

Spectrophotometric determination of Mn (II) ion by Pyridine 2, 6 dicarboxylic acid.

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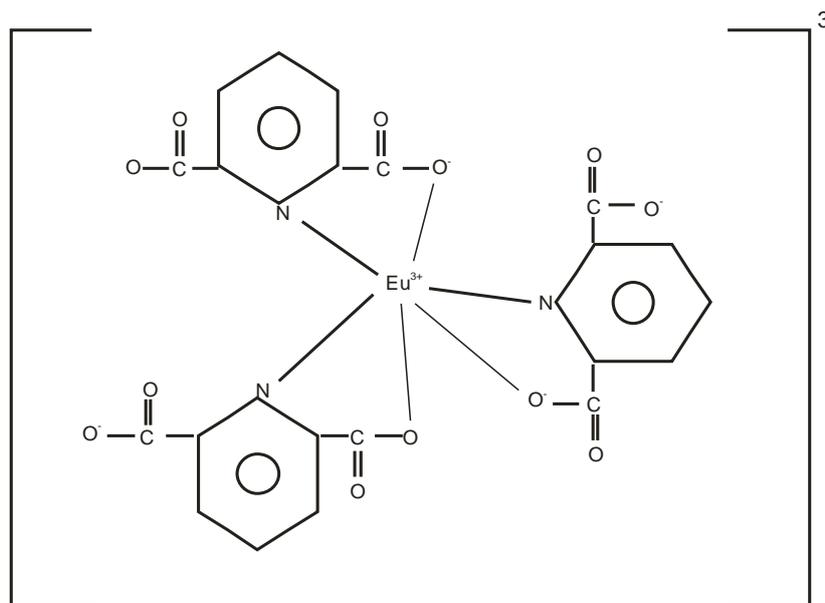
ABSTRACT: A new Spectrophotometric method is developed for the determination of Mn (II) in an aqueous solution. The metal ion forms a pink colored complex with pyridine 2,6 dicarboxylic acid in acidic medium i.e. at pH 1.5 to 2.5. The complex shows maximum absorbance at 500 nm. Job's method for continuous variation and mole ratio method shows metal ligand ratio in the complex to be 1:1. The complex is stable after 2.0 minutes. The pink colored complex obeys the Beer's law in the concentration range of 50 to 225 μg s of manganese. The molar absorptive (E) is found to be $9.89 \times 10^2 \text{ l mole}^{-1} \text{ cm}^{-1}$. The method has been used for the determination of Mn^{+2} in synthetic samples.

