



Complexation of 1,4-bis (3-(2-pyridyl) pyrazol-1-ylmethyl) benzene (1,4-PPB) with Cu (II), Co (II), and Ni (II): Spectrophotometric Studies in Mixed Solvent (EtOH-H₂O)

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Abstract: The stability and composition of the complexes of 1,4-bis (3-(2-pyridyl) pyrazol-1-ylmethyl) benzene (1,4-PPB) with Cu (II), Co (II), Ni (II): have been investigated using spectrophotometric method in mixed (1:1) solvent of ethanol and water. Various experimental parameters, which include pH, ionic strength, solvent composition, and time, have been studied. The stoichiometry and formation constant of each complex have been evaluated using Job's method. Spectrophotometric results show the formation of 1:1 complexes with stability order of Co > Ni > Cu. Molar absorptivity values of the complexes have also been determined.

Keywords: Pyrazole Based Ligands, Spectrophotometry, Cu, Co, Ni.

Subject Classification: Inorganic Chemistry, Complexation in Solutions

Type (Method/Approach): UV-VIS Spectrophotometric Study of Metal ion Complexes

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Introduction

The study of metal complexes with pyrazole based ligands has a practical and theoretical significance because of their biological, medicinal, and agricultural applications [1,2]. They are used in some products that have potential antitumor activity [3,4]. Also, they are used in agriculture as pesticides [5,6]. Those ligands containing unsaturated nitrogen atoms from pyrazole and pyridine rings could be regarded as soft Lewis bases. They have a high tendency to form stable complexes with many transition metal ions, especially those metals which are considered to be as soft Lewis acids [7].

UV-Visible absorption is used to monitor titrations and to study the composition of complex ions [8-10]. Spectrophotometry is a valuable tool for determining the composition of complex ions in solution and for determining their formation constants. The power of the technique lies in the fact that quantitative absorption measurements can be performed without disturbing the equilibria under consideration.

The study of complex formation in aqueous and non-aqueous media is considered to be an efficient tool to design a number of analytical systems like potentiometric sensor [11], bulk and supported liquid membrane transport [12], optical sensor [13], solid phase and cloud point extraction [14]. Different methods can be used to study the composition and formation constants of the complexes; such as: spectrophotometric [15], potentiometric [16], conductometric [17], and kinetic methods [18].

The stoichiometry and formation constant of metal complexes are frequently determined from the spectrophotometric measurements and the analytical data are treated using various methods. These methods include Job [19], Yoe and Jones [20], and other methods as well as stoichiometric [21] and non-stoichiometric [22] dilution methods.

In our previous work, we have studied the effect of solvents and pH on absorption spectra of pyrazole based ligands [23,24]. In the present study, spectrophotometric investigations of complexation between 1,4-bis(3-(2-pyridyl)pyrazol-1-yl)methyl benzene (1,4-PPB) and Cu (II), Co (II), and Ni (II) were studied and the formation constants were determined.

Materials and Methods

Preparation of ligand

The ligand was prepared by reaction of 3-(2-pyrazol-1-yl)pyridine with 1,4-bis(bromomethyl)-benzene under basic conditions by the procedure described elsewhere [25,26].

Spectrophotometric measurements

The UV absorption spectra were recorded in the range from 200 to 400 nm in mixed solvent (1:1 – ethanol: water) using the Agilent Cary 60 UV-Vis Spectrophotometer. Spectra were recorded at 25°C.

Preparation of complex solutions

The stock solution of PPB was prepared by dissolving 0.0300 – 0.0400 g in 25 ml of a solvent. 1.00×10^{-3} M stock solutions of Cu (II), Co (II), Ni (II) were prepared by dissolving an appropriate amount of chloride metal in 25 ml milli-Q water. Other standard solutions were prepared by dilution of stock solution with mixed solvent (1:1 EtOH:H₂O). Each metal complex solution was prepared by mixing the desired volume of ligand and metal solutions and the final volume was made by the mixed solvent.

pH measurements

The pH measurements were performed using an Jenway pH 3505 pH meter. The pH of the solution was adjusted by 0.10 M HCl and 0.10 M NaOH.

Reagents

All chemicals used were analytical-reagent grade, and deionized water (or pure ethanol) was used for preparation of solutions. Reagent grade metal chlorides of copper, cobalt, and nickel (all from Merck) were used without any further purification. Ethanol was HPLC or spectroscopic grade (99.9 %) and used without further purification. The Milli-Q water was used in this study.



