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 **Subrata Das** 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.

Countersigned

Supervisor

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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, **Subtata Das**, 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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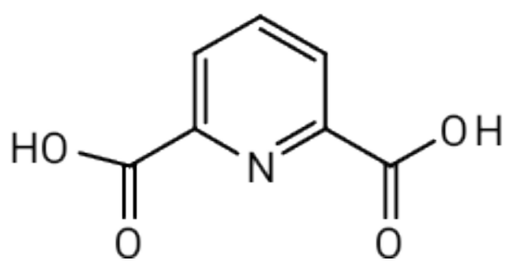
CONTENTS

COORDINATION CHEMISTRY AND COORDINATION COMPLEX WITH DIPICOLINIC ACID AS LIGAND

INTRODUCTION:

The review focuses on the interesting properties of p-, d-, and f-block elements when coordinated with 2,6-pyridinedicarboxylic acid (dipicolinic acid, H2 dipic) and its derivatives as ligands, with a focus on their use as inorganic pharmaceuticals. 2,6-Pyridinedicarboxylic acid (dipicolinic acid, H2 dipic), I, is a widely used building block in coordination and supramolecular chemistry (Froidevaux et al. 2000, Muller et al. 2001, Hunag et al. 2003, Storm and Luning 2003, Haino et al. 2005). It is a versatile, strong, nitrogen-oxygen, multimodal donor ligand, which forms stable complexes with diverse metal ions, sometimes in unusual oxidation states (Renaud et al. 1997a,b, Jackson et al. 2001, Devereux et al. 2002, Ouali et al. 2002, Kapoor et al. 2005, Tse et al. 2006, Kirillova et al. 2007).

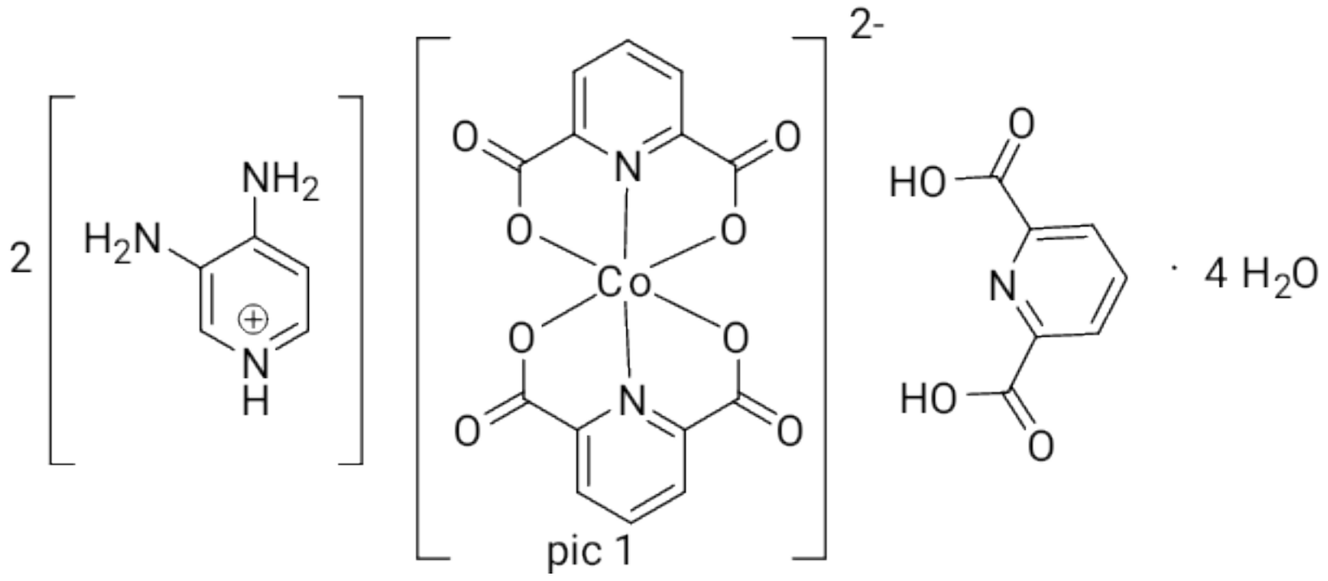


The crystal structure of dipicolinic acid was first solved by Takusagawa et al. (1973). Lately, the pharmacological studies on dipicolinic acid have been given pertinent attention because of its low toxicity and amphophilic nature. Dipicolinic acid is also present in natural systems as a product of oxidative degradation of vitamins, coenzymes, and alkaloids, to name a few (Siddiqi et al. 2010). Furthermore, it is constituent of fulvic acid, and is an intermediate during l-tryptophan degradation as well as a precursor for the NAD enzyme (Siddiqi et al. 2010). Dipicolinic acid and its derivatives are now being featured as ligands in coordination complexes that have medicinal uses. The readers are encouraged to read reviews and articles for information regarding the solution chemistry of dipicolinic acid, its derivatives, and its coordination complexes (Buglyo et al. 2005, Smee et al. 2009, Kirillov and Shul’ pin 2013). Please see the following review “ Pyrazinecarboxylic acid and analogs: Highly efficient co-catalysts in the metalcomplex-catalysed oxidation of organic compounds” (Kirillov and Shul’ pin 2013). In this report, the reviews and featured articles have been published on the following topics: antidiabetic effects of a series of vanadium dipicolinate complexes in rats with streptozotocin (STZ)-induced diabetes (Willsky et

al. 2011); how environment affects drug activity: localization, compartmentalization, and reactions of a vanadium insulin-enhancing compound, dipicolinatooxidovanadium (V) (Crans et al. 2011); and metal speciation in health and medicine represented by iron and vanadium (Crans et al. 2013).

LITERATUREREVIEW:

The syntheses of Co(II) and Co(III) dipicolinate complexes were reported via solid-state X-ray characterization of [Co(H2 dipic)(dipic)].3H2 O 7 and [Co(dipic)(μ-dipic) Co(H2 O)5]·2H2 O 8, respectively, in which two new coordination modes were observed (Yang et al. 2002). Solution studies show a high stability of the Co(III) complex, whereas the Co(II) complexes undergo pH-dependent ligand exchange in the presence of excess ligand (Yang et al. 2002). The [Co(dipic)2] 2- anion was found to be effective in reducing the hyperlipidemia of diabetes using oral administered aqueous solutions to rats with STZ-induced diabetes (Yang et al. 2002).

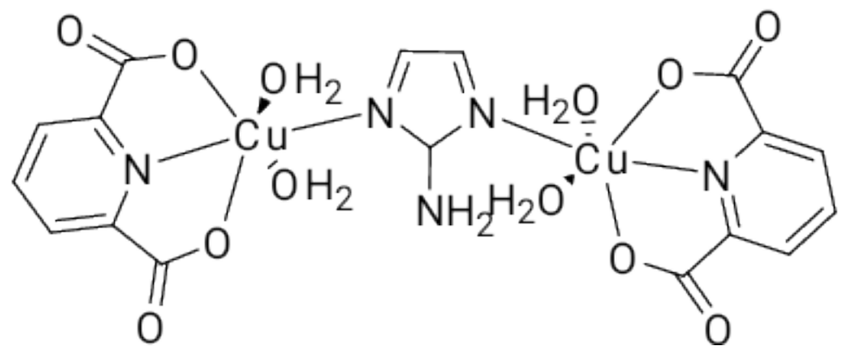


pic 1

In another report by Azadbakht et al., (H2 dap) [Co(dipic)2]·H2 dipic·4H2 O 9 (where dap = 3,4-diaminopyridine) was screened for its antimicrobial activities against Bacillus cereus (ATCC 11778), Bacillus subtilis (ATCC 12711), Staphylococcus aureus (ATCC 25923), Escherichia coli (ATCC 25922), and Pseudomonas aeruginosa (ATCC 27853). However, the screening data revealed that compound 9 exhibited only inhibitory results against S. aureus (MIC > 14 mg cm-3). This finding was of great interest because it seemed to show conflict toward the well-known antimicrobial

characteristic of the pure dipic ligand toward a broad spectrum of bacteria (Chauvin et al. 2006, Gaillard et al. 2013). The confirmation of this observation was done via a comparison of independent data reported by Derikvand et al. (2012), Siddiqi et al. (2010), and Soleimani (2011). It is seen that the dipicolinic acid complexes show a varied resistance to bacterial growth. These data were further supported from the data retrieved from the antifungal studies of Siddiqi et al. (2010) and also showed similar inhibitory results for the complexes containing dipicolinic acid as a ligand. 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.

