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SPECTROPHOTOMETRIC DETERMINATION OF Fe (II) BY ISOCINCHOMERIC ACID - A STUDY OF SYNTHESIS AND CHARACTERIZATION

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ABSTRACT

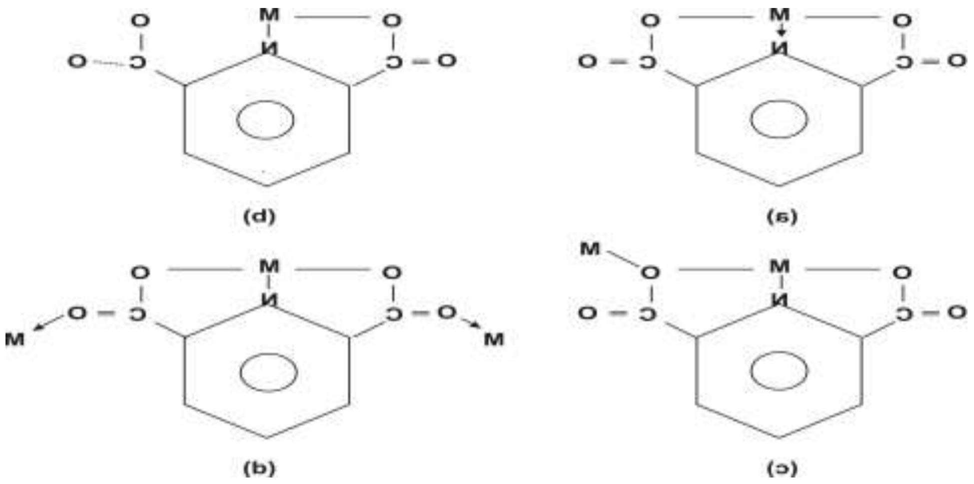
A new spectrophotometric method is developed for the determination of Fe (II) in an aqueous solution. The metal ion forms a red colored complex with pyridine 2, 5 dicarboxylic acid in the pH 4.0 to 7.0. The complex shows maximum absorbance at 492 nm. Job's method for continuous variation and mole ratio method shows metal ligand ratio in the complex to be 1:2. The complex is stable for days. The red colored complex obeys the Beer's law in the concentration range of 225 to 500 μgs of iron. The molar absorptivity (ξ) is found to be 1.55 x 10^2 lmole^{-1}cm^{-1}. The method has been used for the determination of Fe^{+2} in synthetic samples. The complex has been synthesized and FTIR studies have been carried out.

KEYWORDS: Pyridine2, 5 di carboxylic acid, Fe (11), spectrophotometry.

INTRODUCTION

Pyridine dicarboxylic acids are good complexing agents. Pyridine 2,3-, 2,4-, 2,5-, 2,6-, 3,4-, 3,5- dicarboxylic acids exhibit various co-ordination modes. Pyridine 2, 6- dicarboxylic acid can act as partly or fully deprotonated and shows diverse coordination modes. 2, 6 pyridinedicarboxylic acid is found to be suitable ligand as it is well known versatile N, O chelator in coordination chemistry due to its diverse coordination modes.[1-5] It is also reported that this ligand is used to develop more effective anti HIV agents.[6-8] Pyridine dicarboxylic acids are found in the metabolic pathways of animals and they are used for the transport and scavenging of metal ions by the body. Pyridine 2, 6 dicarboxylic acid is reported to be present in bacillus spores, which is responsible for high thermal and UV stability of Bacillus spores.[9] Pyridine dicarboxylic acid has important biological function in the metabolism such as enzyme inhibitor,[10] plant preservative,[11] and food sanitizer,[12] These properties have attracted the interest of scientist not only in the field of coordination chemistry but also in inorganic and bioorganic chemistry.

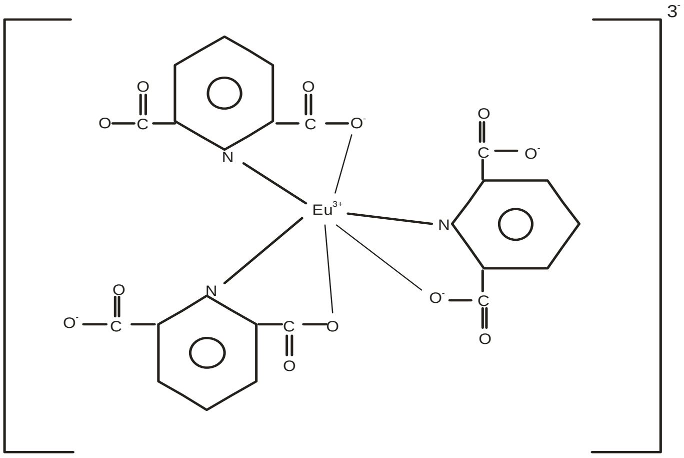
The coordination modes of pyridinedicarboxylate can be predicated as shown in fig.