Keywords: Pyridine-2,6-dicarboxylic acid, Mn (II) complex, spectrophotometry

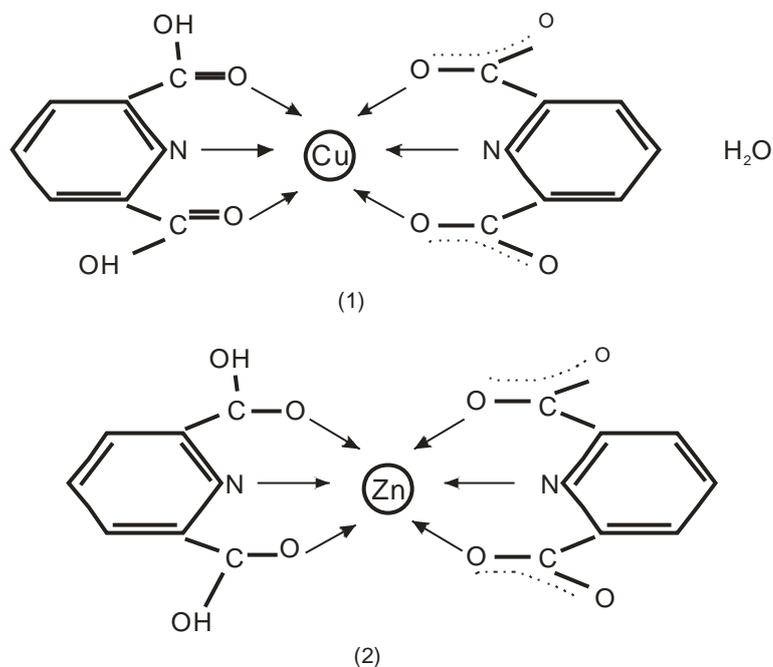
I. INTRODUCTION

Pyridine 2, 3-, 2, 4-, 3, 4-, 2, 5-, 2, 6- dicarboxylic acids have proved to be interesting and important ligand and may exhibit various co-ordination modes. Pyridine 2, 6- dicarboxylic acid can act as partly or fully deprotonated and shows diverse coordinatin 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 modes¹⁻⁵. It is also reported that this ligand is used to develop more effective anti HIV agents⁶⁻⁸.

Europium aquoions 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 reported⁹. These complexes have distorted octahedral geometries.



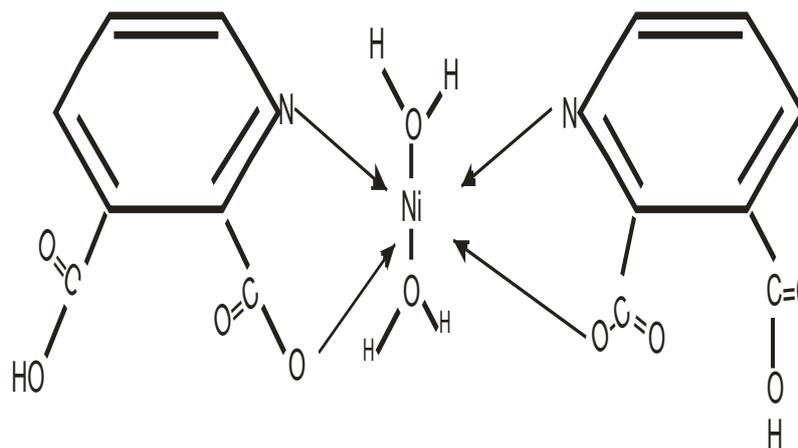
The complexes of Cobalt (II), nickel (II), rhodium (II) and rhodium (III) has been synthesized and their spectral and magnetic properties been studied¹⁰. Nickel is reported forming 1:2 complex i.e. Ni(dpCH)₂ • 3H₂O. Cobalt forms 1:1 complex i.e. Co (dpc) • 3H₂O which is six coordinate and contain co-ordinate water. Anhydrous polymeric [Co-(dpc)]_n has also been reported¹⁰. Rhodium (II) and rhodium (III) forms Rh(dpc).3H₂O and Na [Rh(dpc)₂].2H₂O 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 crystallography¹¹. These dimeric complexes have been reported to have hexa coordinated environment with two different type of donor atoms i.e. nitrogen and oxygen¹¹. Manganese (II) has been reported to form a dinuclear complex i.e. hexaaquabis (Pyridine – 2, 6 – dicarboxylato) dimanganese (II) complex¹². 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 possess a distorted pentagonal bipyramidal coordination¹².

Chromatographic separation of transition metals by pyridine 2, 6 dicarboxylic acid (used as eluent) has been reported. The metals (Cu, Ni, Zn, Co, Cd, Mn) are separated as anionic chelates¹³.

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 potentiometrically¹⁴. Lanthanum, Dysprosium and Gadolinium (La, Dy, Gd) reacts with 2, 6 pyridine dicarboxylic acid in aqueous alkaline solution to give Ln (Pdc) (HPdc) m.H₂O. The thermal dehydration of these lanthanum compounds have been studied¹⁵. The study of complex formation of Dysprosium (III) and pyridine 2, 6 dicarboxylic acid has been reported¹⁶. Electron Spin Resonance studies of complexes of silver (I) and copper (II) with pyridine 2, 6 dicarboxylic acid have been reported¹⁷.