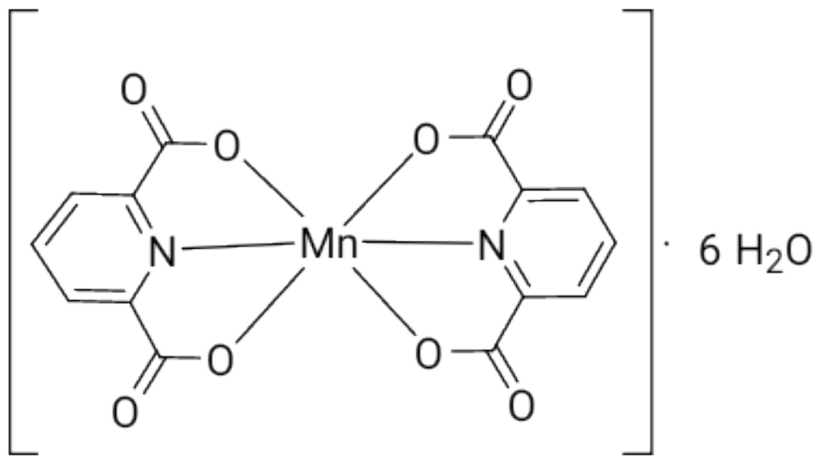
A copper complex, pic-2, was tested for their ability to bind to DNA, and it was seen that there was π-π stacking between the ligands of the complex and the base pairs of DNA (Tabatabaee et al. 2013).[13]



Pic2

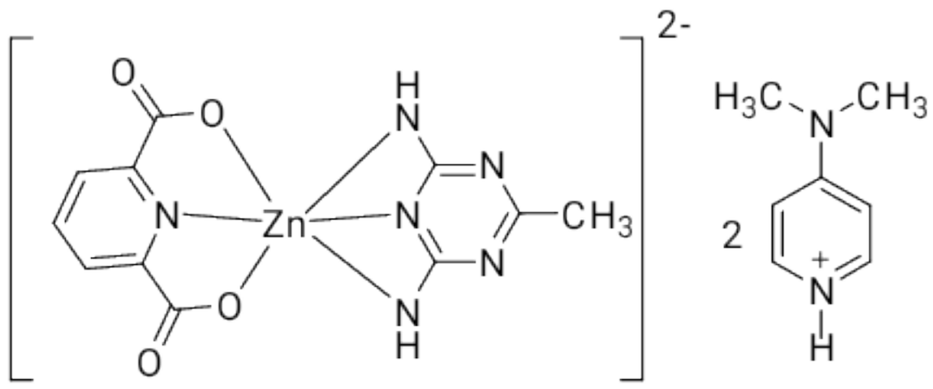
It is seen that the di-picolinic acid complexes show a varied resistance to bacterial growth. It was therefore the general conclusion from these results that showed the overall structure of the tested compounds to be the principal factor influencing the antimicrobial activity.

A manganese complex, $[Mn(dipic)_2]\cdot 6H_2O$,(Pic-3) 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.[11]



Pic-3

The ternary complex formation of some potent insulinlike zinc(II) complexes of bidentate ligands, maltol and 3-hydroxy-1,2-dimethyl-pyridinone with (O,O), 2-picolinic acid and 6-methylpicolinic acid with (N,O), and the tridentate dipicolinic acid with (O,N,O) coordination modes, was studied in aqueous solutions by pH potentiometry and spectroscopic [UV-visible, circular dichroism (CD), and electrospray ionization-mass spectrometry (ESI-MS)] methods in the presence of critical cell constituents such as reduced l-glutathione (GSH) and adenosine 5' -triphosphate (ATP) (Enyedy et al. 2008). The results showed that the formation of the ternary complexes was hindered in the case of dipicolinic acid, especially with ATP, while it was favored with the bidentate ligands in the physiological pH range (Enyedy et al. 2008).

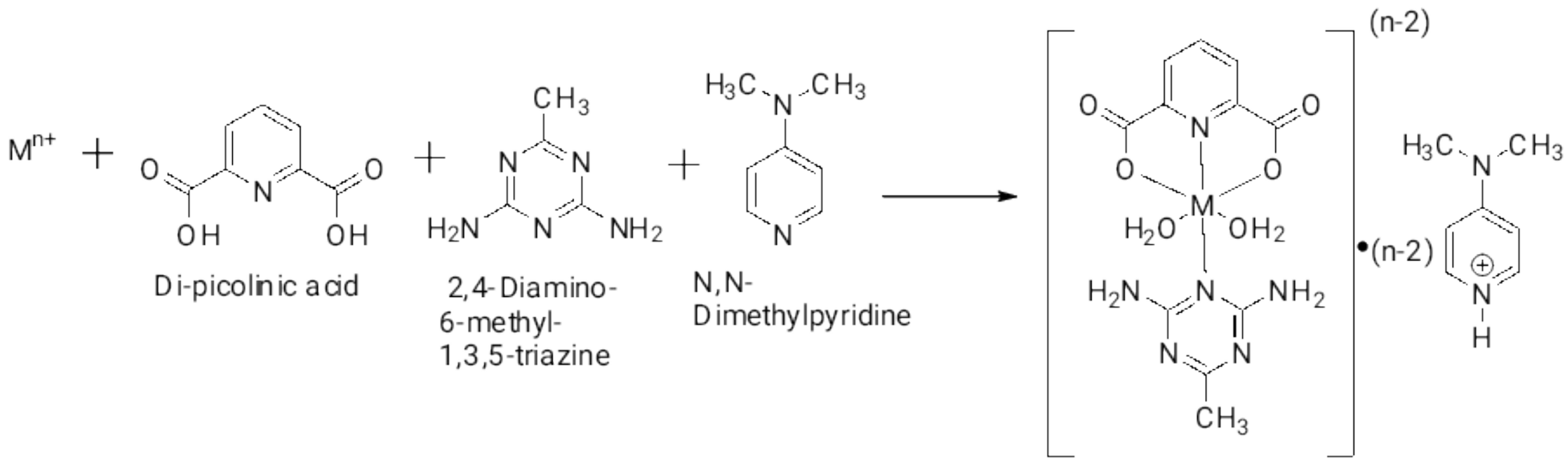


AIM OF THE RESEARCH WORK:

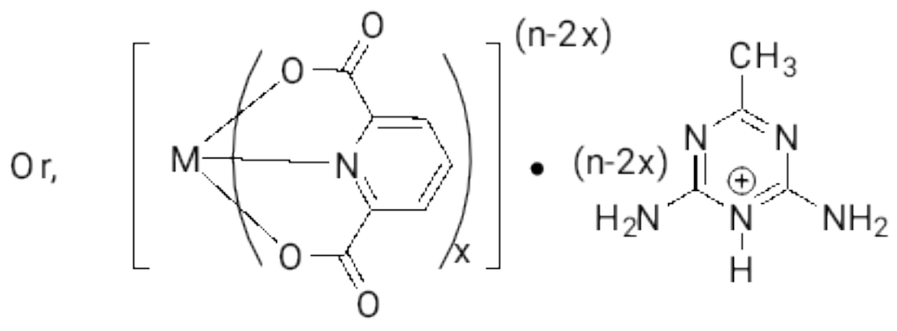
1. Preparation of Schiff base from di-picolinic acid
2. Synthesis of complexing agent.
3. Investigate the activity of the complexing agent.

