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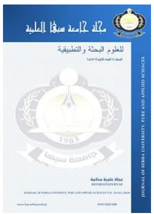

Determination of Stoichiometry and Stability Constant of Cd(II) and Zn(II) Complexes with Pyrazole Based Ligands in Mixed Solvent (EtOH-H2O)

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Keywords:
Pyrazole based ligands
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ABSTRACT

A Spectrophotometric investigation was applied on the complexation of 1,3-bis (3-(2-pyridyl) pyrazol-1-ylmethyl) benzene (1,3-PPB) and 1,4-bis (3-(2-pyridyl) pyrazol-1-ylmethyl) benzene (1,4-PPB) with Zn(II) and Cd(II) ions in a mixed (1:1) solvent of water and ethanol. The mole ratio methodology was used to calculate the stoichiometry, molar absorptivity, and stability constant values. Some experimental conditions have been investigated, including pH, ionic strength, solvent composition, and time. The results revealed the production of 1:1 complexes. In terms of ligands, 1,4-PPB was more stable than 1,3-PPB, whereas Cd(II) complexes were more stable than Zn(II) complexes. The complexes' molar absorptivity values were determined to be 5744, 10019, 9414, and 17716 l.mol-1.cm-1 for Cd-1,3-PPB, Cd-1,4-PPB, Zn-1,3-PBB, and Zn-1,4-PBB, respectively. The sensitivities for Cd and Zn estimation by complexation with 1,3-PPB and 1,4-PPB, respectively, were determined to be 0.051, 0.089, 0.114, and 0.271 mg.l-1.

تقدير نسبة الارتباط وثابت الاستقرارية لمعقدات Cd(II) وZn(II) مع متصلات حاوية على البيرازول في مذيب مختلط (إيثانول-ماء)

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الملخص

تم تطبيق القياسات الطيفية لأجل دراسة تكوين معقدات 1,3-bis (3-(2-pyridyl) pyrazol-1-ylmethyl) benzene (1,3-PPB) و 1,4-bis (3-(2-pyridyl) pyrazol-1-ylmethyl) benzene (1,4-PPB) مع أيونات Zn(II) و Cd(II) مذيب مختلط (1:1) من الماء و الإيثانول. طريقة النسبة المولية أستخدمت لحساب قيم نسبة الارتباط، الامتصاصية المولارية، و ثابت الاستقرارية. تم دراسة تأثير بعض الظروف العملية والتي تشمل: pH ، القوة الأيونية، نسبة المذيب، و الزمن. أوضحت النتائج أن المعقدات تكونت بنسبة 1:1. لوحظ أن معقدات المتصلة 1,4-PBB أكثر استقرارا من معقدات 1,3-PBB، بينما معقدات Cd(II) كانت أكثر استقرار من معقدات Zn(II). قيم الامتصاصية المولارية للمعقدات كانت كالتالي: 5744، 10019، 9414، 17716 لتر/مول.سم للمعقدات: Cd-1,3-PBB، Cd-1,4-PBB، Zn-1,3-PBB، و Zn-1,4-PBB، على التوالي. قيم الحساسية لتقدير Cd و Zn باستخدام 1,3-PBB و 1,4-PBB كانت على التوالي: 0.051، 0.089، 0.114، 0.271 ملجم/لتر.

الكلمات المفتاحية:
متصلات حاوية البيرازول
كادميوم
زنك
نسبة الارتباط
قياسات طيفية

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Introduction

The chemistry of nitrogen-containing heterocycle-based ligands is of particular interest since they represent a significant class of natural and synthesized compounds, many of which have beneficial biological effects [1-5]. F. Blau [6] pioneered the coordination chemistry of transition metals and nitrogen-containing heterocyclic ligand 2,2'-bipyridine. Because they are excellent π-acceptors, bidentate and tridentate nitrogen-containing heterocyclic ligands such as 1,10-phenanthroline and 2,2':6',2''-terpyridine have been widely employed in transition and non-transition metal complexes. As a result, they serve as soft sites for metal coordination [7, 8]. The growth of the coordination chemistry of nitrogenous ligands, as well as their applications in a broad range of fields such as chemical structure and catalysis, has inspired us to utilize a nitrogen-containing multidentate ligand. Imidazole, pyrazole, and oxazole derivatives are well-known π-excessive five-member nitrogen-containing heterocyclic compounds that are poorer π-acceptors, but better π-donors and hence operate as hard donor sites [9, 10].

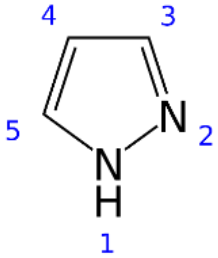

Fig. 1: Pyrazole ring

Pyrazole is a five-membered heterocyclic aromatic ring with three carbon atoms and two nitrogen atoms at positions 1 and 2, as illustrated in Fig. 1. Because of the proton, the N(1)-H is acidic, but the N(2) is basic due to the lone pair in the sp2 orbital. As a result, the pyrazole molecule has a basic property. Because the rupture of the N-C bond is more difficult than that of the N-H bond, tautomerism exists in the event of a symmetrical substitution, or non-substitution on the ring, unless the substituent is at position 1 [10]. Transition metal complexes with pyrazole-based ligands have a wide range of applications. There are already a number of articles accessible in the literature on pyrazole-containing ligands and their complexes [11-18]. Several methods for determining stability constants have been developed, including potentiometric titration, spectrophotometry, capillary electrophoresis, and many others [19-22]. Spectrophotometric methods are often quite sensitive, making them ideal for investigating chemical equilibria in solution. When the components of a chemical equilibrium exhibit unique spectral responses, their concentrations may be measured directly, and determining the equilibrium constant is simple [23,24].