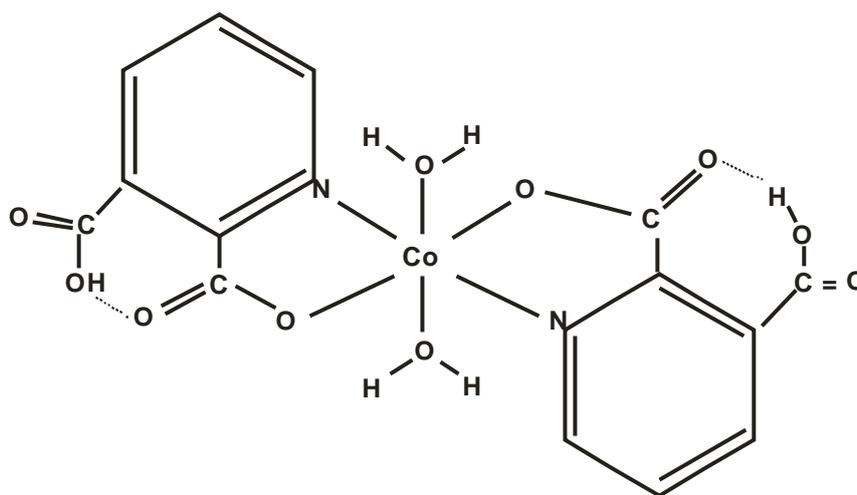
The complex of copper with pyridine 2, 3- dicarboxylic acid i.e. [Cu (2, 3- pydcH)₂] has been reported¹⁸. It is a chain polymer. Two ligand occupy the equatorial plane of each tetragonally elongated Cu⁺² coordination sphere, chelating through the pyridine nitrogen and one oxygen of the deprotonated 2- 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 data¹⁹. 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 ligands¹⁹.

The complexes of the type M (H-Quin)₂.2H₂O (M = Mn, Co, Ni and Zn) where H₂ – Qin = Quinolinic acid i.e. Pyridine 2, 3 dicarboxylic acid have been prepared and characterized²⁰. 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 molecules²⁰. The structure of Ni(II) with quinolinic acid can be represented as.

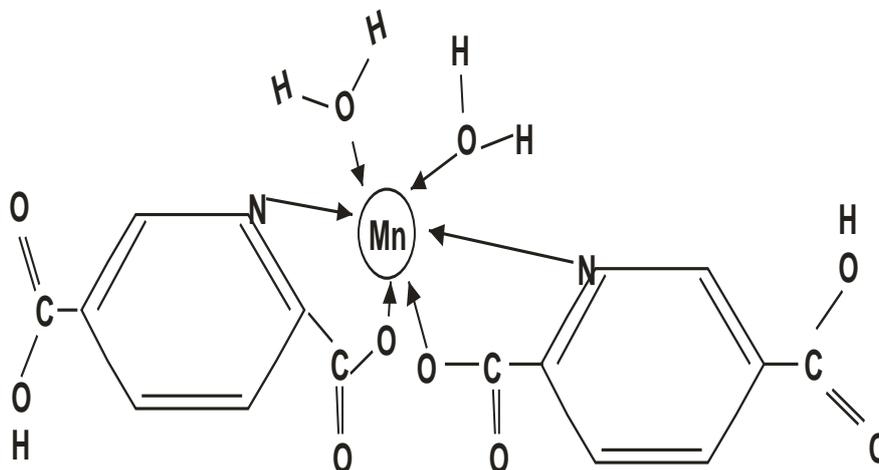


The complex $\text{Mn}(\text{H-Quin})_2 \cdot 2\text{H}_2\text{O}$ has been formulated as $[\text{Mn}(\text{H}_2\text{O})_6][\text{Mn}(\text{H-Quin})_3]_2$. The octahedral $[\text{Mn}(\text{H-Quin})_3]^-$ and $[\text{Mn}(\text{H}_2\text{O})_6]^{2+}$ units lie on different three fold axis.²⁰ Lanthanide (III) quinolate complexes have been prepared and reported and evidence is presented which indicates that these complexes may be six-coordinated.²¹ Calcium (II) complexes with pyridine 2, 3- dicarboxylate (Quinolinic acid) has been synthesized and crystal structure has been reported²². The complexes of uranium (IV) with quinolinic acid has been synthesized and reported²³. Two types of complexes of cadmium with quinolinic acid has been synthesized and reported²⁴. They are $[\text{cd}(2, 3 \text{ pydcH}_3)[\text{cd}(\text{H}_2\text{O})_6]$ and $[\text{cd}(2, 3 \text{ pydc})(\text{H}_2\text{O})_3]_n$. The chromium (III) – quinolinato complexes $[\text{Cr}(\text{quinH}_3)]^{+3}$, $[\text{Cr}(\text{QuinH})_2(\text{H}_2\text{O})_2]^+$ and $[\text{Cr}(\text{quinH})(\text{H}_2\text{O})_4]^{2+}$ have been obtained and characterized in solution²⁵.