SCHEME OF THE REACTION :

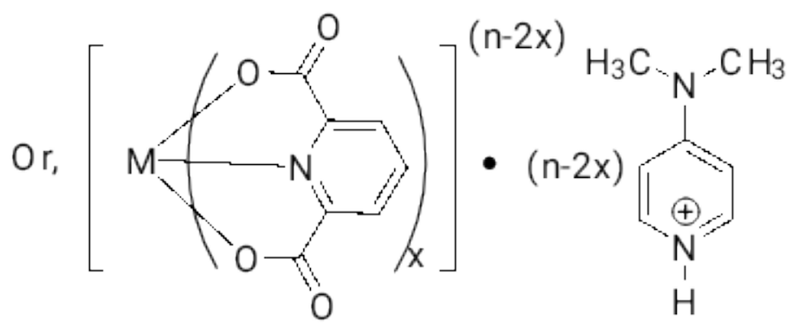
SCHEME:1



COMPLEX 1

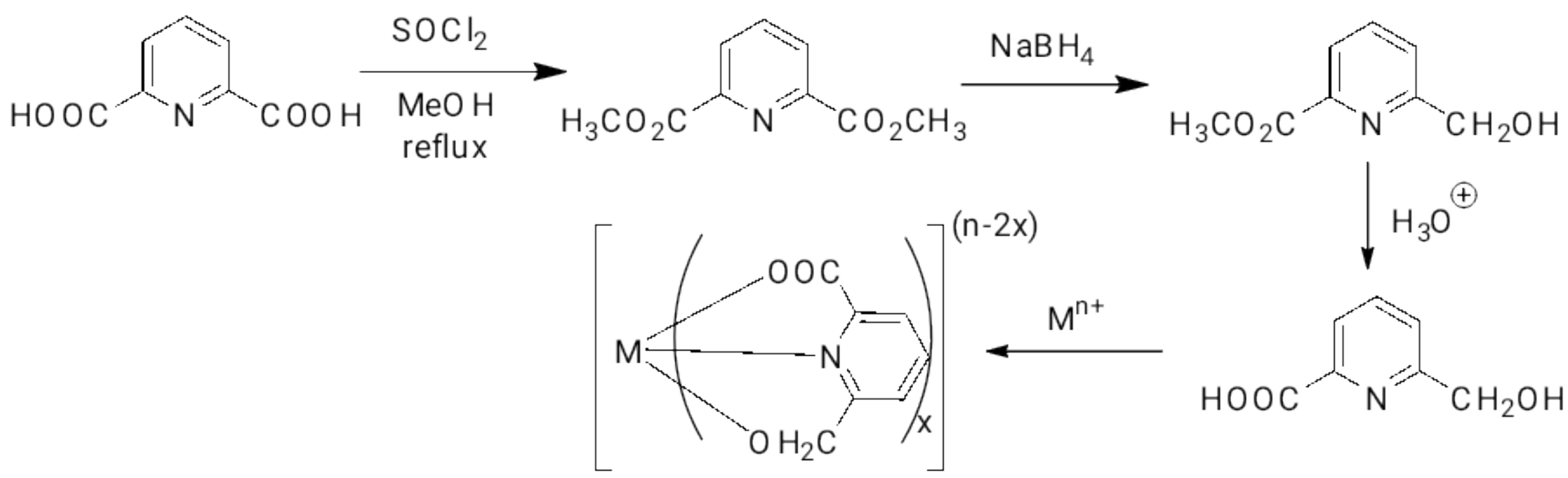


COMPLEX 2



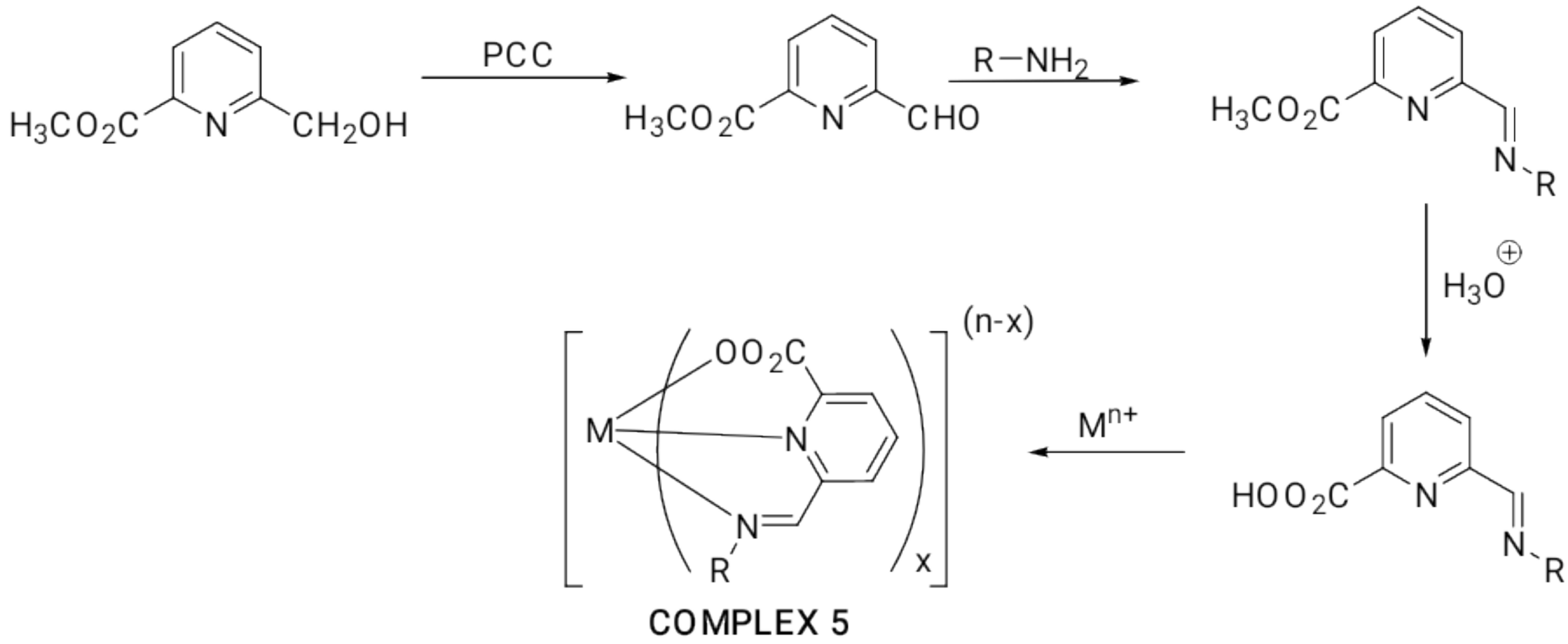
COMPLEX 3

SCHEME:2



COMPLEX 4

SCMEME:3



COMPLEX 5

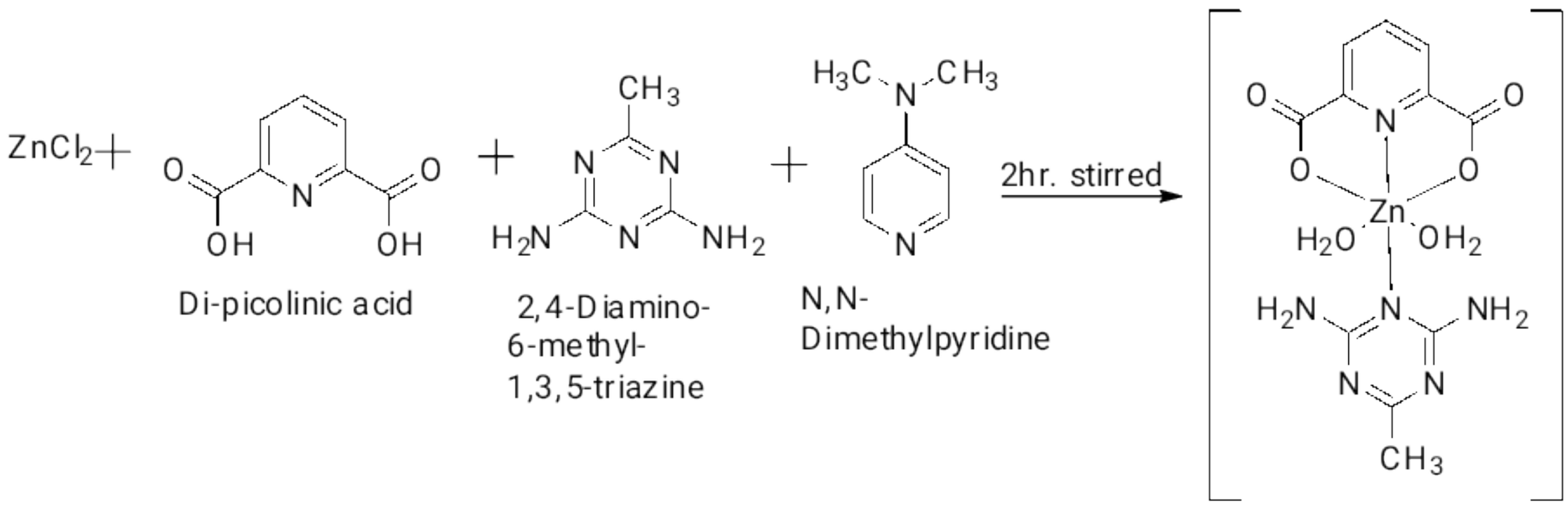
Where , M = Fe, Cr, Mn, Co... .etc.