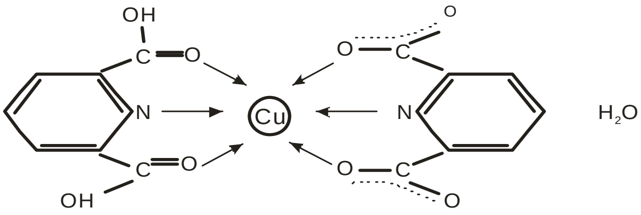
Most of the transition metals are reported to form fig (a) type of complexes . A comparative study of the luminescent properties of europium and terbium coordinated with pyridine 2, 6 dicarboxylic acid in aqueous solutions has been described by Nadine Arnaud, Eric Vaquer and Joseph Georges.

It is also reported that this ligand is used to develop more effective anti HIV agents. Pyridine dicarboxylic acids are found in the metabolic pathways of animals and they are used for the transport and scavenging of metal ions by the body. Pyridine 2, 6 dicarboxylic acid is reported to be present in bacillus spores, which is responsible for high thermal and UV stability of Bacillus spores. Pyridine dicarboxylic acid has important biological function in the metabolism such as enzyme inhibitor.[42] plant preservative.[43] and food sanitizer.[44] These properties have attracted the interest of scientist not only in the field of coordination chemistry but also in inorganic and bioorganic chemistry.

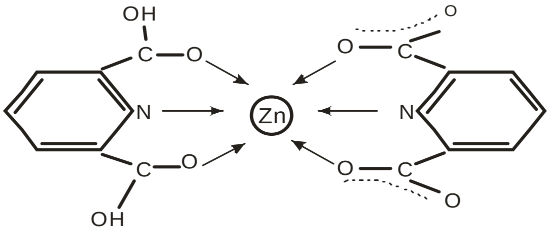
Europium aquoion form chelate complexes with pyridine 2, 6 – dicarboxylic acid,[8] The structure of the complex is given as.



The 1:2 complexes of copper (II) and Zinc (II) with pyridine 2, 6 – dicarboxylic acid has been reported (13). These complexes have distorted octahedral geometries.



(1)



(2)

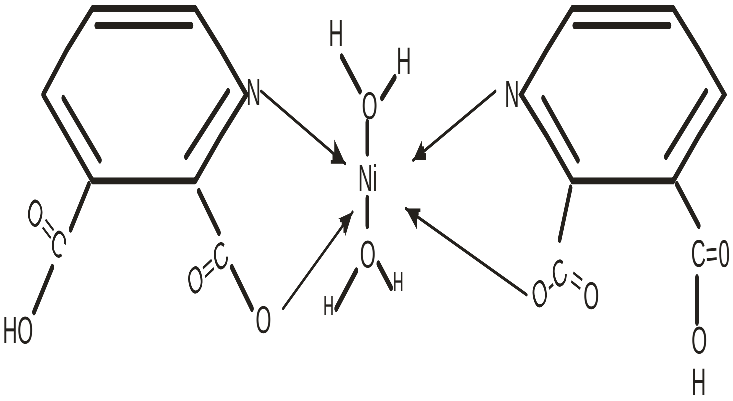
The complexes of Cobalt (II), nickel (II), rhodium (II) and rhodium (III) has been synthesized and their spectral and magnetic properties been studied (14). Nickel is reported forming 1:2 complex i.e. Ni (dpCH) $_2$ $3H_2O$. Cobalt forms 1:1 complex i.e. Co (dpc) $3H_2O$ which is six coordinate and contain co-ordinate water. Anhydrous polymeric [Co-(dpc)] $_n$ has also been reported (14). Rhodium (II) and rhodium (III) forms Rh (dpc).$3H_2O$ and Na [Rh (dpc) $_2$].$2H_2O$ respectively. Another study reports the dimeric complexes of Ni and Co with pyridine 2, 6 di-carboxylic acid. The structure of these complexes has been determined by single crystal x-ray crystallography.[15] These dimeric complexes have been reported to have hexa coordinated environment with two different type of donor atoms i.e. nitrogen and oxygen.[15] Manganese (II) has been reported to form a binuclear complex i.e. hexaaquabis (Pyridine – 2, 6 – dicarboxylato) dimanganese (II) complex,[16] Each Mn (II) ion is coordinated by three oxygen atoms and one Nitrogen atom from the pyridine 2, 6 dicarboxylate ligand and by three water oxygen atoms. Each manganese possesses distorted pentagonal bipyramidal coordination.