Water and alcohol mixtures have been frequently employed in both experimental and theoretical studies to understand the sort of interaction between aqueous and non-aqueous polar molecules via hydrogen bonding [25]. The complexation reaction and stability of a synthesized Pyrazole Based Ligands with Cd(II) and Zn(II) ions in a mixed (1:1) water-ethanol mixed solvent was studied in the present research because the nature of the solvent can strongly influence the stoichiometry and complexation of transition metal complexes in solution.

Materials and Methods

Reagents

All chemicals used were analytical-reagent quality, and solutions were prepared with deionized water (or pure ethanol). Without additional purification, reagent-grade cadmium chloride and zinc chloride (from Merck) were utilized. HPLC or spectroscopic grade ethanol (99.9%) was used without further purification. This study made use of Milli-Q water.

Stock solutions

PPB stock solutions were made by dissolving 0.0300-0.0400 g in 25 ml of solvent. Cd(II) and Zn(II) stock solutions of 1.00 x 10^{-3} M were produced by dissolving a suitable amount of cadmium chloride and zinc chloride in 25 ml milli-Q water. Other standard solutions were made by diluting the stock solution using a mixture of solvents (1:1 EtOH: H_2O). Each metal complex solution was created by combining the desired volume of ligand and metal solutions, and the ultimate volume was determined by the solvent mixture.

Synthesis of ligand

The two ligands were synthesized using the method previously described [26,27] by reacting 3-(2-pyrazol-1-yl)pyridine with 1,3 bis (bromomethyl)-benzene (or 1,4 bis (bromomethyl)-benzene) in basic circumstances and they have also been characterized.

Spectra analysis

Using the Agilent Cary 60 UV-Vis Spectrophotometer, the UV absorption spectra were obtained in the range of 200 to 400 nm in a mixed solvent (1:1 ethanol: water). At 25°C, spectra were recorded.

pH adjusting

The Jenway pH 3505 pH meter was used to measure the pH. 0.10 M HCl and 0.10 M NaOH were used to alter the pH of the solution.

Factors Affecting the Absorbance

Effect of Acidity

To investigate the effect of acidity on complex absorbance, experiments were carried out by mixing equal volumes of metal ion and ligand solutions to produce a series of 25 ml solutions. The pH of the solutions was adjusted using 0.1 M hydrochloric acid and sodium hydroxide solutions. The absorbance of the solutions was measured at the optimal wavelength to investigate the effect of pH.

Effect of Time

The complexes solutions were made by mixing equal volumes of metal ion and ligand solutions, then monitoring the absorbance of each complex at 5-minute intervals and up to 150-minute intervals to investigate the effect of time on the stability of the prepared complexes.

Effect of ionic strength

The absorbance of solutions containing a given quantity of metal ion complexes was found to be affected by the content of various NaCl solutions (0.01, 0.02, 0.05, 0.1, 0.2, 0.5 M). By altering the concentration of the salt solution, this impact was investigated

Complex composition and stability

The mole ratio method [28] was used to calculate the formation constant. The approach was also used to identify the type of complexes generated in the solution.

In a typical mole ratio methodology experiment, 10.0 ml of ligand solution ($5.0x10^{-5}$ mol/L) in mixed water: ethanol was placed in the spectrophotometer cell and the absorbance of the solution was measured. Then, using a micropipette, a known amount of the concentrated solution of metal ions in the same solvent ($1.0x10^{-3}$ mol/L) was added sequentially. After each addition, the absorbance of the solution was measured. The metal ion solution was added in steps until the required metal to ligand mole ratio was reached.

By using the mole ratio method to fit the observed absorbance, A_{obs}, at different metal ion/ligand mole ratios, the formation constant Kf and the molar absorptivity (ε) of the resulting 1:1 (metal ion to ligand) complexes between the two ligands (1,3-PBB and 1,4-PBB) and two cations (Cd and Zn) were determined.

Results and Discussion

Fig. 2 depicts the structures of 1,3-PPB and 1,4-PPB. Fig. 3 displays the electronic absorption spectra of the complexes of Cd(II) and Zn(II) with the two ligands. The absorption maxima for the free two ligands are around 250 and 280 nm. The first (250 nm) is caused by two phenyl groups (π→π* transitions), while the second is caused by pyridine-pyrazole groups (π→π* and n→π* transitions). The second absorbance maxima (λ_{max}) for the two complexes changed to (287 and 288 nm) for Cd(II) and to (286 nm and 287 nm) after chelating with metal ions. Because of the steric effect, the displacement of the 1,4-PBB ligand is more than that of the 1,3-PBB, and it is slightly larger in cadmium complexes, which may be related to the smaller size of the cadmium ion.