Results and Discussion

The structure of 1,4-PPB is shown in Figure 1. The electronic absorption spectra of Cu (II), Co (II), and Ni (II) complexes with 1,4-PPB are shown in Figure 2. The free ligand has an absorption maximum (λ_{max}) wavelength at 281 nm. Upon chelating with metal ions, the absorption maxima (λ_{max}) were shifted to 296, 291, 292 nm for Cu (II), Co (II), and Ni (II) complexes, respectively.

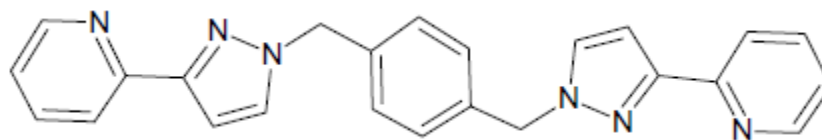


Figure 1. Structure of 1,4-bis (3-(2-pyridyl) pyrazol-1-ylmethyl) benzene (1,4-PPB)

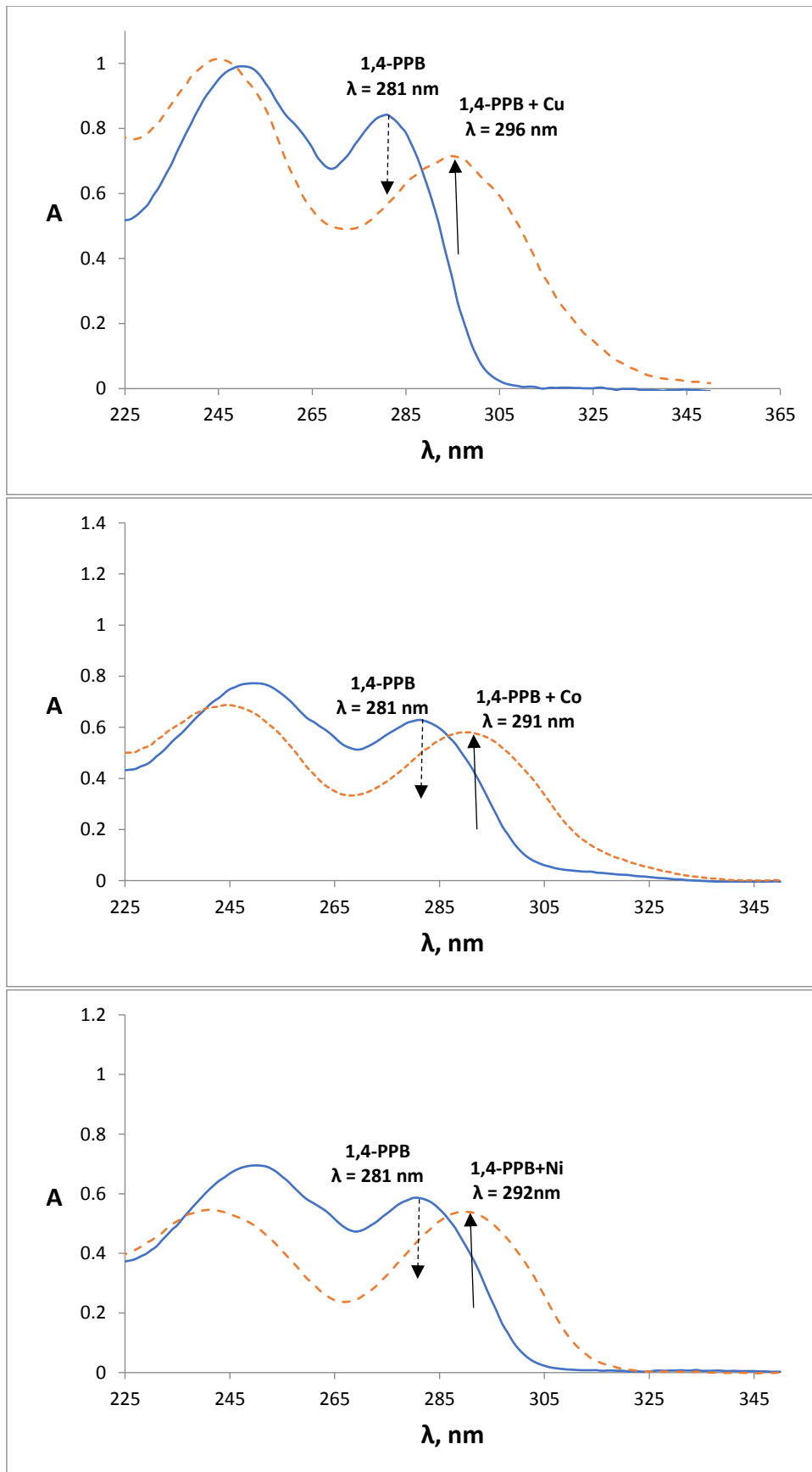


Figure 2. The spectra of free 1,4-PPB and 1,4-PPB metal complexes in mixed solvent (1:1)