Chromatographic separation of transition metals by pyridine 2, 6 dicarboxylic acid (used as eluent) has been reported. The metals (Cu, Ni, Zn, Co, Cd, and Mn) are separated as anionic chelate.[17]

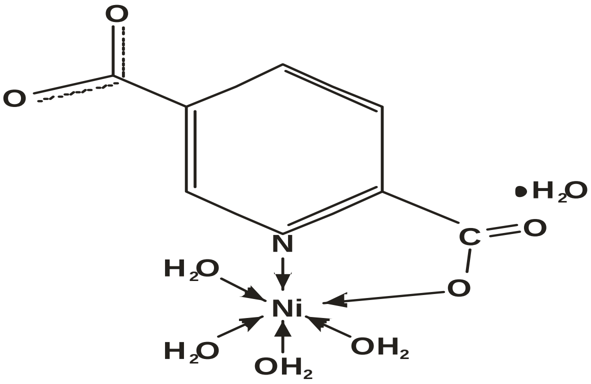
The complex formation studies of large number of cations are reported. Mixed ligand complexes of Nickel (II) and Cadmium (II) with Pyridine 2, 6 dicarboxylic acid have been studied potentiometrically.[18] Lanthanum, Dysprosium and Gadolinium (La, Dy, and Gd) reacts with 2, 6 pyridine dicarboxylic acid in aqueous alkaline solution to give Ln (pdc) (HPdc) m.H_2O. The thermal dehydration of these lanthanum compounds have been studied .[19] The study of complex formation of Dysprosium (III) and pyridine 2, 6 dicarboxylic acid has been reported,[20] Electron Spin Resonance studies of complexes of silver (I) and copper (II) with pyridine 2, 6 dicarboxylic acid have been reported.[21]

The complex of copper with pyridine 2, 3- dicarboxylic acid i.e. [Cu (2, 3- pydcH) $_2$] has been reported.[22] It is a chain polymer. Two ligand occupy the equatorial plane of each tetragonally elongated Cu^{+2} coordination sphere, chelating through the pyridine nitrogen and one oxygen of the deprotonated 2- carboxylic acid group, the axial positions are occupied by long bonds to a 3-carboxylic acid oxygen of adjacent Cu (2, 3 PydcH)$_2$ repeat unit. The coordination polymer of Mn with pyridine 2, 3 dicarboxylate has been synthesized and crystal structure has been proposed based on the experimental data.[23] According to this report Mn^{+2} ion is coordinated in a distorted octahedral environment by the O atoms of two water molecules, one N and one O atoms of the chelating pyridine 2, 3- dicarboxylate (PDC) dianion, and two axial bridging carboxylate O atoms from two adjacent PDC ligands.[23]

The complexes of the type M (H-Quin) $_2$. 2H_2O (M = Mn, Co, Ni and Zn) where H_2 – Qin =Quinolinic acid i.e. Pyridine 2, 3dicarboxylic acid have been prepared and characterized .[24] All these reported complexes have octahedral distorted structure. The nickel atom in Ni (H-Quin) $_{2.2H2O}$ is octahedrally coordinated by two nitrogen atoms and two oxygen atoms belonging to the two H-Quin$^-$ anions and two trans-aqua molecules.[24] The structure of Ni (II) with Quinolinic acid can be represented as,

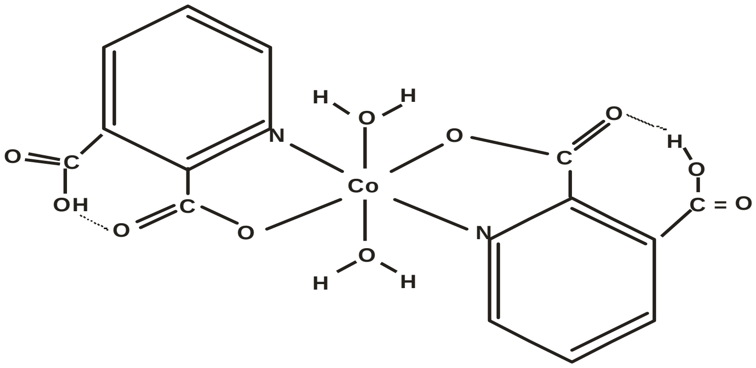


The crystal structure of Ni (II) with pyridine 2, 5 dicarboxylic acid has been reported,[25] This compound i.e. [Ni ($C_7H_3No_4$) (H_2O) 4].H_2O is synthesized by reaction of Ni (II) with pyridine-2, 5-dicarboxylic acid and piperazine in water. The compound contains a six coordinate Ni (II) ion which has a distorted octahedral structure. Following is the reported structure.