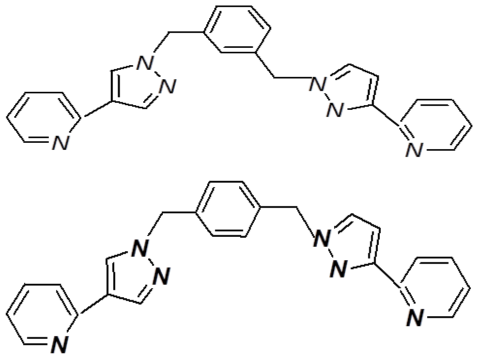

Fig. 2: Structure of 1,4 and 1,3-bis (3-(2-pyridyl) pyrazol-1-ylmethyl) benzene (1,3-PPB and 1,4-PPB)

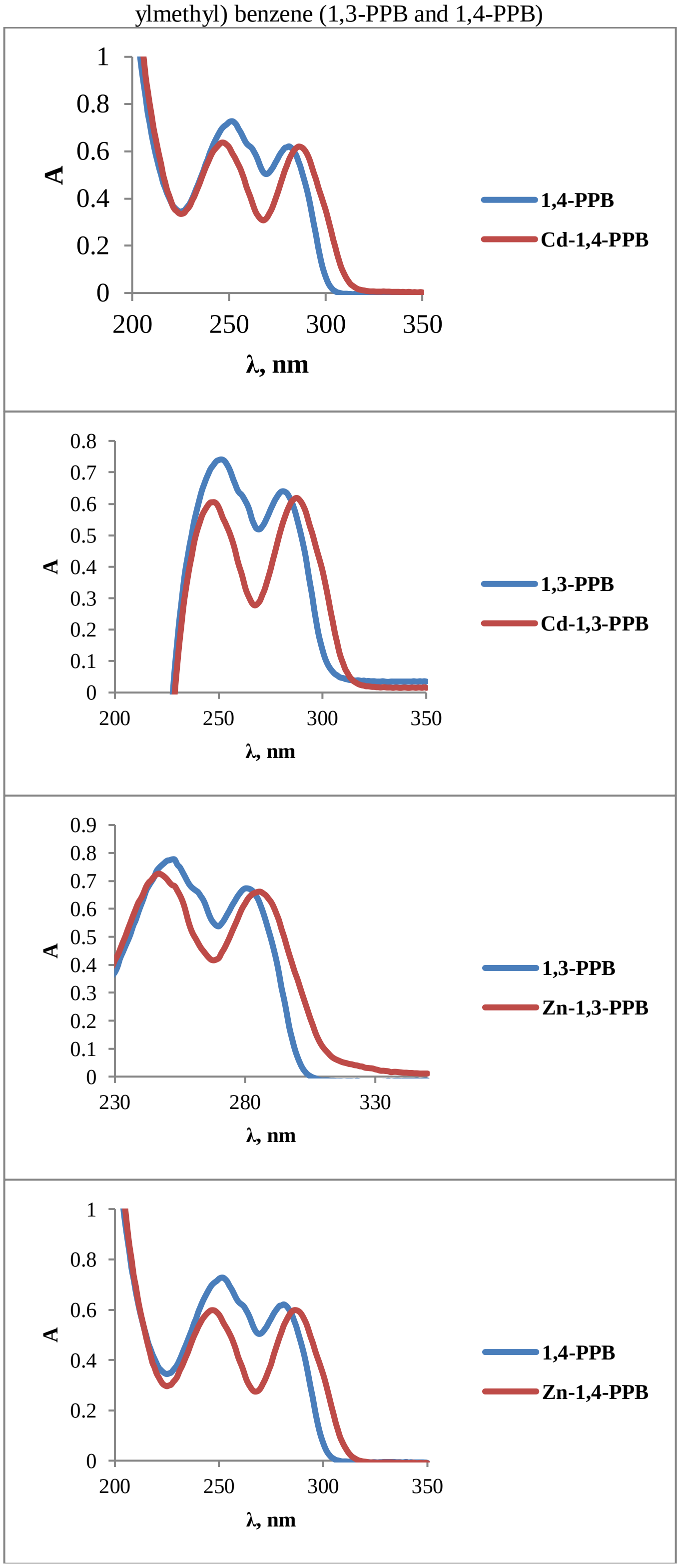

Fig. 3: The spectra of free 1,3-PPB, 1,4-PPB, and Cd(II) and Zn(II) complexes in mixed solvent (1:1) (EtOH-H_2O)

Due to the pyrazole-pyridyl system in the ligand, which includes π→ π* and n→ π* transitions, the absorption reaches its highest around 280 nm. Complexation alters the energy levels n, π, π*, which changes the maximal amount of absorption. It is essential to investigate the various factors that could influence the complex formation, such as pH, ionic strength, time, and solvent. We have looked into these parameters and how they affect the stability of our compounds.