The absorption maximum around 280 nm is due to pyrazole-pyridyl system in the ligand which include $\pi \rightarrow \pi^*$ and $n \rightarrow \pi^*$ transitions. The energy levels n , π , π^* are affected by complexation and therefore the absorption maximum have been shifted. Various parameters could affect the complex formation, which include: pH, ionic strength, time, and the solvent, should be studied. These parameters and their effects on the stability of our complexes have been investigated.

Solvent Effect

The impact of water on the stability of the complexes have been examined utilizing distinctive ethanol to water proportions. In general, as the water percent expands, the complex absorption decreases as shown in Figure 3. This could be a result of the dissociation of the complex in aqueous medium. With nickel complex, the absorption achieved a maximum at 50 % water after that begin to diminish. The water influences the complexation in two ways: firstly, because the water itself is a complexing agent and could replace our ligand. Secondly, the water as a solvent can form a hydrogen bond with nitrogen lone pairs in pyrazole and pyridine rings and therefore the ligand could lose the ability to coordinate with metal ions. Also, the absorption maxima of the complexes are blue shifted (about 2 nm)

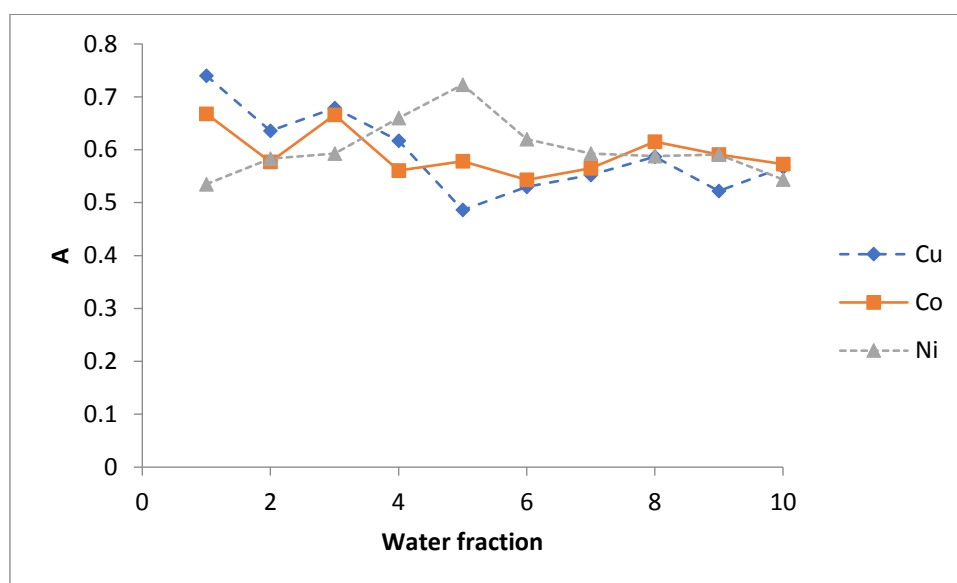


Figure 3. Effect of water fraction on absorption maxima of metal complexes

Time Effect

The study of the complex stability with time is an essential parameter since some complexes are not so stable and could dissociate after generation. The two components (metal ion and ligand) are mixed at room temperature, and the absorbance is measured directly. To examine whether the complex being dissociated or still created with time, the absorption of the complex is measured each 15 min and till 200 min as shown in Figure 4. The absorbance of our complexes remains stable with time indicating the stability of our complexes.

