimethylpyridine were added to this solution. Then the solution was stirred for 2hours and the solution became blue coloured. after the solution was heated and it's became transparent . After cooling, the solution was filtered and kept undisturbed. After 14 days a blue coloured crystal was obtained.

Reaction:



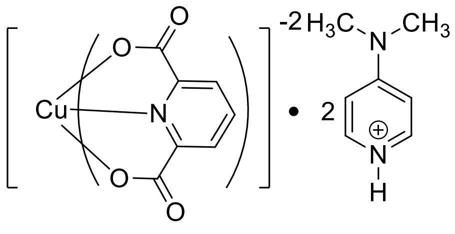
COMPLEX 1.4

Or,



COMPLEX 2.4

Or,



COMPLEX 3.4

Spectrum analysis:

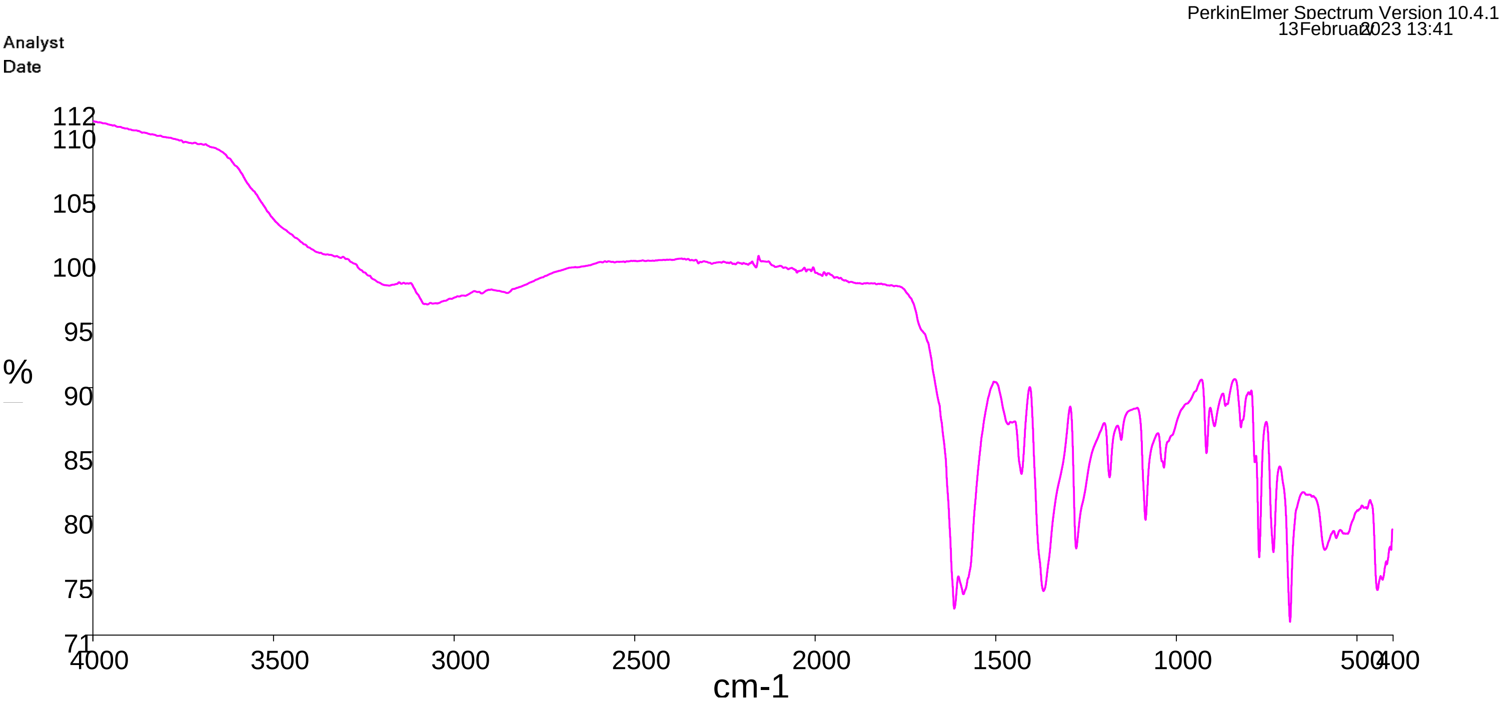
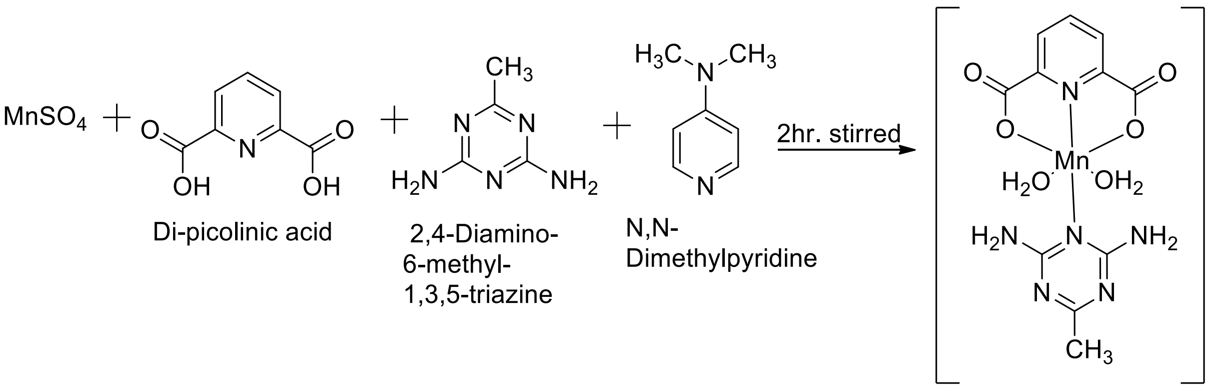