Solvent Effect

The influence of water on the stability of the complexes was investigated using various ethanol/water ratios. As demonstrated in Figs. 4 & 5, the larger the proportion of water in the mixture, the lower the absorbance of the complex. This is due to two factors: one, the complex's solubility reduces in aqueous media, and second, water molecules are thought to be complementary ligands for metal ion complexation. Furthermore, because water can establish hydrogen bonds with nitrogen lone pairs in pyrazole and pyridine rings, the ligands may lose their capacity to bind with metal ions.

In contrast, the influence of the water percentage on the absorption peak of the formed complexes is observed to have varying effects on the complexes formed. In the case of Cd(II) complexes, a blue shift is detected with increasing water fraction in the mixture, but a red shift occurs with 1,4-PBB. In the case of Zn(II) complexes, a blue shift occurs with an increase in the proportion of water up to 50%, after which a red shift begins.

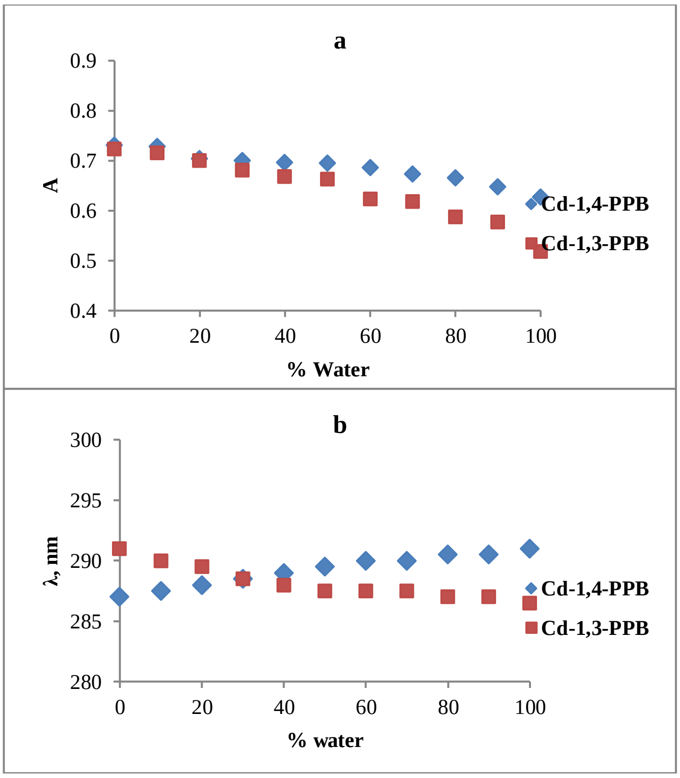

Fig. 4: Effect of water fraction on absorption and λ_{max} of Cd(II) complexes

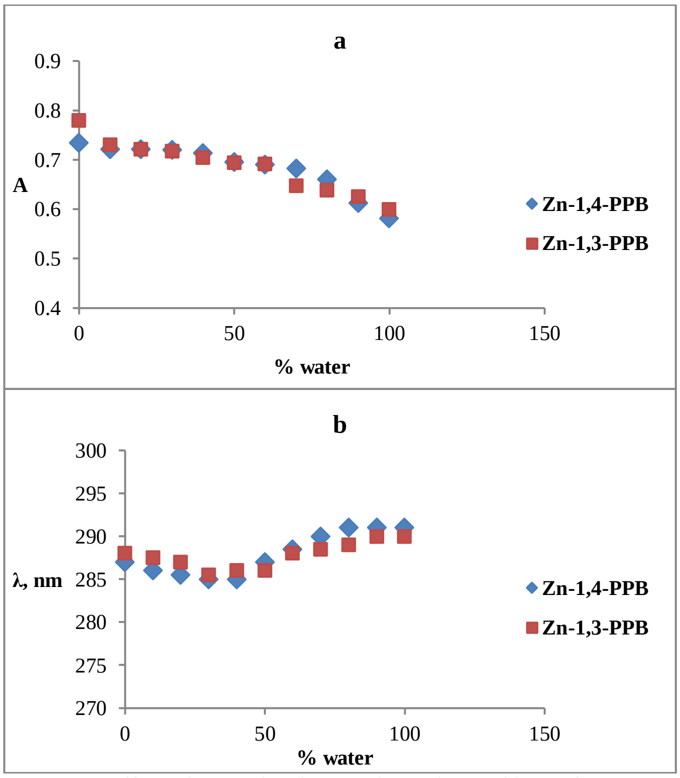

Fig. 5: Effect of water fraction on absorption and λ_{max} of Zn(II) complexes

Time Effect

The study of complex stability with time is an important characteristic because some complexes are unstable and may dissociate after creation. The absorption of the complex is monitored every 15 minutes to 200 minutes to determine if the complex is being dissociated or continuing being to be produced with time, as illustrated in Fig. 6. The figure shows that the absorption of the two complexes develops with time till 60 minutes, when the increase becomes minimal, suggesting that the complex formation process has achieved an equilibrium state.