WORK DONE :

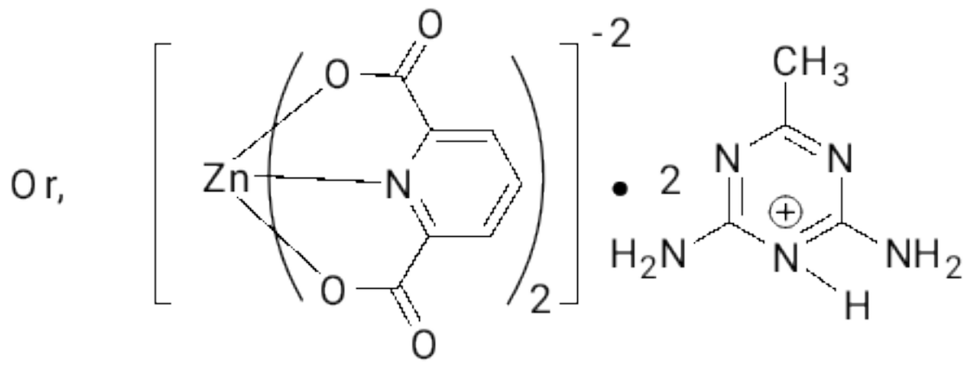
- **Preparation of Zn (II) complex:**

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.

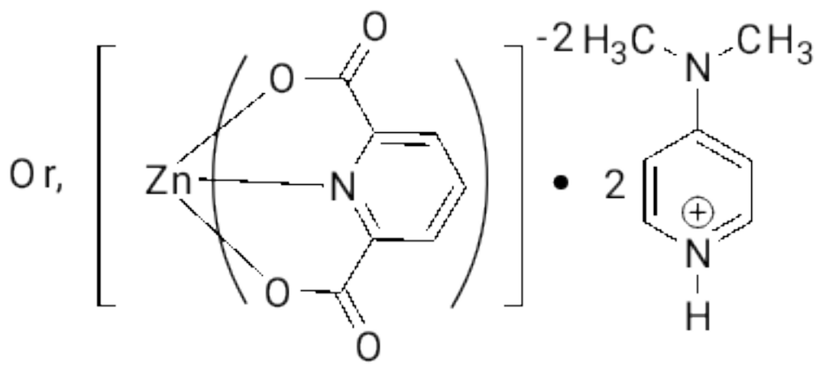
Reaction:



COMPLEX 1.1



COMPLEX 2.1



COMPLEX 3.1

SPECTRUM ANALYSIS:

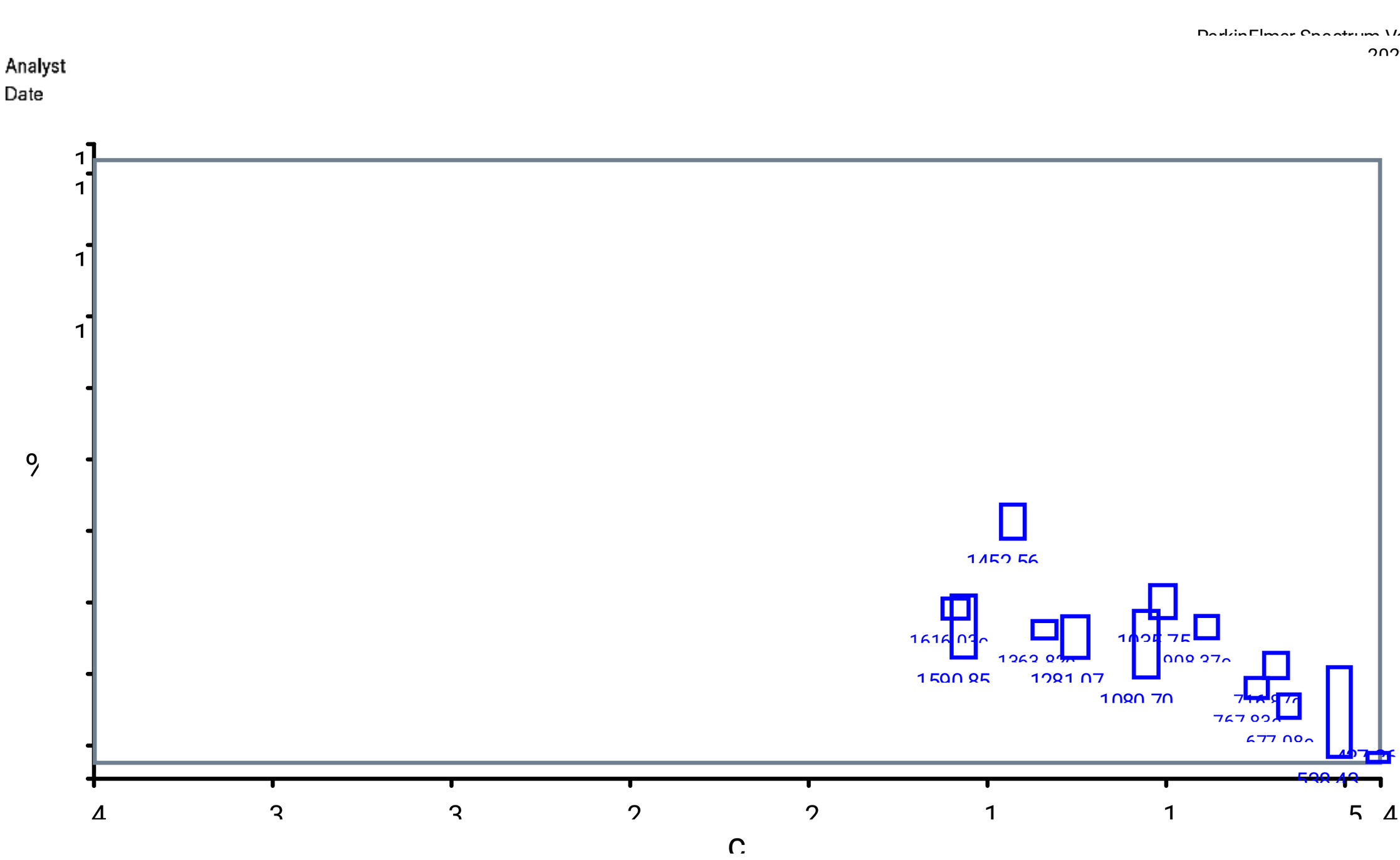
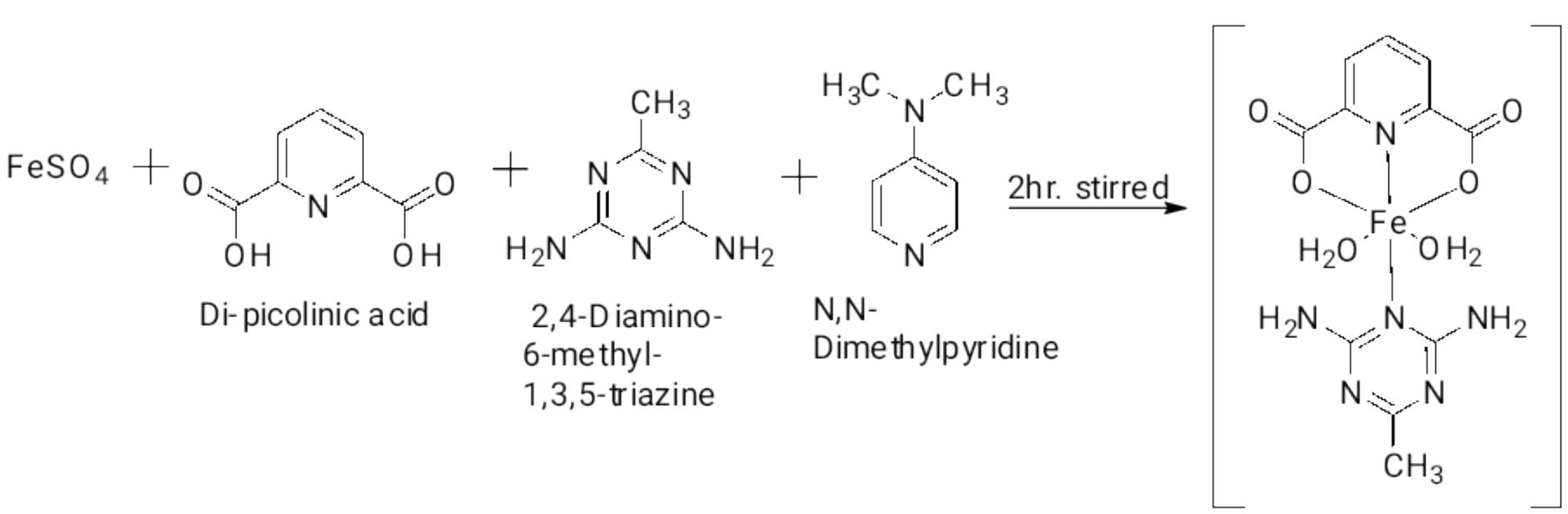