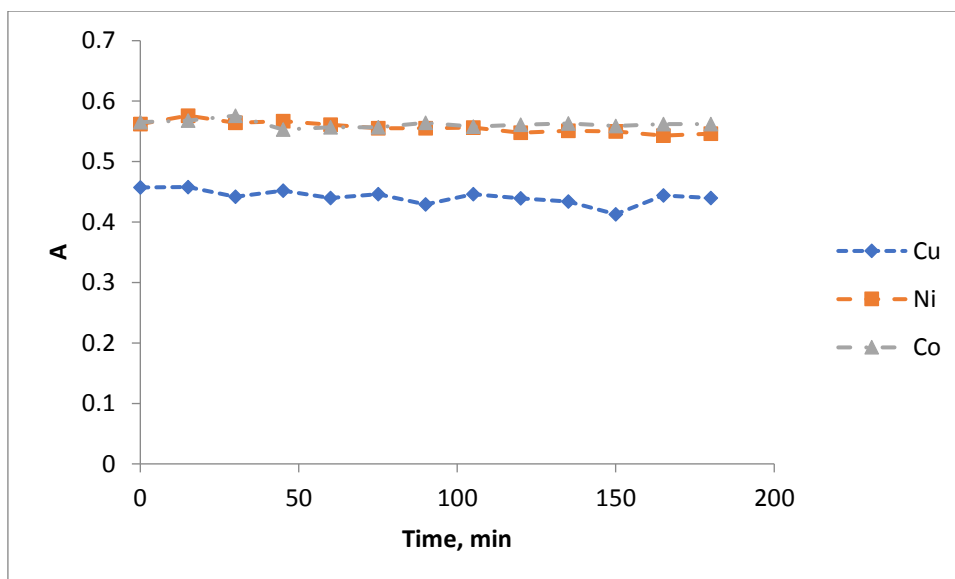


Figure 4. Effect of time on absorption maxima of metal complexes

Ionic Strength Effect

The effect of ionic strength on the complex formation was studied using different concentrations of sodium chloride (from 0.005 – 1.0 M). The absorption of the complex is measured with each ionic strength and shown in Figure 5. No effect of the ionic strength on complex formation can be detected

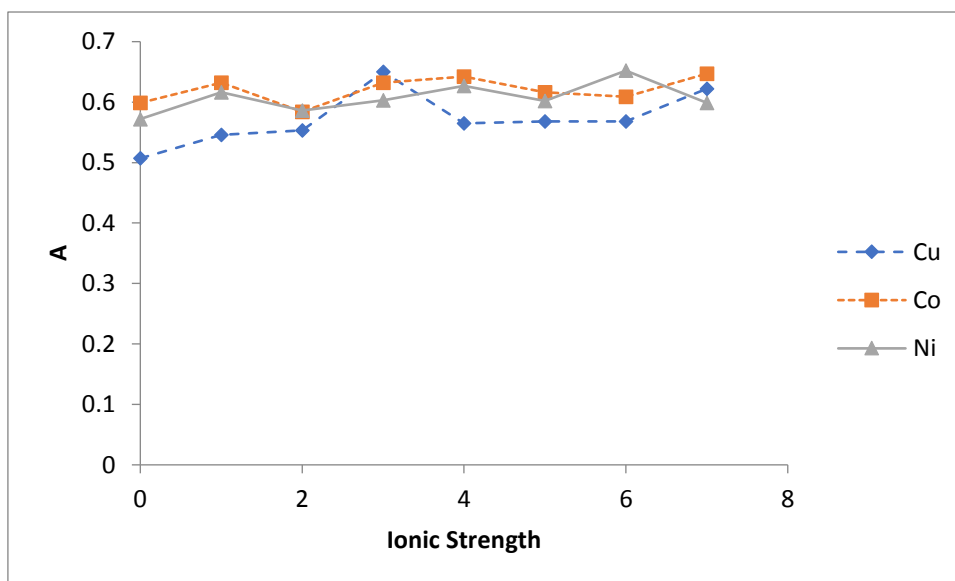


Figure 5. Effect of ionic strength on absorption maxima of metal complexes

Effect of pH

The spectra of metal complexes (Cu, Co, and Ni) were recorded at different pH values. pH values were adjusted using 0.1 M HCl and 0.1 M NaOH solutions. The pH is a very important parameters that affect the metal complex formation because of all ligands are weak acids or weak bases which can be protonated or de-protonated depending on the pH of the solution. Our ligand (1,4-PPB) is considered to be a weak base [24] and can be protonated at pH value of (2-3). The protonation of the ligand will limit its ability to complex with metal ion by making the nonbonding electron-pairs unavailable for complexation and therefore diminishing the tendency to form complexes with the metal ions. Therefore, the complex formation equilibria could be affected by pH value of the solution. The optimum value for complexation of our ligand



would be at $\text{pH} > 5$. The second factor that control the optimum pH for complexation is the precipitation of metal ion as hydroxide at higher pH . The absorption of the complex at different pH values is shown in Figure 6. As can be seen from the figure, the best pH values were: 4.0 – 4.5 for Co (II), 5.5 – 6.0 for Cu (II), and 4.5 -5.0 for Ni and these values are given in Table 1.