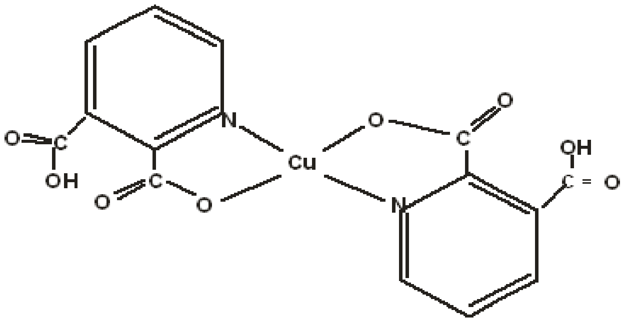


The complex Mn (H-Quin) $_{2.2H2O}$ has been formulated as [Mn (H_2O) $_6$] [Mn (H-Quin) $_3$]$_2$. The octahedral [Mn (H-Quin)$_3$]$^-$ and, [Mn(H_2O)$_6$]$^{2+}$ units lie on different three fold axis.[24] Lanthanide (III) quinolinate complexes have been prepared and reported and evidence is presented which indicates that these complexes may be six-coordinated.[26] A calcium (II) complex with pyridine 2, 3- dicarboxylate (Quinolinic acid) has been synthesized and crystal structure has been reported.[27] The complexes of uranium (IV) with quinolinic acid has been synthesized and reported,[28] Two types of complexes of cadmium with quinolinic acid has been synthesized and reported.[29] They are [Cd (2,3 pydcH)$_3$][Cd(H_2O)$_6$] and [Cd (2, 3 pydc) (H_2O)$_3$]n. The chromium (III) – quinolinato complexes [Cr(quinH)$_3$]$^{+3}$ [Cr(QuinH)$_2$(H_2O)$_2$]$^+$ and [Cr(quinH)(H_2O)$_4$]$^{2+}$ have been obtained and characterized in solution.[30]

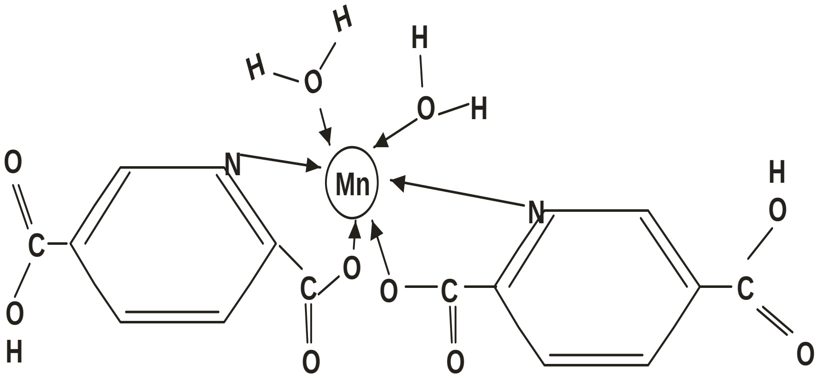
The structure of some Cu (I), Ag (II) and Cu (II) compounds with quinolinic acid have been established based on X-ray crystallographic studies.[31-33] In each case, quin is bonded as a monoanion through pyridine nitrogen and carboxyl ate oxygen atoms forming the 5-membered chelate ring. The same coordination mode is postulated for other quin-complexes with Cr (III), Cd (II), Fe (II),[34, 37] though no structural studies were conducted. The spectrophotometric evaluation of iron (II) quinolinic acid complex (1:2) metal ligand system has been reported.[38] Quinolinic acid i.e. pyridine 2, 3 dicarboxylic acid forms a 1:2 complex with Fe (II) at 5.9 pH which absorbs at 420 nm. The complex of cobalt with quinolinic acid has been synthesized and structure has been reported.[39] The following structure of hydrated cobalt (II) complex of quinolinic acid has been reported.[39]



The crystal structure of copper with pyridine 2, 3 dicarboxylic acid has been investigated.[40] Following structure has been reported.



The complex formed by Mn (II) and pyridine 2, 5 dicarboxylic acid has been synthesized and characterized by elemental analysis, IR, electronic spectra, thermo gravimetric analysis and x-ray diffraction techniques.[41] The Mn (II) ion is coordinated by two water molecules and two chelated Pyridine 2, 5 dicarboxylic ligands. Water molecules coordinate with Mn (II) ion in cis mode.



Conductometric and Potentiometric methods of quantitative determination of Aluminum (III), Indium (III), and Lanthanum (III) with pyridine 2, 6 dicarboxylic acids have been reported,[42] Uranium (VI) and Vanadium (III) forms complexes with pyridine 2, 6 dicarboxylic acid which has been used for quantitative determination by conductometric and Potentiometric methods.[43]

Nickel (II) has been determined spectrophotometrically with pyridine 2, 6 dicarboxylic acid. Ni (II) forms 1:2 colored complexes which are stable and independent of pH and its $\lambda_{\max}$ is at 1025 m.[44] Iron (II) has been determined spectrophotometrically with pyridine 2, 6 dicarboxylic acid. Fe (II) forms 1:2 complexes at pH 5.2 and maximum absorption is at 510 nm.[45] Cr (III) forms 1: 2 complexes with pyridine 2, 6 dicarboxylate in aq. Solution. The stability constants of the metals as Ba^{2+}, Ca^{2+}, Cd^{2+}, Ce^{3+}, Co^{2+}, Cu^{2+}, Dy^{3+}, Er^{3+}, Eu^{3+}, Fe^{2+}, Fe^{3+}, Gd^{3+}, Ho^{3+}, La^{3+}, Lu^{3+}, Hg^{2+}, Mg^{2+}, Mn^{2+}, Nd^{3+}, Ni^{2+}, Pb^{2+}, Pr^{2+}, Pr^{3+}, Sm^{3+}, Sr^{2+}, Tb^{3+}, Tm^{3+}, Y^{3+}, Yb^{3+} and Zn^{2+} with pyridine 2, 6 dicarboxylic acid have been reported.