Figure 1: IR spectra for Zn(II) complex : 3090 cm^{-1}(aromatic C-H stretch);1616-1452 cm^{-1}(C=C, C=N pyridine ring stretch).

- **<u>Preparation of Fe(II) complex:</u>**

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:



Spectrum analysis:

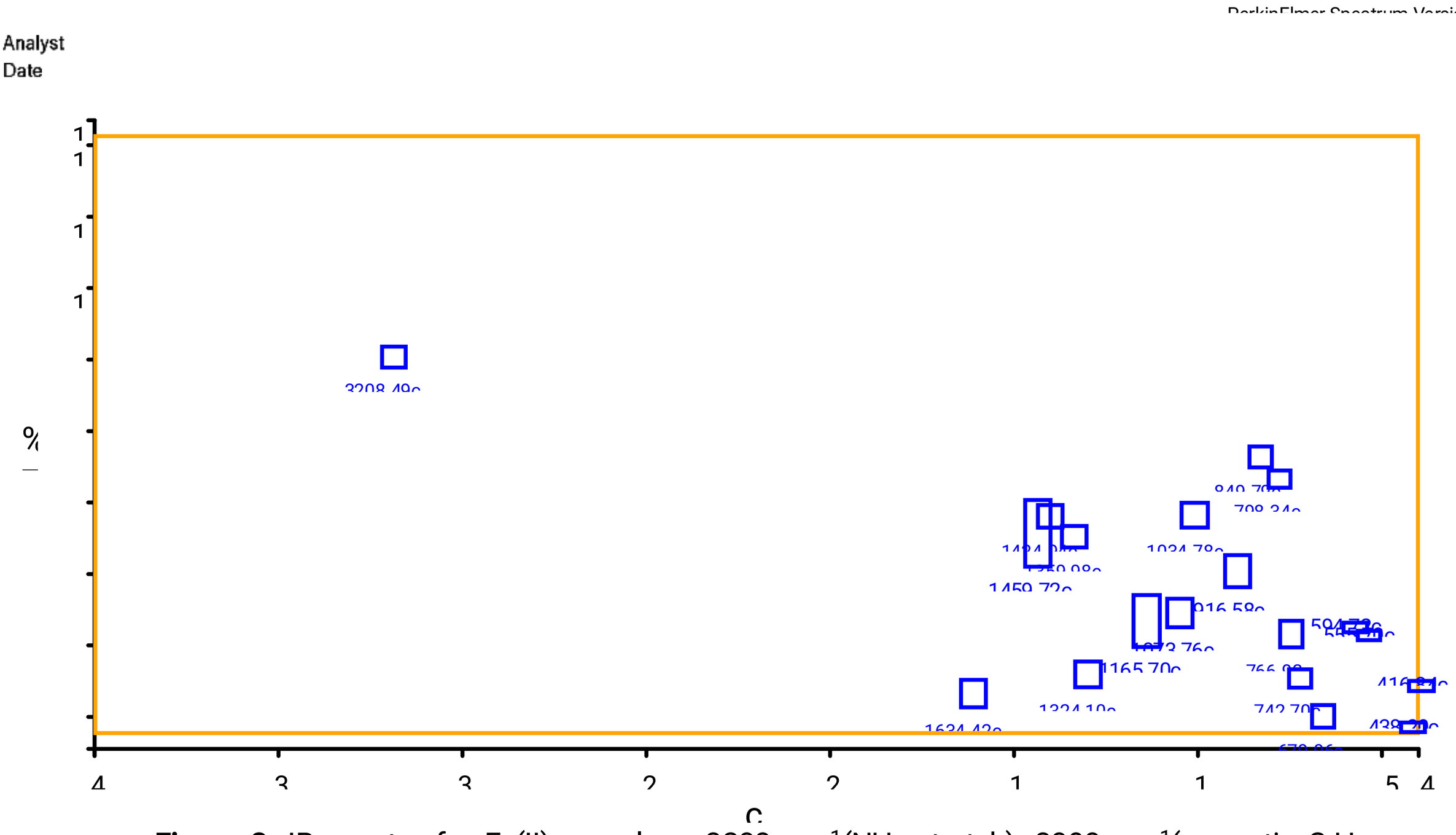
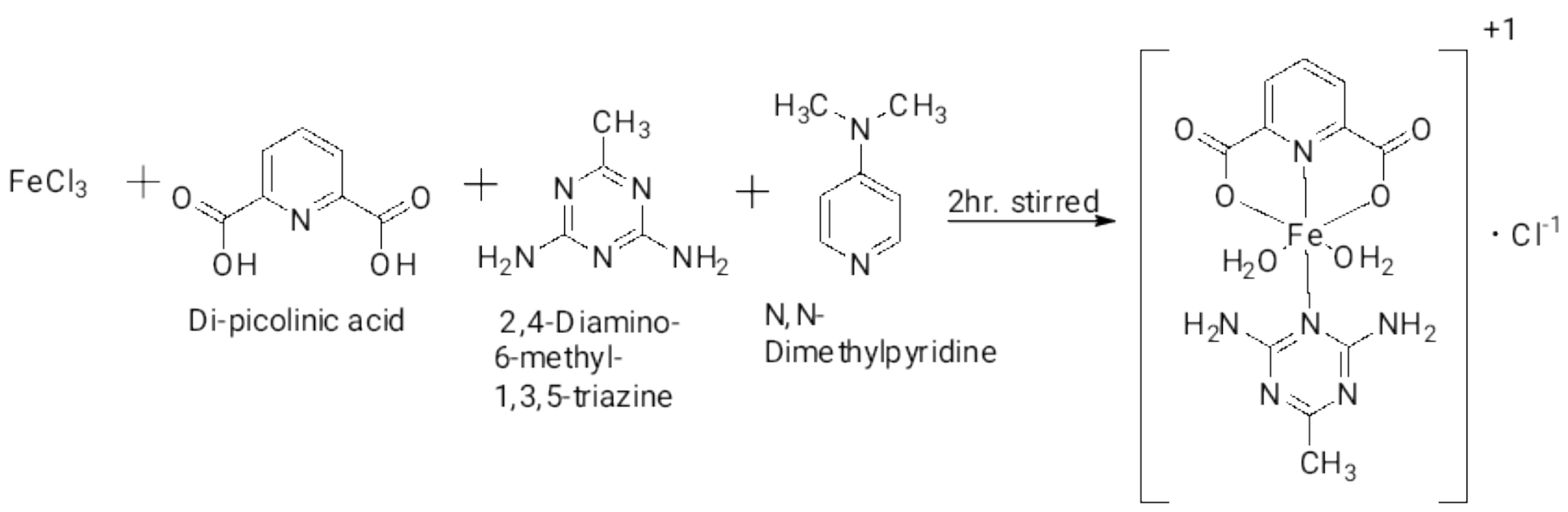