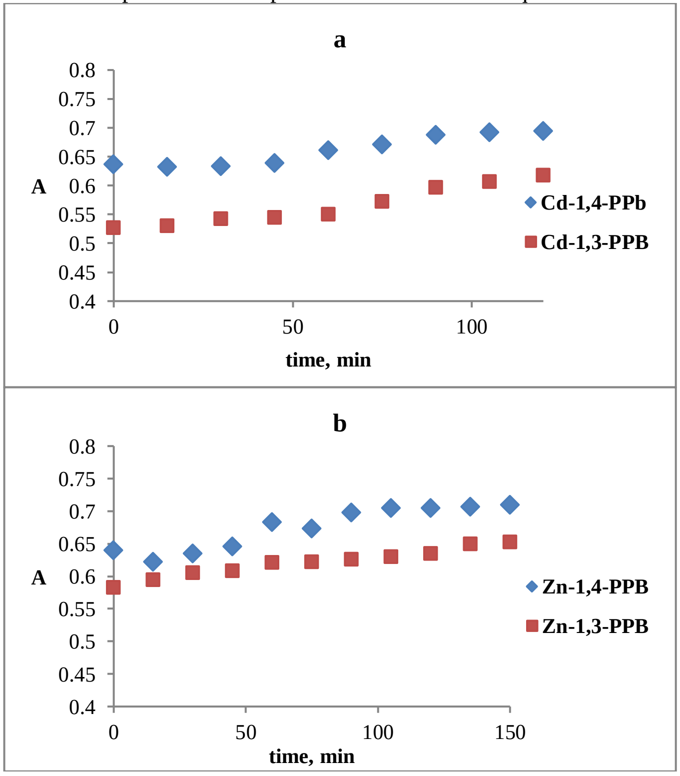

Fig. 6: Effect of time on absorption maxima of Cd(II) and Zn(II) complexes

Ionic Strength Effect

To investigate the influence of ionic strength on complex stability, different concentrations of NaCl solution were utilized (from 0.005 – 0.5 M). Fig. 7 depicts the complex's absorption as it varies with ionic strength. The absorption of complexes minor changes at low concentrations. At a 0.5 M concentration of NaCl solution, the absorption of the cadmium complex with 1,3-PBB decreases by only 7%, whereas the absorption of the cadmium complex with 1,4-PBB decreases by 30%. In the case of zinc complexes, at a concentration of 0.5 M sodium chloride solution, the rate of reduction in absorption approaches 30% for 1,3-PBB and 15% for 1,4-PBB. Because the ions participating in the process have a low effective concentration, increasing the ionic strength of the solution diminishes the likelihood of complex formation.

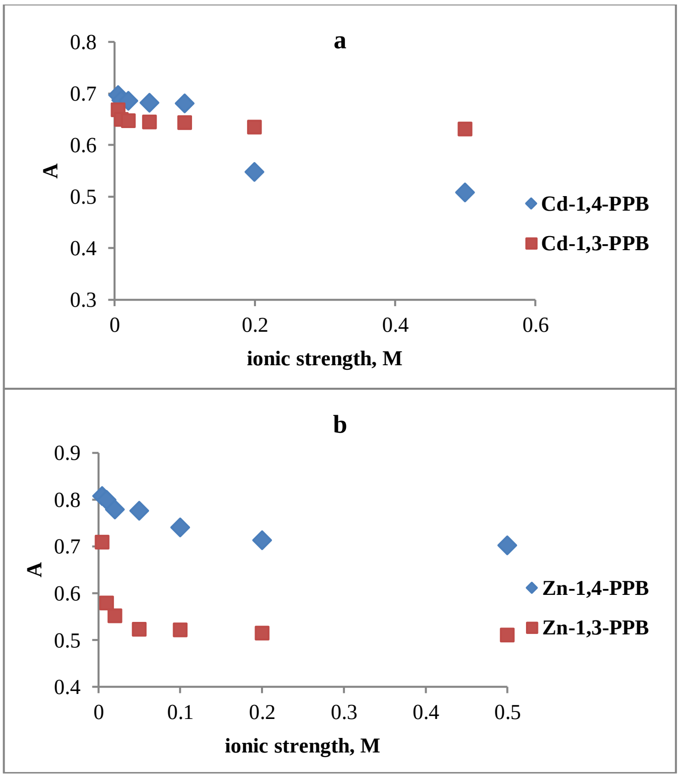

Fig. 7: Effect of ionic strength on absorption maxima of Cd(II) and Zn(II) complexes

Effect of pH

At various pH levels, the spectra of the generated complexes were detailed (from 2-12). pH levels were adjusted using 0.1 M HCl and 0.1 M NaOH solutions. Because all ligands are weak acids or weak bases that may be protonated or de-protonated depending on the pH of the solution, pH is an important issue that affects metal complex formation. Our ligands (1,3-PPB and 1,4-PPB) are considered weak bases [6, 7] and may be protonated at pH values as low as 7. (2-3). The ligand's potential to react with metal ions is limited by protonation, which makes nonbonding electron pairs accessible for complexation and so reduces the propensity to form complexes with metal ions. As a result, the complex formation equilibria may be altered by the pH of the solution. As illustrated in Fig. 8, the optimal value for the complexation of our ligands with Cd(II) and Zn(II) was as follows: (6-8), (7.5-9), (8-10), and (8-11.5), respectively, for Cd(II)-1,3-PBB, Cd(II)-1,4-PBB, Zn(II)-1,3-PBB, and Zn(II)-1,4-PBB. A second aspect that influences the optimal pH for complexation is the precipitation of metal ions as hydroxide at higher pH (pH>9 in this study). The optimal pH values are shown in Table 1.