The structure of some Cu(I), Ag(II) and Cu(II) compounds with quinolinic acid have been established based on X-ray crystallographic studies.²⁶⁻²⁸ In each case, quin is bonded as a monoanion through pyridine nitrogen and carboxylate 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)²⁹⁻³² though no structural studies were conducted. The spectrophotometric evaluation of iron (II) quinolinic acid complex (1:2) metal ligand system has been reported³³. The complex of cobalt with quinolinic acid has been synthesized and structure has been reported³⁴. The following structure of hydrated cobalt (II) complex of quinolinic acid has been reported³⁴.



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 techniques³⁵. The Mn(II) ion is coordinated by two water molecules and two chelated Pyridine 2, 5 dicarboxylic ligand. Water molecules coordinate with Mn(II) ion in cis mode.



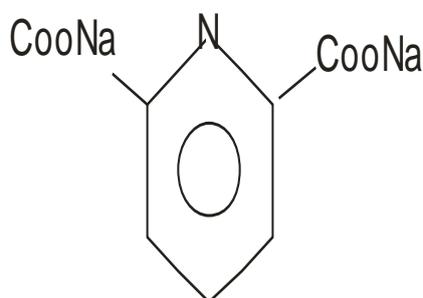
Conductometric and potentiometric methods of quantitative determination of Aluminium (III), Indium (III), and Lanthanum (III) with pyridine 2, 6 dicarboxylic acid has been reported³⁶. Uranium (VI) and Vanadium (III) forms complexes with pyridine 2, 6 dicarboxylic acid which has been used for quantitative determination by Conductometric and potentiometric methods³⁷. Nickel (II) has been determined spectrophotometrically with pyridine 2, 6 dicarboxylic acid. Ni (II) forms 1:2 colored complex which is stable and independent of pH and its λ_{max} is at $1025 \text{ m}\mu$ ³⁸. Iron (II) has been determined spectrophotometrically with pyridine 2, 6 dicarboxylic acid. Fe (II) forms 1:2 complex at $\text{pK} > 52$ and maximum absorption is at 510 nm ³⁹. Cr(III) forms 1: 2 complex 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.

A further literature survey showed that the solution studies of Mn(II) has not been reported. A study of complexation of Mn(II) with pyridine 2, 6 dicarboxylic acid and its application for quantitative determination have been carried out.

II. 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, 6 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.

Mn (II) solution :- A 0.01 M stock solution of $\text{MnCl}_2 \cdot 4\text{H}_2\text{O}$ 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 Mn (II) and reagent solution were taken, the pH was maintained (1.5 to 2.5) and made up to the mark with distilled water. The absorbance was measured at 500 nm against the reagent blank. The calibration curve was prepared by plotting absorbance against the amount of Mn. (II)

III. RESULTS AND DISCUSSIONS

(1) Determination of λ_{max} of the complex,

The absorption spectra of pink colored complex solution were recorded in the wavelength region 400-900nm as shown in the fig. It was observed that the complex showed the maximum absorbance at 500 nm where as the reagent blank is colorless solution and does not absorb in the visible region. The absorption spectra of $\text{MnCl}_2 \cdot 4\text{H}_2\text{O}$ has also been recorded. The λ_{max} of $\text{MnCl}_2 \cdot 4\text{H}_2\text{O}$ occurs at 472 nm. The λ_{max} of complex is shown in Fig 1.

(2) Effect of pH

Studies on the effect of variation in pH shows that the complex has maximum absorption in the pH range.1.5 to 2.5 pH. This is shown in Fig – 2.