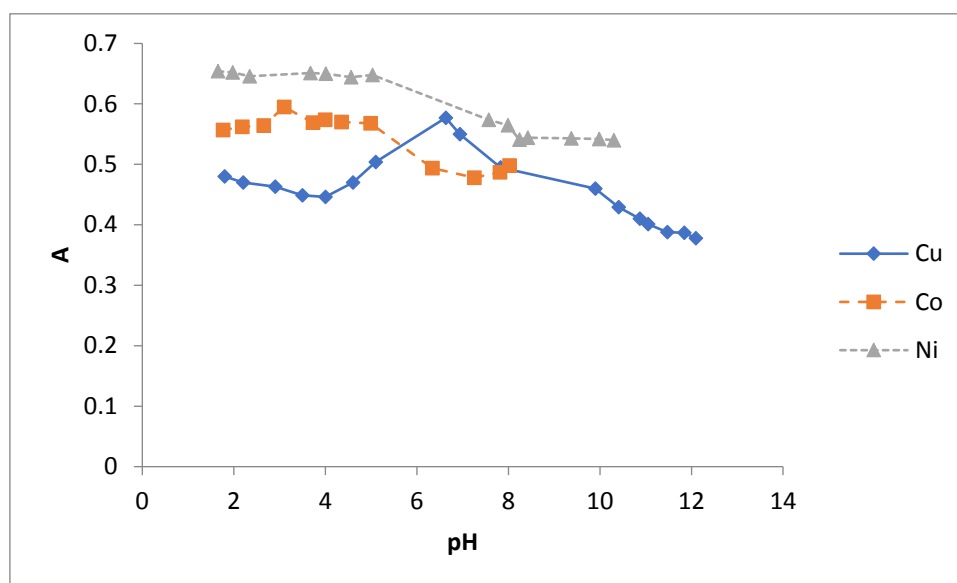


Figure 6. Effect of pH on absorption maxima of metal complexes

The Composition of the Complexes and their Formation Constants (K_f)

The composition of our complexes was determined by the “Job's” method (method of continuous variation). Nine solutions with a final volume of 10 ml were prepared using the same concentration of metal ion and ligand of 10^{-4} M solutions. Each solution contains different fraction of each constituent. Starting from the first solution which contain 1 ml of metal ion solution and 9 ml of 1,4-PPB solution to the final one with 9 ml of metal ion and 1 ml of 1,4-PPB solution. The absorbance of each mixture was measured at the appropriate wavelength. These absorbance values for each mixture were plotted against ligand mole fraction and the stoichiometry of each complex was determined. Also, the formation constant of each complex was determined using Job's plot. Job's plot for each complex is shown in Figure 7. The molar absorptivity ϵ of the complex can also be determined using Job's method by calculating the concentrations of the complex at each point and plotting the concentration against the absorbance as shown in Figure 8. The complex stoichiometry, formation constant, and molar absorptivity values are given in Table 1.