Figure 2: IR spectra for Fe(II) complex : 3208 cm^{-1}(NH_2 stretch); 3090 cm^{-1}(aromatic C-H stretch);1634-1424 cm^{-1}(C=C, C=N pyridine ring stretch);

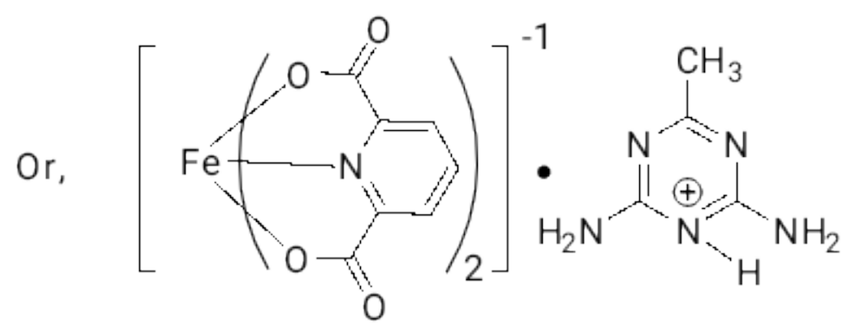
- **Preparation of Fe(III) complex :**

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.

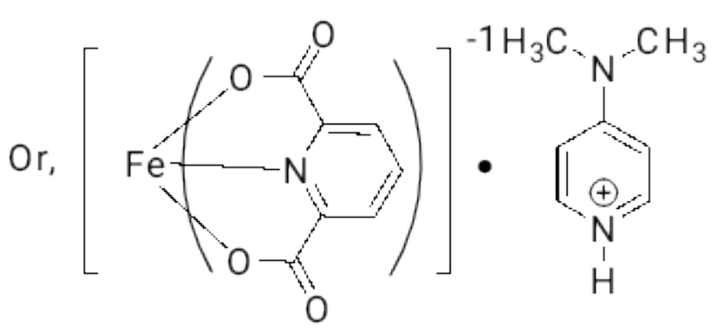
Reaction:



COMPLEX 1.3



COMPLEX 2.3



COMPLEX 3.3

Spectrum analysis:

PerkinElmer Spectrum Version 10.4

Analyst
Date

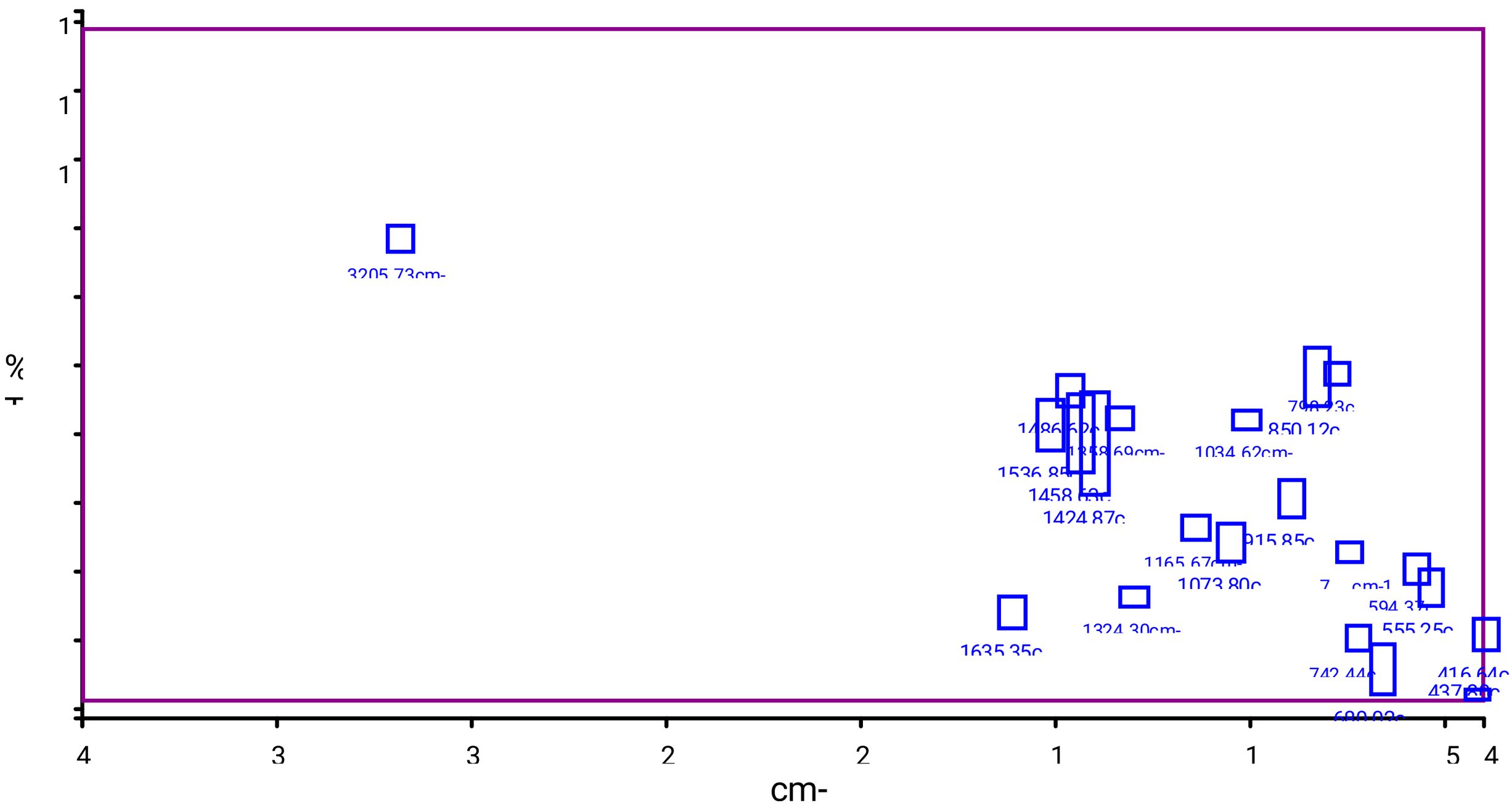
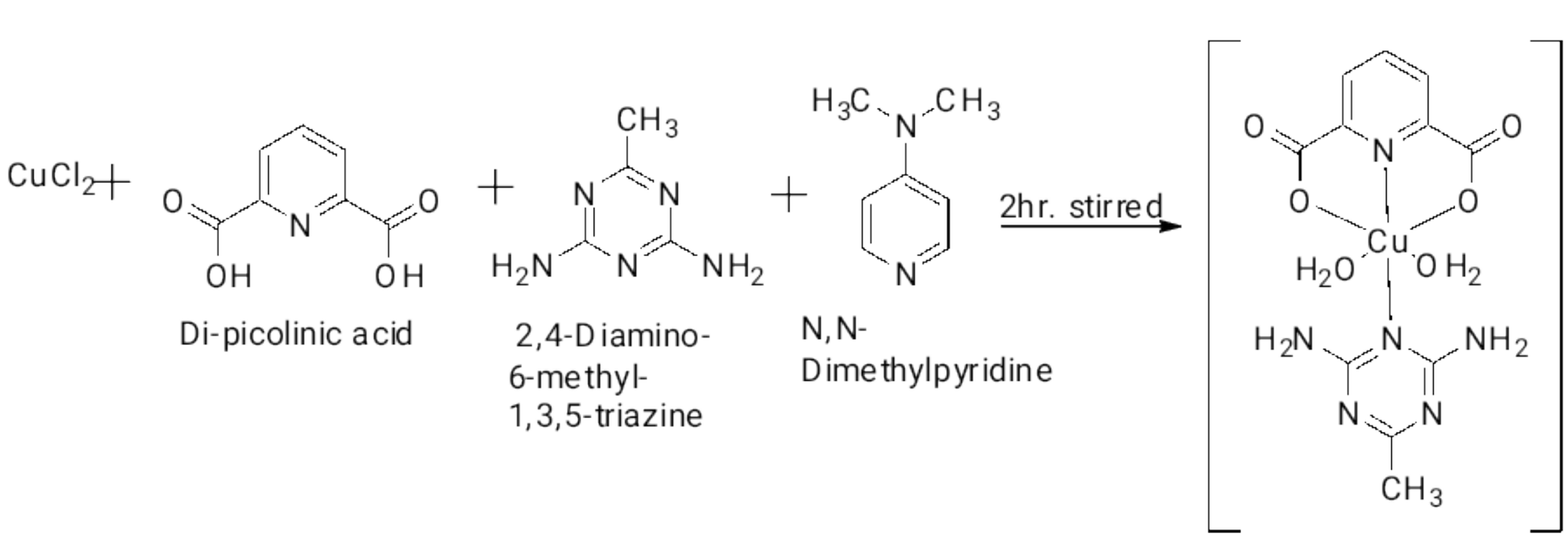