(3) Effect of time :-

The Manganese (II) – Pyridine 2, 6 dicarboxylate complex takes 2.0 minutes to complete the reaction and there after it is stable.

(4) Effect of Temperature

The Mn (II) complex is stable in the temp. range of 30 – 70⁰ C Fig - 3.

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

It seems that the complex formation requires the same concentration of the ligand This is shown in Fig – 4.

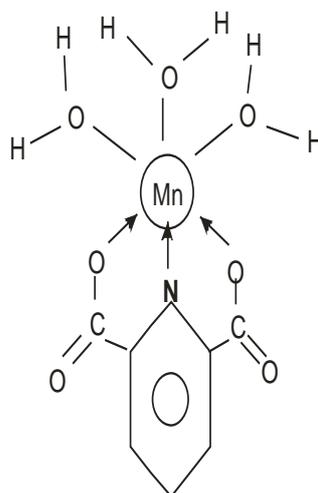
(6) Job's Method

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 – 5.

(7) The Beer's Law

The beer's law is obeyed in the concentration range 50 to 225 μ gms of Mn (II). The method that has been developed has moderate sensitivity. Calibration graph Fig – 6.

Solution studies of Mn(II) shows that it forms pink colored complex in the acidic pH with pyridine 2, 6 dicarboxylic acid. The reaction is pH sensitive. The complex formed is stable for days. Pyridine 2, 6 dicarboxylic acid has proved to be interesting and versatile ligand and may exhibit various coordination modes. Pyridine 2, 6 dicarboxylic acid (2, 6 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^{1, 3, 4, 19}. It is predicted that Pyridine 2, 6 dicarboxylic acid may be forming 1:1 complex with Mn(II) in solution. The following structure may be assigned in solution.



IV. EFFECT OF FOREIGN IONS IN THE SPECTROPHOTOMETRIC STUDIES

The effect of various anions and cations on the determination of Mn(II) under optimum conditions was studied. It was noticed that Cu^{+2} , Fe^{+2} , Ni^{+2} and Ba^{+2} interfere only when present in the same concentration range. They do not interfere when present in ten fold less concentration than the analyte solution. Ions such as V^{+3} , Sn^{+2} , K^+ , Na^+ , NH_4^+ , Zn^{+2} , Cl^- , Br^- , SO_4^{2-} , CO_3^{2-} , F^- does not interfere even when present in large excess. (i.e. ten fold excess)

Validity of the method;

A number of synthetic samples were prepared for the analysis. Spectrophotometric determination was carried out by the proposed method. The results are given in the table.

Sample	Mn(II) taken μgs	Abs Average	Mn(II) found μgs	Relative error %
Synthetic Sample – 1	55	0.108	54	-1.8
Synthetic Sample – 2	110	0.224	112	+1.8
SyntheticS-3	220	0.43	215	+2.2