Figure 4: IR spectra for Cu(II) complex : 3090 cm^{-1}(aromatic C-H stretch);1630-1424 cm^{-1}(C=C, C=N pyridine ring stretch);

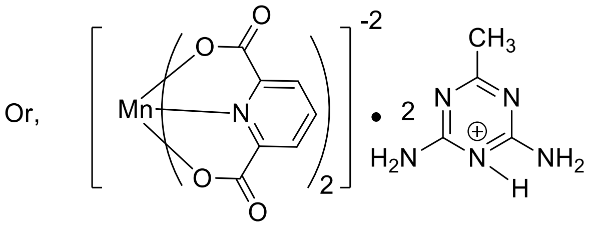
- **Preparation of Mn(II) complex :**

Procedure : At first a 100 ml cleaned beaker was taken and 40 ml of distilled water was added to it. Then 0.170 g (1mmol) of $MnSO_4$ salt was added to this water and the solution was placed on a magnetic stirrer. After that 0.338 g (2mmol) of 2,6-Pyridinedicarboxylic acid and 0.125 g (1mmol) of 2,4-Diamino-6-methyl-1,3,5-triazine and 0.126 g (1mmol) of N,N-Dimethylpyridine were added to this solution. Then the solution was stirred for 2hours and the solution became purple coloured. after the solution was heated and it's became transparent . After cooling, the solution was filtered and kept undisturbed. After 14 days a coloured crystal was obtained.

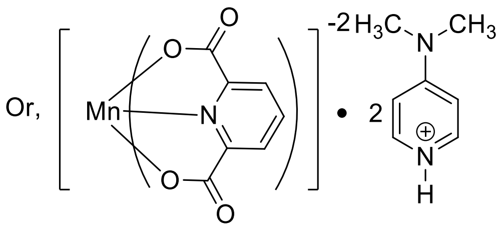
Probable Reaction:



COMPLEX 1.5



COMPLEX 2.5



COMPLEX 3.5

SPECTRUM ANALYSIS :