This work is in continuation with the following work that we have already completed. We have developed a method for the spectrophotometric determination of Mn (II) by pyridine2,6 dicarboxylic acid.[46] Synthesis characterizations and spectrophotometric determination of Ni(II) by pyridine2,3 and 2,5 dicarboxylic acid has also been studied.[47,48] Synthesis, characterization, antimicrobial studies and spectrophotometric determination of Mn(II) by pyridine2,3 dicarboxylic acid has been done.[49] We have also carried out studies of some novel chromium pyridine dicarboxylate Complexes.[50]

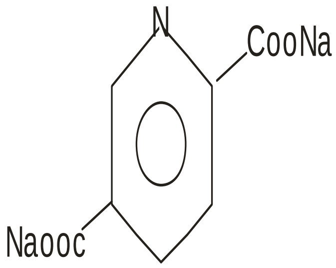
A further literature survey showed that the solution studies of Fe (II) with pyridine 2, 5 dicarboxylic acids have also not been reported.

Therefore a study of complexation of iron (II) metal with pyridine2, 5 dicarboxylic acids and its application for quantitative determination has been carried out. The complex is synthesized and an FTIR study has also been carried out.

MATERIALS AND METHODS

An UV-VIS spectrophotometer-108 equipped with 1cm quartz cell was used for spectrophotometric measurements. The pH measurements were made with an Elico LI 120 pH meter.

The reagent used was pyridine 2, 5 dicarboxylic acid. The substance was dissolved in minimum amount of NaOH and its sodium salt solution was used.



A 0.01 M solution of the ligand was used.

Fe (II) solution

A 0.01 M stock solution of $FeSO_4 . 7H_2O$ prepared by dissolving in distilled water and was made acidic by adding HCl. The pH was maintained by using dilute NaOH and dilute HCl.

Procedure

In each set of different 50 ml standard flasks, various volumes of Fe (II) and reagent solution were taken, the pH was maintained (4.0 to 7.0) and made up to the mark with distilled water. The absorbance was measured at 492 nm against the reagent blank. The calibration curve was prepared by plotting absorbance against the amount of Fe. (II)

RESULTS AND DISCUSSION

(1) Determination of λmax of the complex,

The absorption spectra of Red colored complex solution were recorded in the wavelength region 400-800nm as shown in the fig. It was observed that the complex showed the maximum absorbance at 492 nm where as the reagent blank is colorless solution and does not absorb in the visible region. The absorption spectra of $FeSO_4 . 7H_2O$ has also been recorded. The ferrous sulphate solution is almost colorless and does not absorb in the visible region.

(2)Effect of pH

Studies on the effect of variation in pH shows that the complex has maximum absorption in the pH range.4.0 to 7.0 pH. This is shown in Fig – 1

(2) Effect of time

The Fe (II) – Pyridine 2, 5 dicarboxylate complex forms readily and there after it is stable.

(4)Effect of Temperatur

The Fe (II) complex is stable in the temp. range of 30 – 70^0 C Fig - 3.

(5)The effect of the reagent concentration (PDC) on the complex.

It seems that the complex formation requires the double concentration of the ligand. This is shown in Fig.

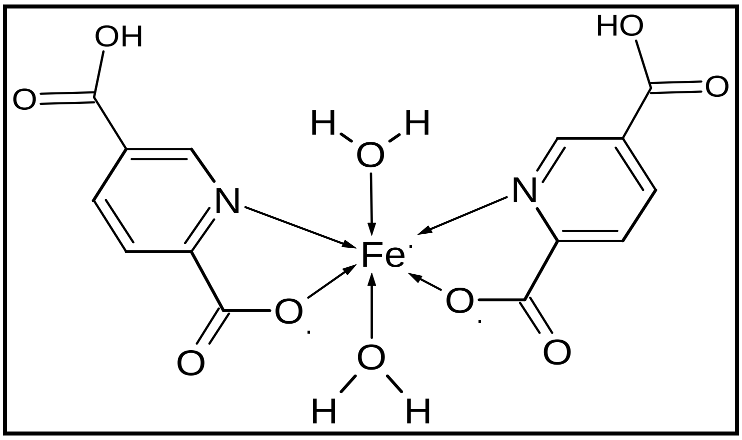
(6) Job’s Method

Composition of the complex as determined by the job’s method and the mole ratio method was found to be 1:1. This is shown in Fig.

(7) The Beer’s Law

The beer’s law is obeyed in the concentration range 225 to 500 μgms of Fe (II). The method that has been developed has moderate sensitivity. Calibration graph Fig – 6.

Solution studies of Fe(II) shows that it forms red colored complex in the range of 4.0 to 7.0 pH with pyridine 2, 5 dicarboxylic acid. The reaction is pH sensitive. The complex formed is stable for few days. Pyridine 2, 5 dicarboxylic acid has proved to be interesting and versatile ligand and may exhibit various coordination modes. Pyridine 2, 5 dicarboxylic acid (2, 5 Pydc H2), being a potential polydentate ligand, has aroused considerable interest of many groups and the literature cites numerous examples of different metal complexes. The Ligand can act as partly or fully deprotonated and shows diverse coordination modes such as monodentate or bridging. It may be due to this reason that contradictory reports for the crystal structure appears in the literature. It is predicted that Pyridine 2, 5 dicarboxylic acid may be forming 1:2 complex with Fe(II) in solution. The following structure may be assigned in solution.