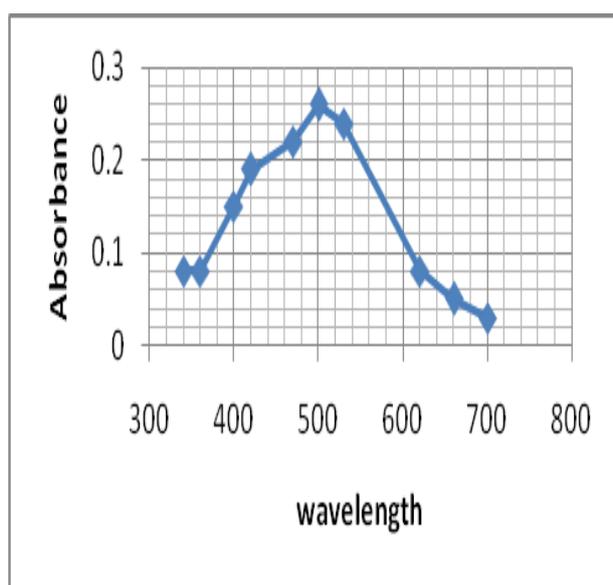


Fig: 1 Absorption spectra of the complex

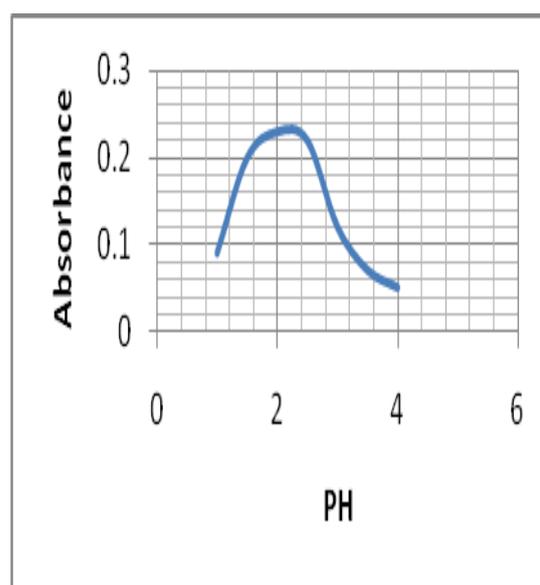


Fig: 2 Effect of PH

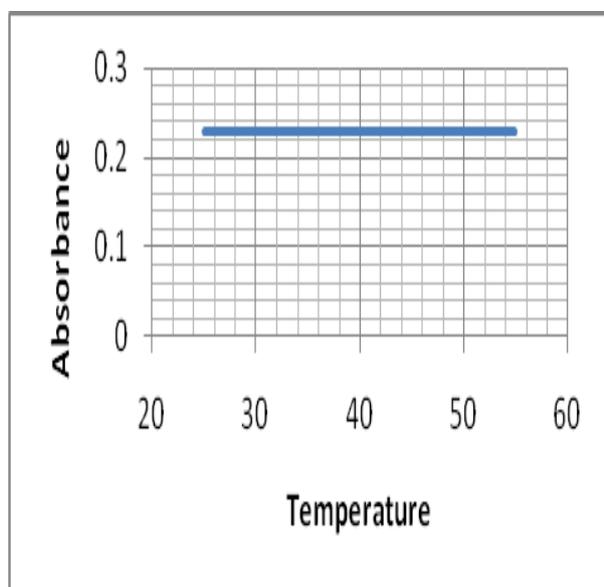


Fig: 3 Effect of temperature

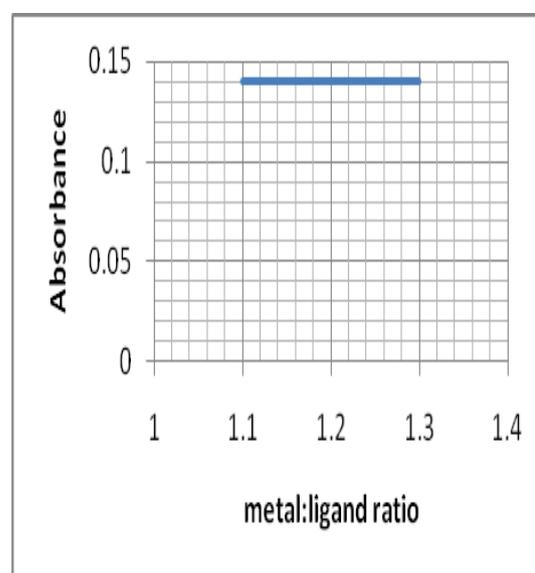


Fig: 4 Effect of ligand con.