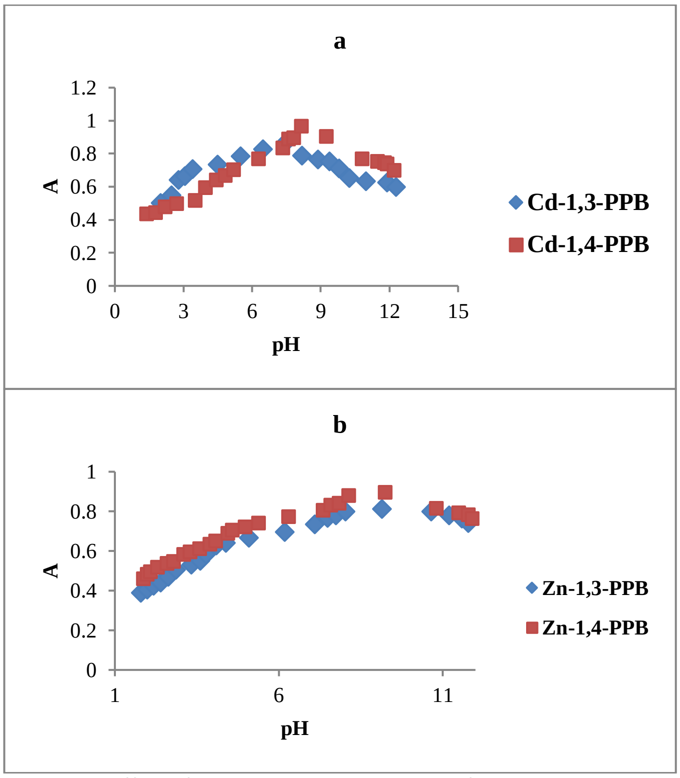

Fig. 8: Effect of pH on absorption maxima of Cd(II) and Zn(II) complexes

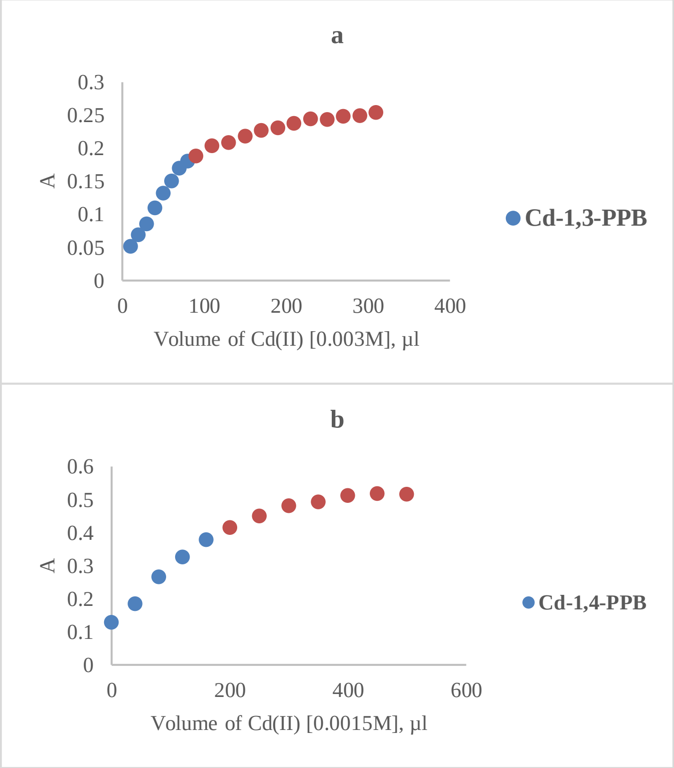

Fig. 9: Titration of two ligand solutions with Cd(II) ion

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

The mole ratio approach was used to estimate the composition of Cd(II) and Zn(II) complexes with PPB ligands. At the λ_{max} value for each complex, the absorbance values of complexes prepared by combining different metal to ligand ratios were measured. The absorbance values for each combination were plotted against the ligand to metal mole ratio (Figs. 9 and 10) and the stoichiometry of each complex was obtained at the point of intersection of the two straight lines (Figs. 11 and 12). The formation constant of each complex was also measured using a mole ratio plot. The complex's molar absorptivity can also be calculated by calculating the concentrations of the complexes at each point and plotting the concentration versus the absorbance, as shown in Fig. 13. Table 1 shows the complex stoichiometry, stability constants, and molar absorptivity values. If the cadmium and zinc ions were measured using these ligands, the sensitivity of the spectrum approach was assessed by graphing the connection between the metal ion concentration and complex absorption, as shown in Fig. 14, and the resultant values are provided in Table 1.