Synthesis and characterization of the complex

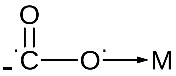
[A] Synthesis of Fe (II) – 2, 5 PDC complexes**.**

10 ml of 0.01 M Fe (II) solution was taken in a container. To this solution 20 ml of 0.01 M pyridine 2, 5 dicarboxylate (Sodium salt) was added. A red colored complex is obtained in one minute of time. The pH of the mixed solution was maintained in between 4.0 to 6.0 pH. The complex precipitate out after ten hours in the pH range 3.5 to 4.0. The complex easily separates out if both the reagent solutions are concentrated. The red colored precipitates obtained in the solution were filtered, washed and dried and FTIR study was carried out.

Vibration Studies

The patterns of IR spectrum show vibrations due to isocinchomeronate ligands.The □□(O-H) vibrations belonging to the H_3O^+ fragments are not observed as bands in the region 3599, 3558, 3474 and 3423 cm^{-1}. Therefore the cation H_3O^+ is absent. The stretching frequencies due to the aromatic rings at 3000 to 3100 cm^{-1} are found. In the IR spectrum of the complex, all the bands involving O – H vibrations of the carboxyl ate are absent, namely the O - H stretching of the COOH groups, the C – OH in plane bonding and out of plane O-H deformation mode, hence showing deprotonation of the COOH group and coordination to the metal. The absorption bands in the region 650 – 780 cm^{-1} are attributed to the vibrations of the co-ordinate pyridine molecules.

The presence of IR bands around 1700 cm^{-1} indicates that all the COOH – carboxylic groups are not deprotonated.

The frequency at 1600, and 1651 cm^{-1} indicates the carbonyl frequency of the carboxyl group which is attached with the metal as -  $\overset{O}{\overset{\|}{C}}-O\rightarrow M$.

The metal – nitrogen (M – N) and metal – Oxygen (M – O) bonds were further confirmed by the presence of the band around 403 cm^{-1} and 528 cm^{-1}.
The presence of IR bands around 1700 cm^{-1} indicates that all the COOH – carboxylic groups are not deprotonated.

The frequency at 1600, and 1651 cm^{-1} indicates the carbonyl frequency of the carboxyl

□□□**Fe-N**	□□□**Fe-O**
403 cm^{-1}	528 cm^{-1}

It is reported that Fe (II) and Ni (II) forms 1:2 complex with pyridine 2, 6 dicarboxylic acid. The structure of Fe (II) PDC 2, 6 complexes has also been reported.[51,52] Based on the above discussed evidences, the above shown structure may be predicted.

Effct of eforeign ions in the spectrophotometric studies

The presence of diverse ions on the determination of Fe (II) with PDC2, 5 has been studied under optimum conditions developed for the determination of Fe (II).

A series of determinations of Fe (II) are carried out in the presence of a number of foreign ions.

The alkali metals such as Na^+, K^+ and Li^+ does not interfere in the iron(II) determination even when present 10 times excess to that of Fe(II) ion concentration. Similarly NH_4^+ ion does not interfere even when present 10 times excess to that of Fe (II).

A marked change in the absorption of Fe (II) PDC2, 5 complex has been observed when the concentration of foreign ions such as Cr (III) and Hg (II) is same or ten times lower than that of Fe (II). Hg (II) strongly interferes even when present in lower concentration than Iron. Cr (VI) is not found to interfere when present in same concentration as that of Fe (II). Vanadium (III) precipitates when present in higher concentrations. Zn (II) gives white precipitates in the solution with pyridine2, 5 dicaoboxylic acid.

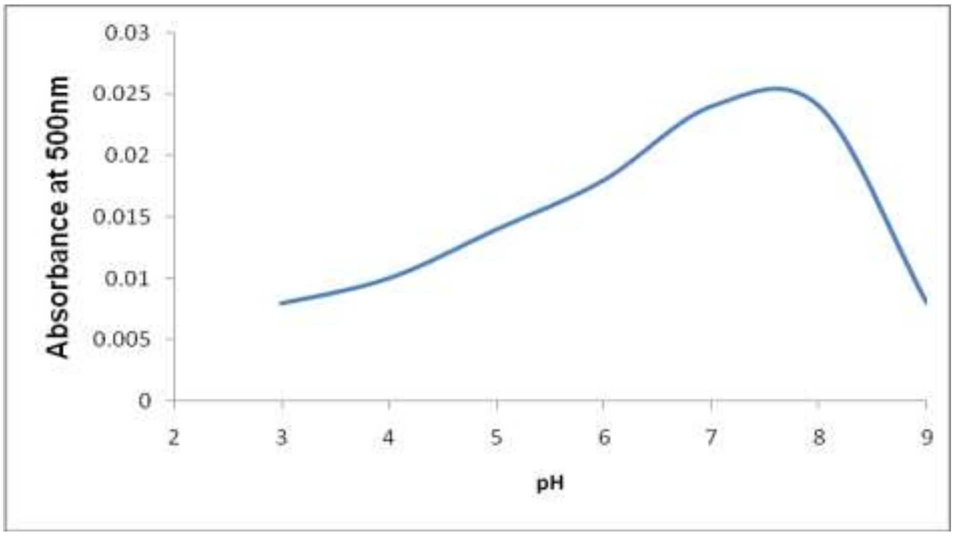
Cl^-, Br^-, I^- does not interfere in the determination even when present 10 times or large excess in Fe (II). Sulphate and carbonate does not interfere even when present in large excess.