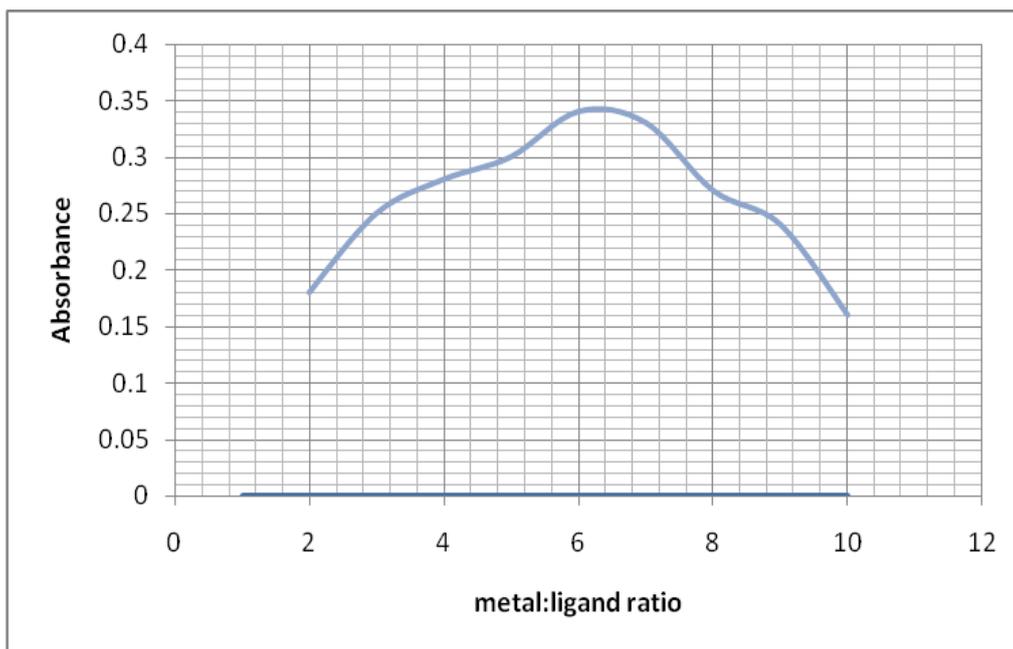


Fig: 5 Jobes method (1:9 to 9:1 M; L ratio)

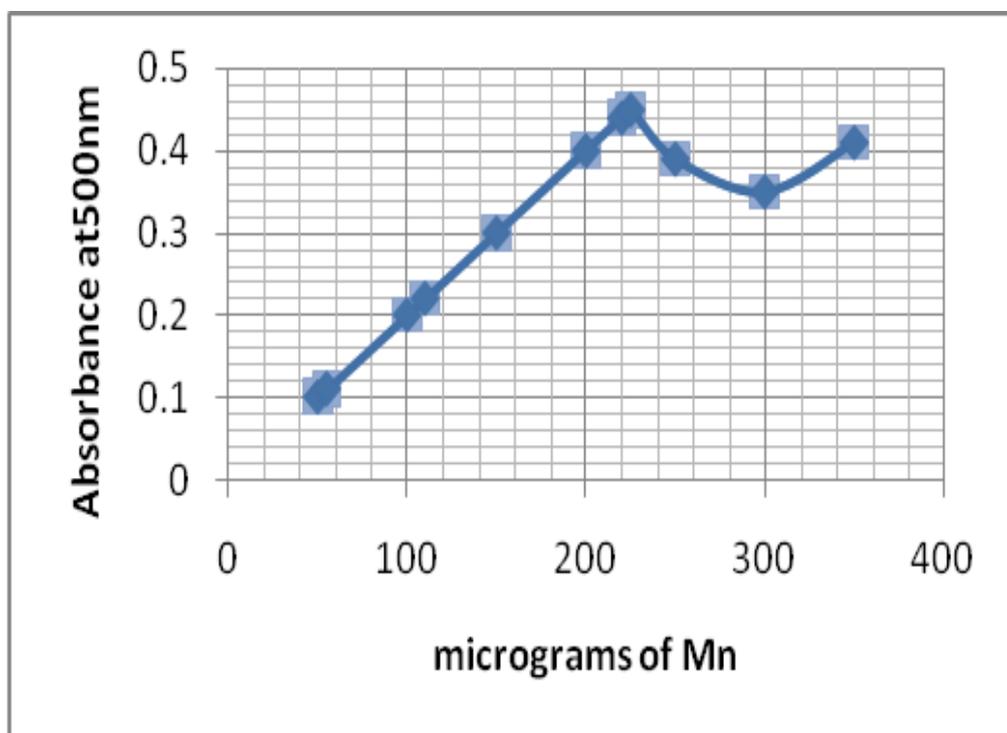


FIG: 6 Beers Law graph

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