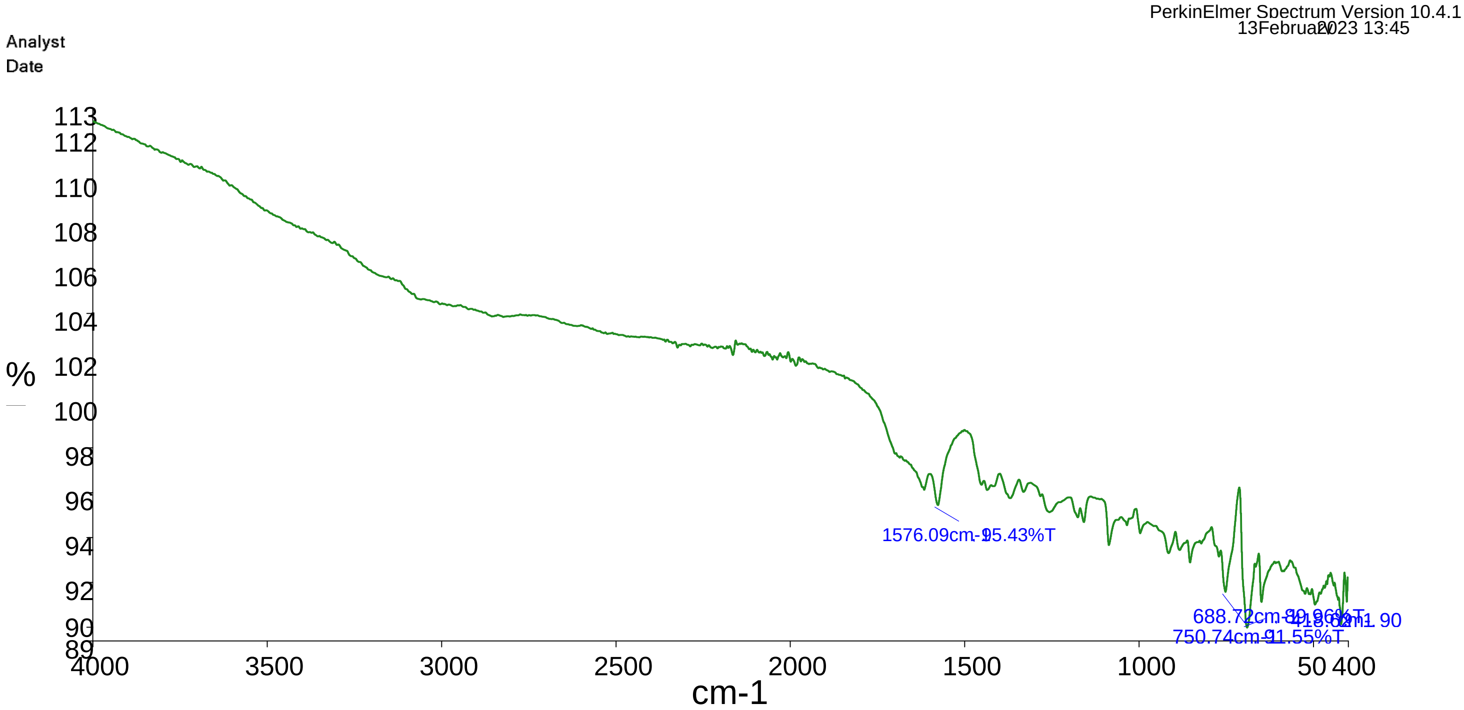


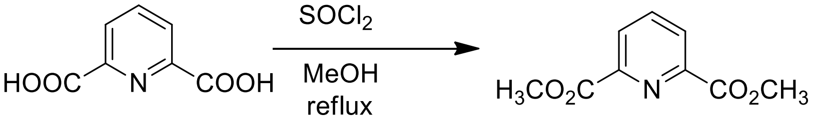
Figure 5: IR spectra for Mn(II) complex: 1630-1424 cm^{-1}(C=C, C=N pyridine ring stretch);

WORK DONE:

❖ Preparation of Di-picolinic acid's derivatives:

Procedure: At first 8 gm of di-picolinic acid was taken in a RB flask and 50 mL methanol was added in it. Then the solution was cooled and placed on magnetic stirrer for stirring. After that 18 mL $SOCl_2$ was added dropwise. Then the solution was refluxed for 1hour and then cooled at room temperature. Next the extra solvent was extracted by vacuum distillation. Then approx. 50 mL ethyl acetate was used to wash the RB flask and the solution was taken in separation funnel. Then saturated aq. $NaHCO_3$ solution was added in the funnel. Then the organic layer solution was collected by passing through Na_2SO_4. After that the collected solution was filtered and dried. Then the solid product was collected.

Reaction:



Experimental yield : 4.36 g

% of Yield : 46.68 %

CONCLUSION:

Our project work synthesis of coordination complex with Schiff base derived from dipiolinic acid and it's derivatives which can be used in pharmaceutical industry. This may be used in bio-inorganic chemistry involving the design of compounds of reduce toxic side-effects and understand their mechanism action.

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