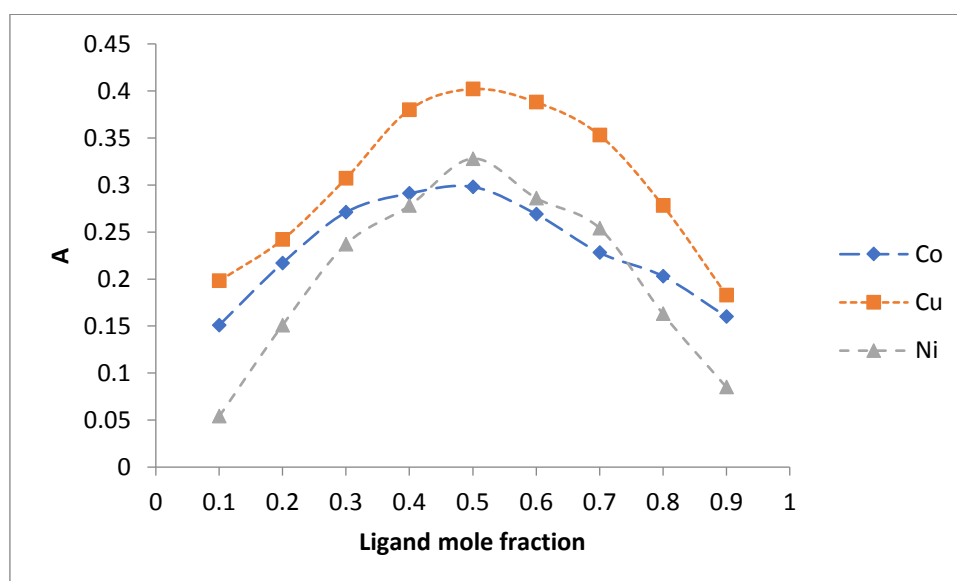




Figure 7. Job's plot for metal complexes

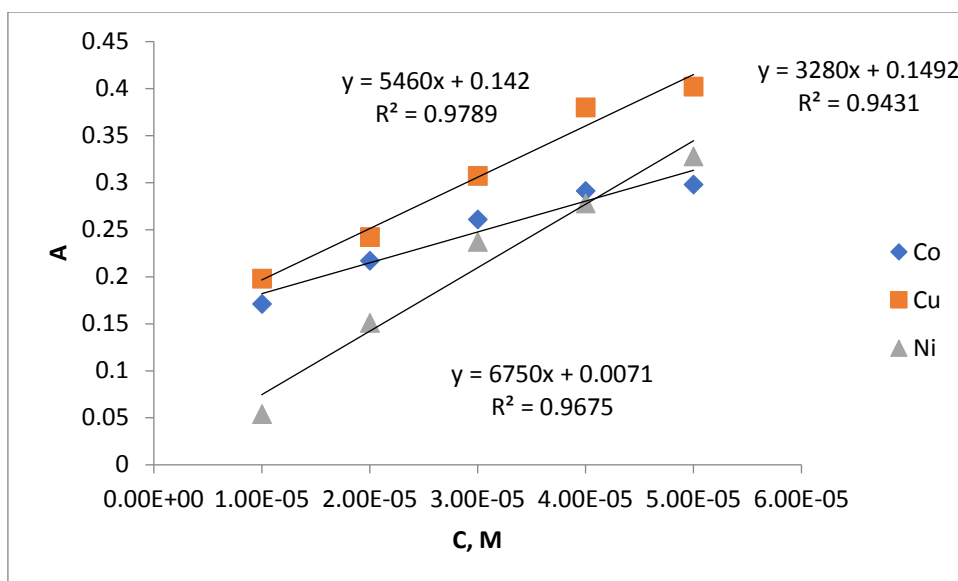


Figure 8. Calibration curve for each metal complex

Table 1. Metal ion complexes stoichiometry and formation constant values

Metal complex	m:n	K_f	ϵ l.mol ⁻¹ .cm ⁻¹	R^2	pH
Cu – 1,4-PPB	1:1	3.23×10^6	5460	0.9789	5.5 – 6.0
Co – 1,4-PPB	1:1	7.20×10^6	3280	0.9431	4.0 – 4.5
Ni – 1,4-PPB	1:1	6.92×10^6	6750	0.9675	4.5 – 5.0

Conclusions

This paper reports spectrophotometric study of the metal complex of Cu (II), Co (II), and Ni (II) with 1,4-bis(3-(2-pyridyl)pyrazol-1-ylmethyl) benzene (1,4-PPB). All studied complexes under optimum conditions were stable for at least 4 hours. Stability constants for Cu (II), Co (II), and Ni (II) complexes have been found to be in the order: Co-1,4PPB > Ni-1,4PPB > Cu-1,4PPB and the values determined using Job method were: 3.23×10^6 , 7.20×10^6 , and 6.92×10^6 respectively. The stability is strongly depended on pH of the solution. The stoichiometric studies by Job method showed that The formation of 1:1 metal to ligand in all complexes. The molar absorptivity values for Cu (II), Co (II), and Ni (II) were found to be 5460, 3280, and 6750 l/mol.cm at $\lambda_{max} = 305$ nm, respectively. $\pi-\pi^*$ and $n-\pi^*$ transitions are responsible for absorption spectra in all complexes indicated by molar absorptivity values.

Conflicts of Interest

Submitting author is responsible for co-authors declaring their interests.

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