Figure 3: IR spectra for Fe(III) complex : 3205 cm^{-1}(NH_2 stretch); 3090 cm^{-1}(aromatic C-H stretch);1635-1424 cm^{-1}(C=C, C=N pyridine ring stretch);

- **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:



Spectrum analysis:

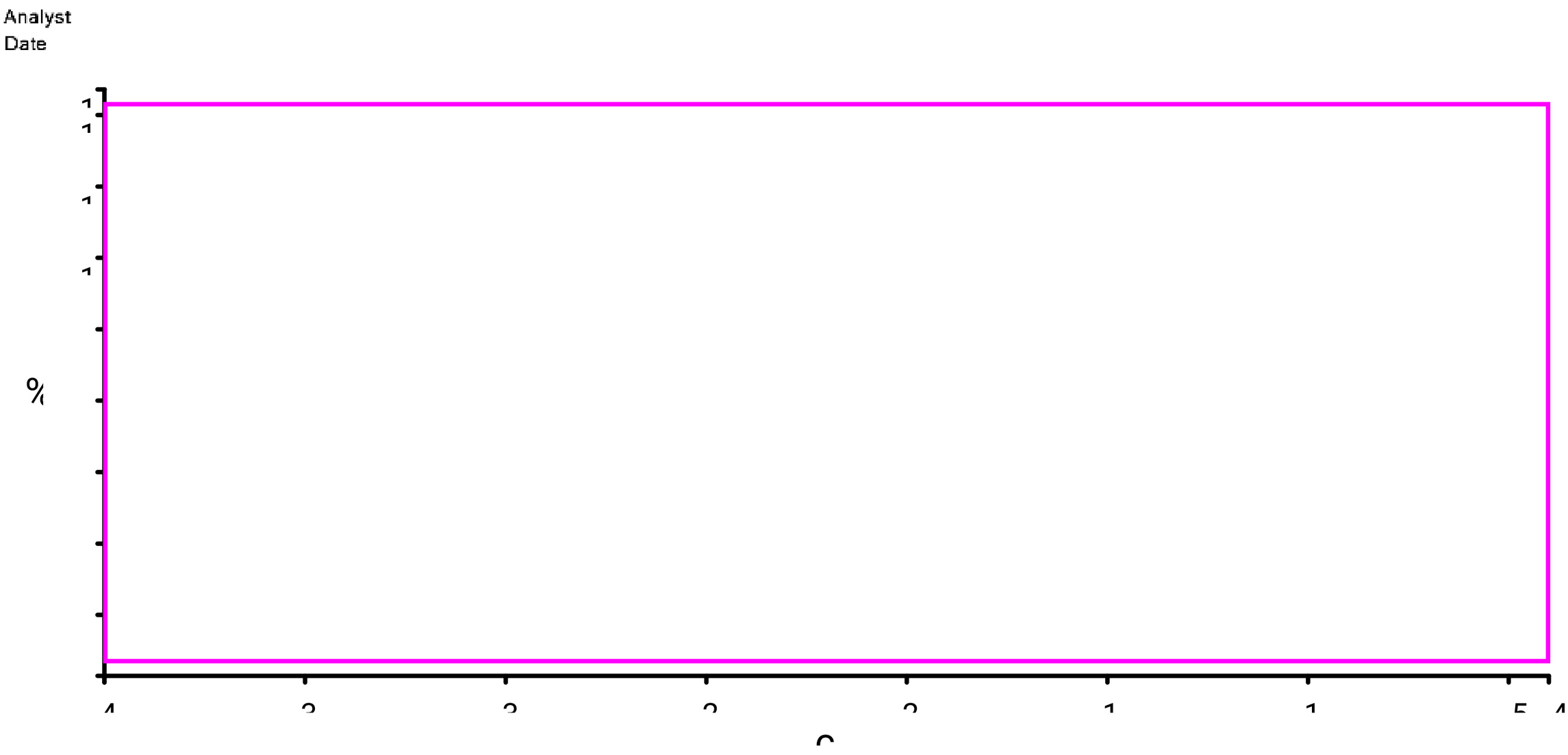
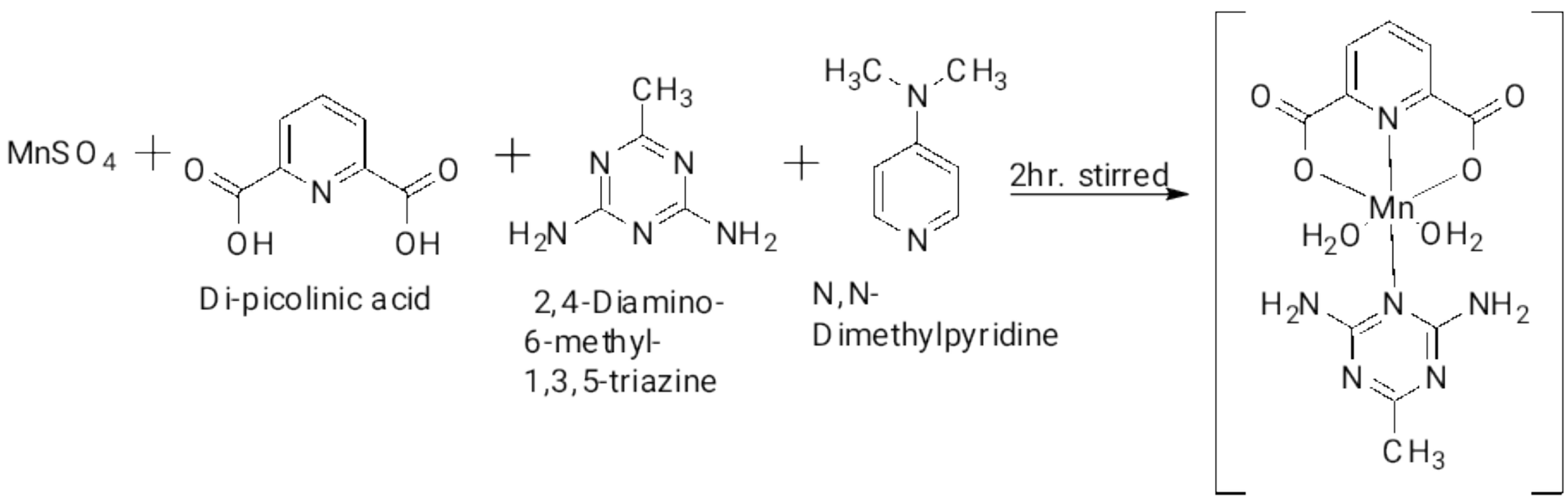


Figure 4: IR spectra for Cu(II) complex : 3090 cm^{-1}(aromatic C-H stretch);1630-1424 cm^{-1}(C=C, C=N pyridine ring stretch);