Validity of the method

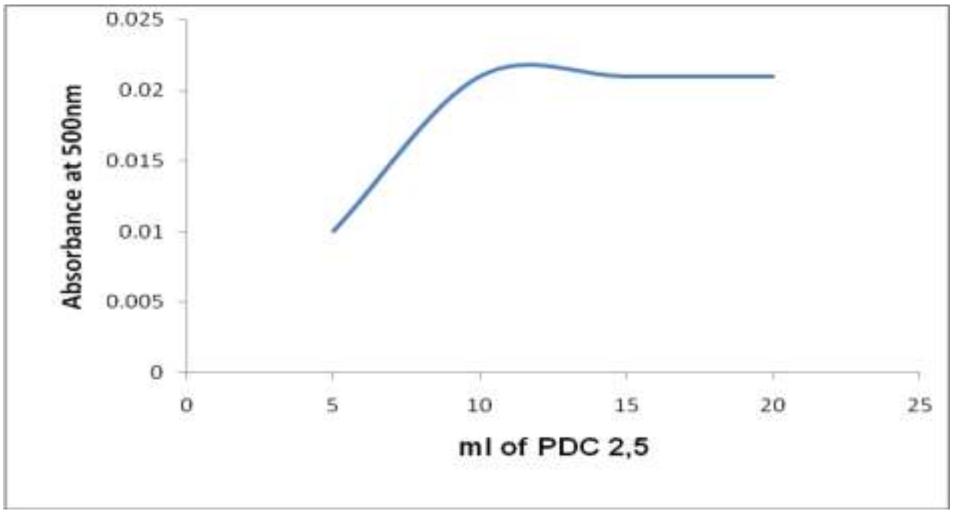
A number of synthetic samples in the range of 250 – 550 µg of Fe (II) are prepared and determined with the help of calibration graph

Sr. No.	Conc. Of Fe (II) taken µg	Absorbance	Conc. of Fe (II) found µg	Relative error
1	224	0.010	216	3.8%
2	280	0.018	290	3.4%
3	336	0.024	347	3.2%
4	392	0.029	400	2.1%
5	448	0.034	456	1.8%
6	504	0.039	513	1.5%

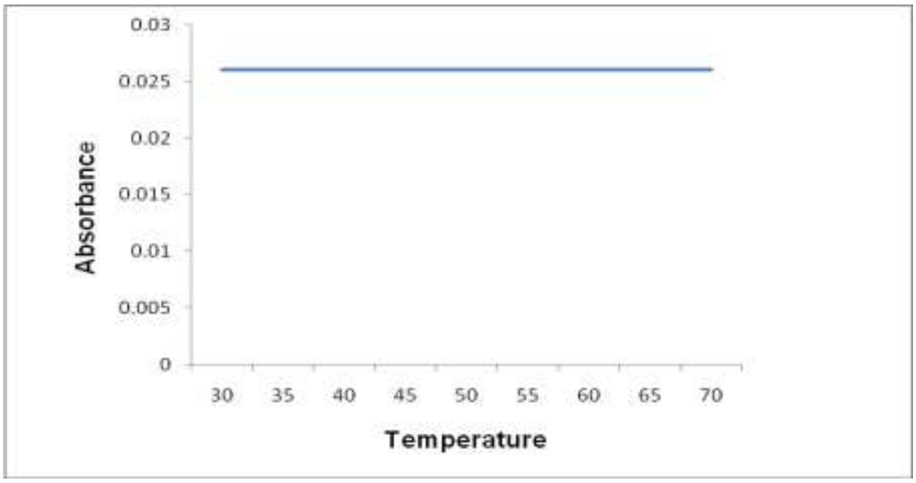
The percentage error for each determination has been calculated and is found to be in the range of 2 to 3.8%. The error decreases with the increase in the analyte concentration.