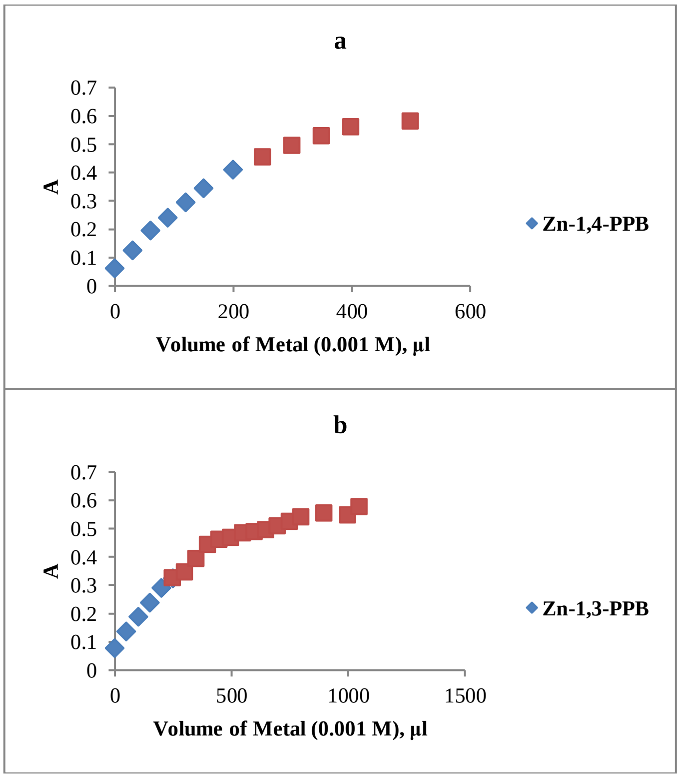

Fig. 10: Titration of two ligand solutions with Zn(II) ion

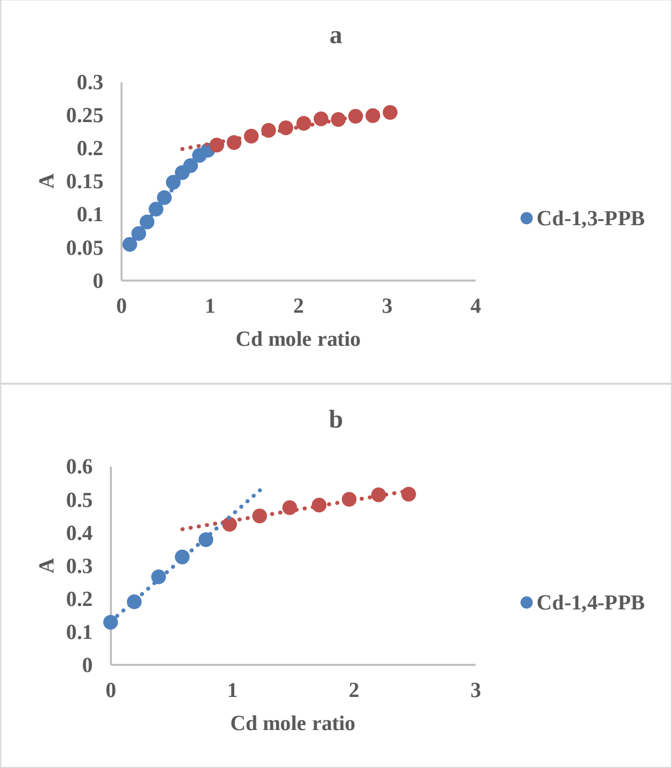

Fig. 11: Stoichiometry of Cd(II) complexes by mole ratio method

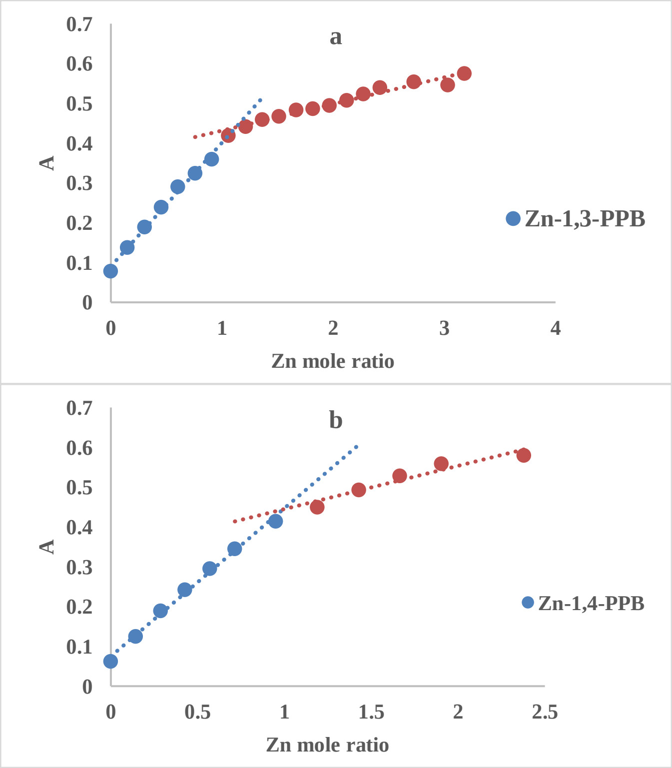

Fig. 12: Stoichiometry of Zn(II) complexes by mole ratio method

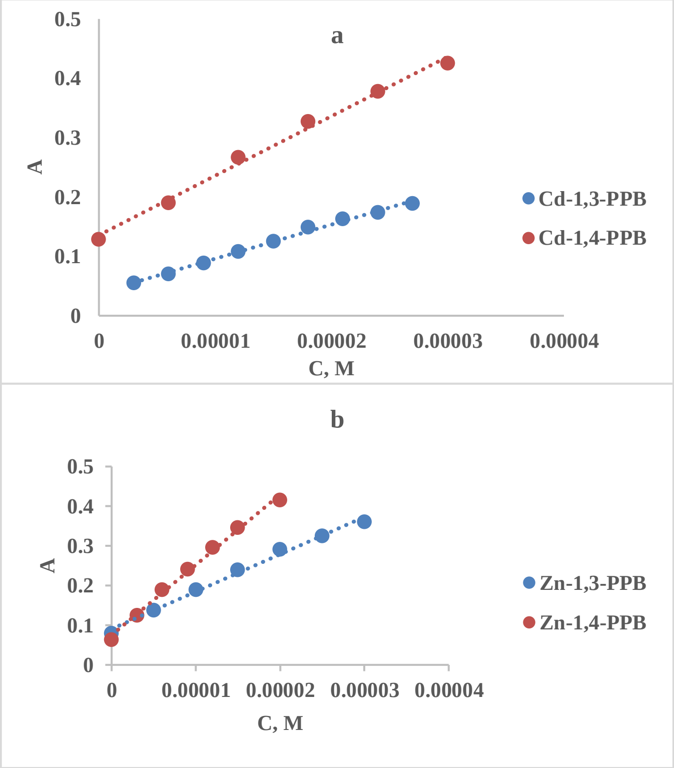

Fig. 13: Calibration curve for Cd(II) and Zn(II) complexes

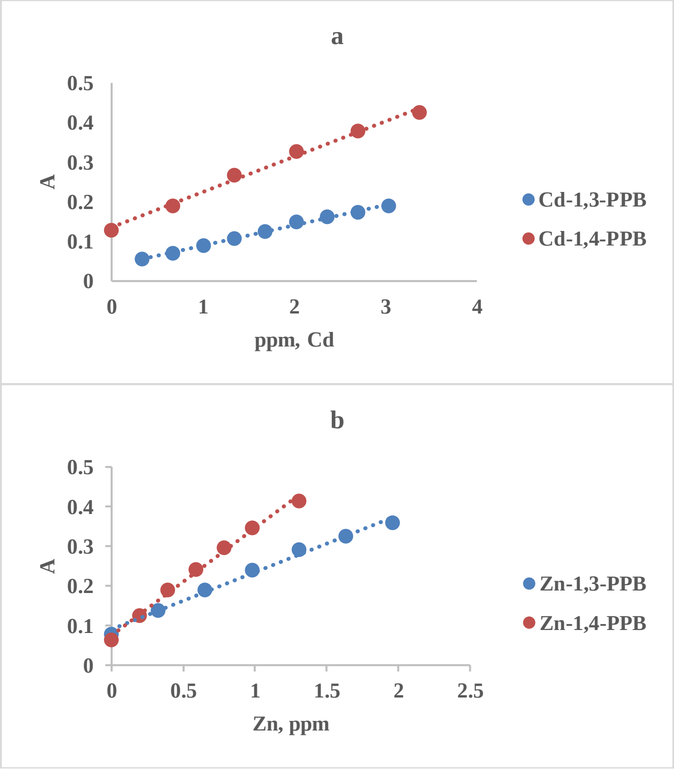

Fig. 14: Calibration curve for Cd(II) and Zn(II) ions

Table 1: Metal ion complexes stoichiometry, formation constant, molar absorptivity, pH range, and sensitivity values

Metal complex		m:n	K_f	ε $l.mol^{-1}.cm^{-1}$	R^2	pH	Sensitivity $mg.l^{-1}$
Cd(II)	1,3-PBB	1:1	$1.16x10^7$	5744	0.995	6.0 – 8.0	0.051
	1,4-PBB	1:1	$8.2x10^7$	10019	0.993	7.5 – 9.0	0.089
Zn(II)	1,3-PBB	1:1	$6.18x10^6$	9414	0.992	8.0-10.0	0.114
	1,4-PBB	1:1	$3.08x10^7$	17716	0.994	8.0-11.5	0.271

Conclusion

The current work describes a spectrophotometric investigation of metal complexes of Cd(II) and Zn(II) with 1,3-PPB and 1,4-PPB ligands. Under ideal conditions, all of the complexes examined were stable for at least 3 hours. The stability constants for the complexes investigated were discovered to be in the order of 1,4-PPB > 1,3-PPB, which might be attributed to steric effects. Cd(II) complexes, on the other hand, were more stable than Zn(II) complexes. The pH of the solution has a considerable influence on the stability. Stoichiometric measurements revealed that the four complexes had a 1:1 metal-to-ligand ratio.

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