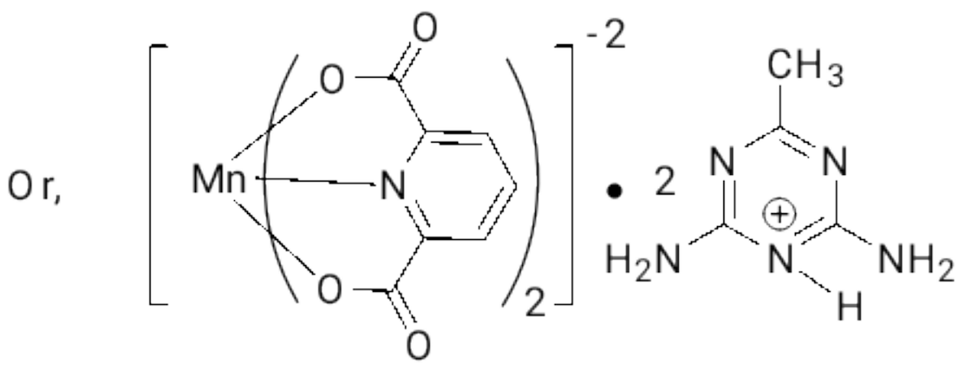
- **Preparation of Mn(II) complex :**

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.

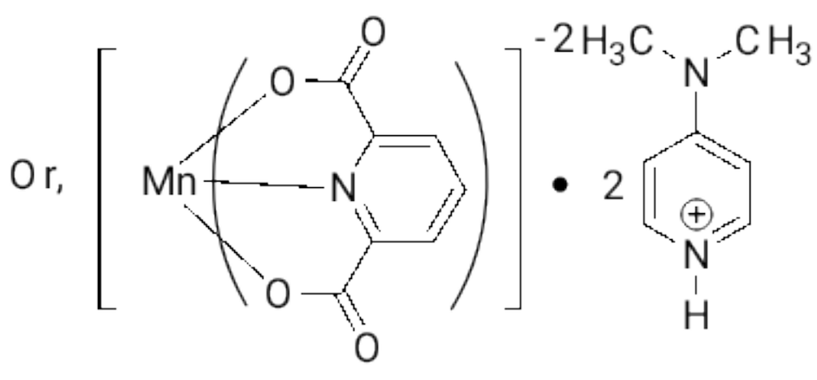
Reaction:



COMPLEX 1.5



COMPLEX 2.5



COMPLEX 3.5

SPECTRUM ANALYSIS:

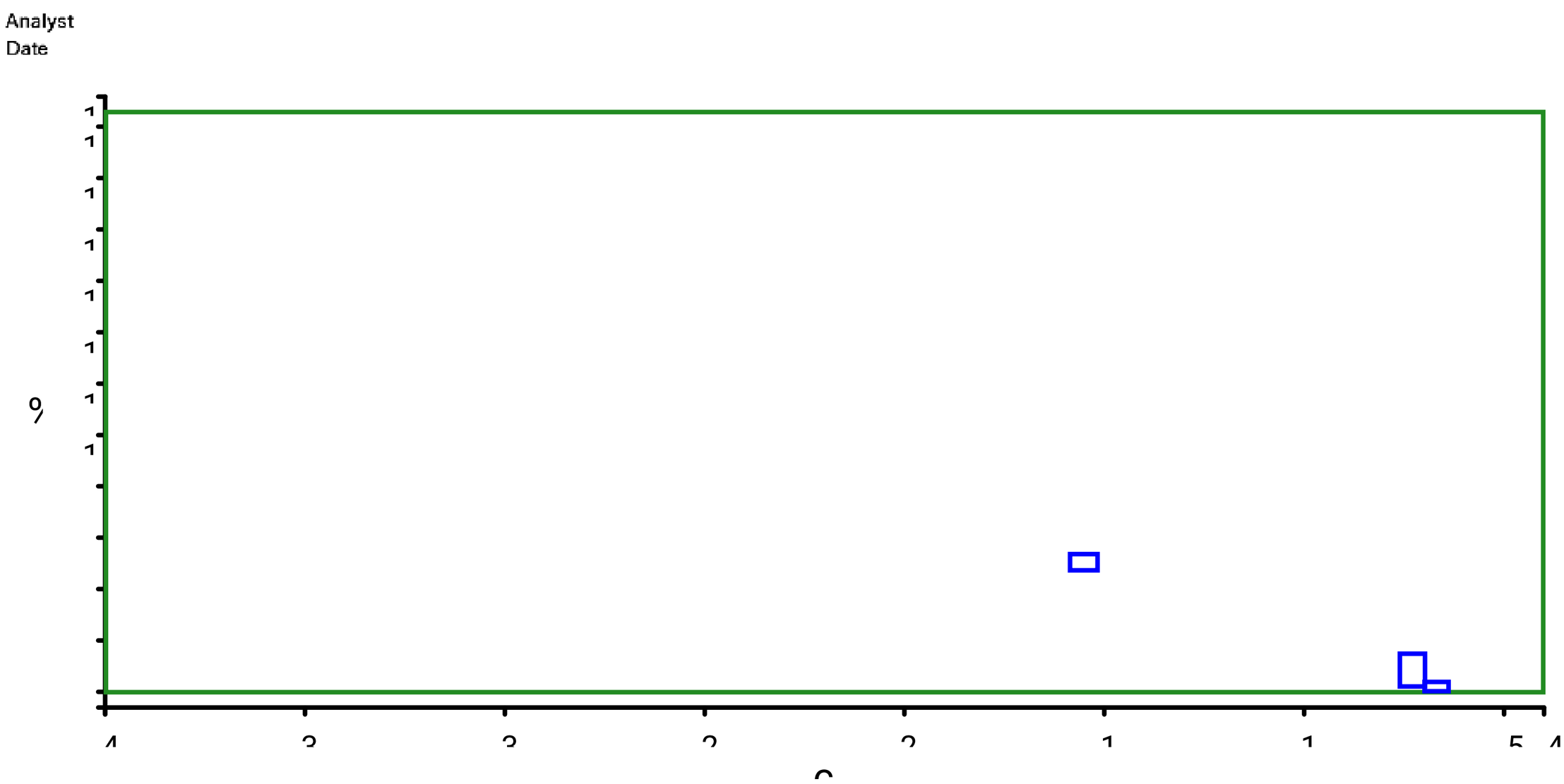


Figure 2: IR spectra for Mn(II) complex: 1630-1424 cm^{-1}(C=C, C=N pyridine ring stretch);

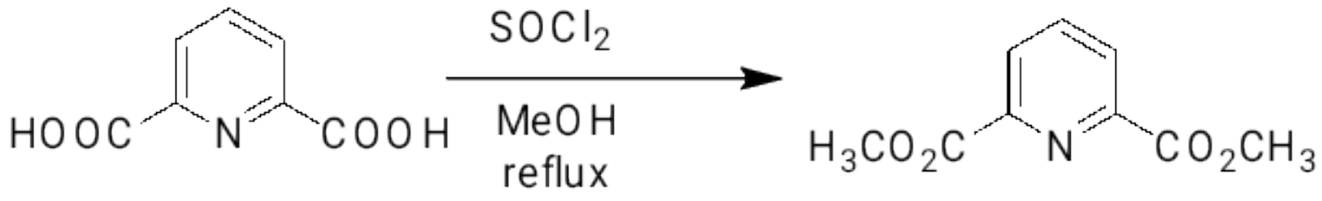
Figure 2: IR spectra for Mn(II) complex: 1630-1424 cm^{-1}(C=C, C=N pyridine ring stretch);

WORK DONE:

- **Preparation of Di-picolinic acetate from Di-picolinic acid:**

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: - 4.36g

% of yield: 46.68%

CONCLUSION:

Our project work synthesis of coordination complex with Schiff base derived from dipiolinic acid and it' s derivatives. We synthesis coordination complex of Zn(II),Fe(II), Fe(III) and Cu(II) derived from di-picolinic acid 2,4-Diamino-6-methyl-1,3,5-triazine. and prepared di-picolinicacetate.

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