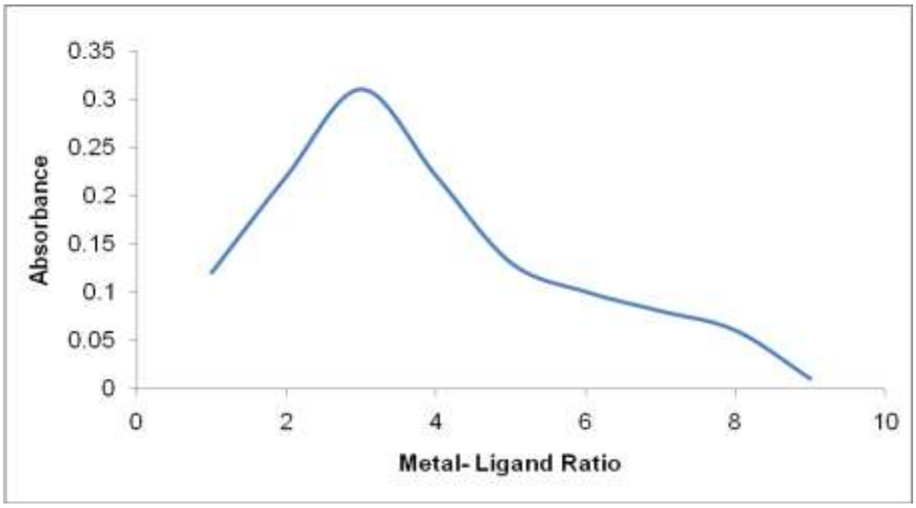
Effect of pH on Fe(II)-PDC complex formation



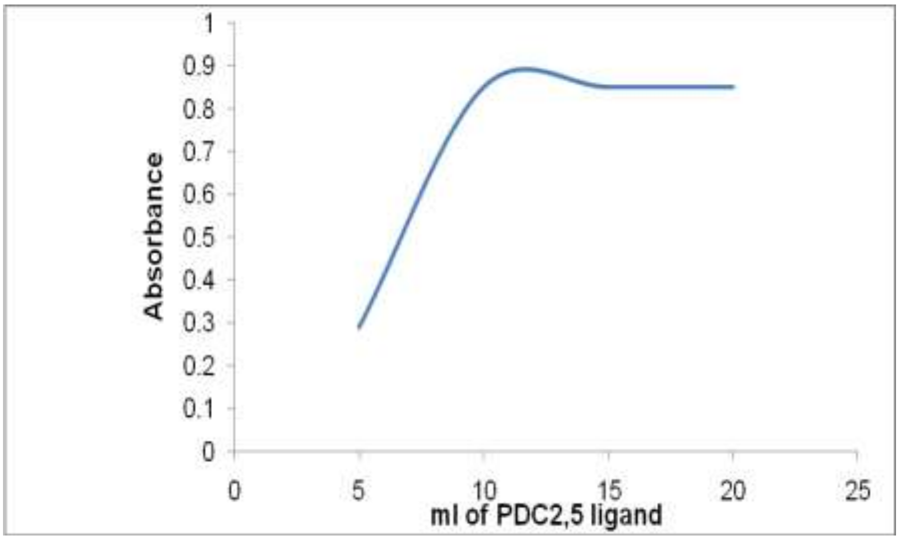
Effect of PDC 2,5 concentration on the complex



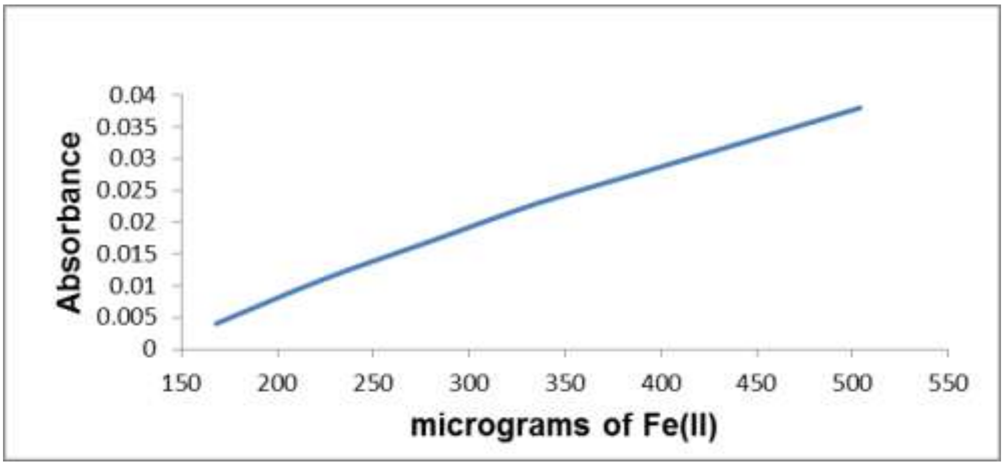
Effect of temperature on the Fe(II)-PDC 2,5complex



Plot of job' curve for Fe(II)-PDC2,5 complex



l fmole-ratio curve for Fe(II)-PDC complex



Beer's Law Graph

CONCLUSION

The results from this study show that proposed work is simple, rapid and sensitive for the determination of Iron (II). No extraction step is required and hence, the use of organic solvents, which are generally toxic pollutants, is avoided.

Studies indicates that Iron (II) - pyridine 2,5dicarboxylate complex may have either octahedral or distorted octahedral geometries. The metal – nitrogen (M – N) and metal-Oxygen (M – O) bonds were further confirmed by FTIR studies.

ACKNOWLEDGEMENT

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