Arabian Journal of Chemical and Environmental Research

Vol. 08 Issue 2 (2021) 236–246

Complexation of Pyrazole Based Ligands with Ag (I): Spectrophotometric Studies in Mixed Solvent (EtOH-H_2O)

K. M. Elsherif [1*], A. Zubi [2], A. Najar [3], H. Bin Ghashir [2]

[1]*Chemistry Department, Faculty of Science, University of Benghazi, Benghazi-Libya.*
[2]*Chemistry Department, Faculty of Science, Misurata University, Misurata-Libya.*
[3]*Chemistry Department, Faculty of Arts and Science - Marj, University of Benghazi, Al Marj-Libya.*

Received 28 May 2021, Revised 15 June 2021, Accepted 20 June 2021

Abstract

The current study aimed to use silver ion (Ag^+) complexes with pyrazole based ligands for developing spectroscopic method of silver ion in its aqueous solution with high sensitivity and low detection limits. The stability and composition of the complexes 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 Ag (I) ion have been investigated applying the 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 spectrophotometrically. Spectrophotometric results indicated the formation of 1:1 complexes with stability order of Ag-1,4-PPB > Ag-1,3-PPB. Molar absorptivity values of the complexes have also been determined and were found to be 5039 and 6320, for Ag-1,3-PPB and Ag-1,4-PPB, respectively. The sensitivities for Ag determination by complexation with 1,3-PPB and 1,4-PPB were evaluated and found to be 0.045 and 0.055 mg.l-1, respectively. The Ag-PPB complexes could be used for Ag^+ determination in aqueous solutions with high sensitivity and low detection limits.

*Keywords: Pyrazole Based Ligands***,** Silver, Stoichiometry, Stability Constant.

*Corresponding author.
E-mail address: elsherif27@yahoo.com

ISSN : 2458-6544

1. Introduction

The chemistry of nitrogen containing heterocycle-based ligands is of particular importance since they establish an important group of natural and synthetic products, numerous of them display valuable biological activities [1–3]. Because they present soft sites for metal coordination [4], the growth of coordination chemistry of nitrogenous ligands and their presentations in the variety of areas such as chemical, structural, catalysis, have led to purpose nitrogen containing multidentate ligand. Imidazole, pyrazole, and oxazole derivatives are widespread well-known π-excessive five-member nitrogen-containing heterocyclic ligands and they are poorer π-acceptors, actually, they are better π-donor and hence operate as hard donor sites [5]. Including these heterocycles, we are presently interested in pyrazole and substituted pyrazole containing ligand because of their variety of applications [6-9]. The focal point of our investigation on metal chelates with pyrazole based ligands because of their importance in theoretical and practical applications [10, 11]. Various commercial commodities or compounds which based on these ligands are in the stage of activity estimation owing to pyrazole derivatives show several biological activities [12, 13]. As pyrazoles easily form complexes, they are suitable agents for inspecting the active sites of biomolecules and for modeling the biosystems of oxygen transfer [14, 15]. Dissociation constant is one of the significant physicochemical parameter offers precarious knowledge about drug properties such as solubility, lipophilicity, acidity, transport behavior, bonding to receptors and permeability [16]. Hence, the relationship between the acid dissociation constants and structure in drug design studies is important. Stability constants of metal ion complexes of various ligands and particularly chelating ligands applying various methods such as potentiometric and spectrophotometric methods have been evaluated [17]. Stability constant of a complex ion is affected by number of issues like ligand type, metal ion type, counter-ions and solvent [18].

In the present study, spectrophotometric investigations of complexation between 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 Ag (I) were studied and the formation constants were determined.

2. Materials and methods

2.1. Reagents

All chemicals used were analytical-reagent grade, and deionized water (or pure ethanol) was used for preparation of solutions. Reagent grade silver nitrate (from Merck) was 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.

2.2. Preparation of ligand

The ligand was prepared by reaction of 3-(2-pyrazol-1-yl)pyridine with 1,3 bis (bromomethyl)-benzene (or 1,4 bis (bromomethyl)-benzene) under basic conditions by the procedure described elsewhere [19,20]. A mixture of 1,3-bis(bromomethyl)benzene (1.20 g, 4.55 mmol), 3-(2-pyridyl)pyrazole (1.35 g, 9.32 mmol), aqueous NaOH (10 M, 20 cm^3), toluene (50 cm^3) and Bu_4NOH (40% aqueous solution, 3 drops) was stirred vigorously at room temperature for 40 min. The mixture was diluted with H_2O (100 cm^3) and the organic layer separated, dried over $MgSO_4$ and concentrated before purification using an alumina column.

2.3. Preparation of complex solutions

The stock solution of PPB (1.00 x 10^{-3} M) was prepared by dissolving 0.0300 – 0.0400 g in 25 ml of a solvent. 1.00 x 10^{-3} M stock solution of Ag (I) was prepared by dissolving an appropriate amount of silver nitrate in 25 ml milli-Q water. Other standard solutions were prepared by dilution of stock solution with mixed solvent (1:1 EtOH:H_2O). Each silver complex solution was prepared by mixing the desired volume of ligand and metal solutions and the final volume was made by the mixed solvent. The absorption maxima of Ag-PPB complexes in (1:1 EtOH:H_2O) solvent were investigated by titration of 1.00x10^{-5} M PPB ligand solution with 1x10^{-3} M Ag(I) solution (20 µl additions) and recording the spectrum (from 200 – 350 nm). The complexes just formed were examined for their stability.

2.4. 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.

2.5. 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.

3. Results and discussion

The structures of 1,3-PPB and 1,4-PPB are shown in Fig. 1. The electronic absorption spectra of Ag(I) complexes with two ligands are shown in Fig. 2. The free two ligands have two absorption maxima around 250 and 280 nm. The first one (250 nm) due to two phenyl groups and the second due to pyridine-pyrazole groups. Upon chelating with metal ions, the second absorption maximum (λ_{max} = 281 nm) were altered to 286 nm for the two complexes. The n electrons of the ligand is donated to metal ion to form

the coordination bond, therefore, the absorption maximum is shifted. Noted that a too little displacement of ligand absorbance as a result of the complex formation. Because the silver ion is a soft acid and also has a relatively large ion size, this may be the reason for the little shift.

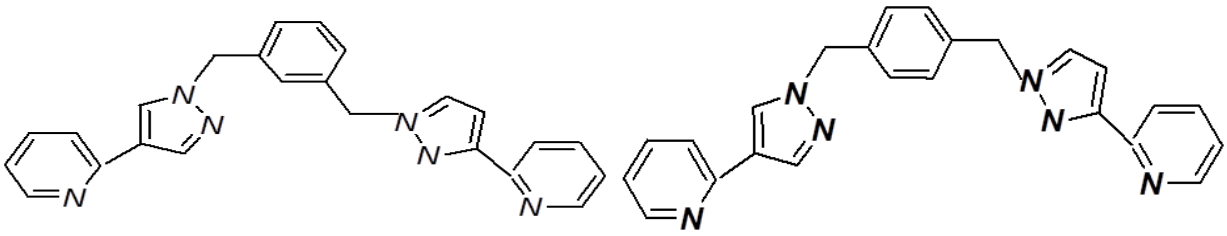

Fig. 1. Structure of 1,3 and 1,4-bis (3-(2-pyridyl) pyrazol-1-ylmethyl) benzene (1,3-PPB and 1,4-PPB)

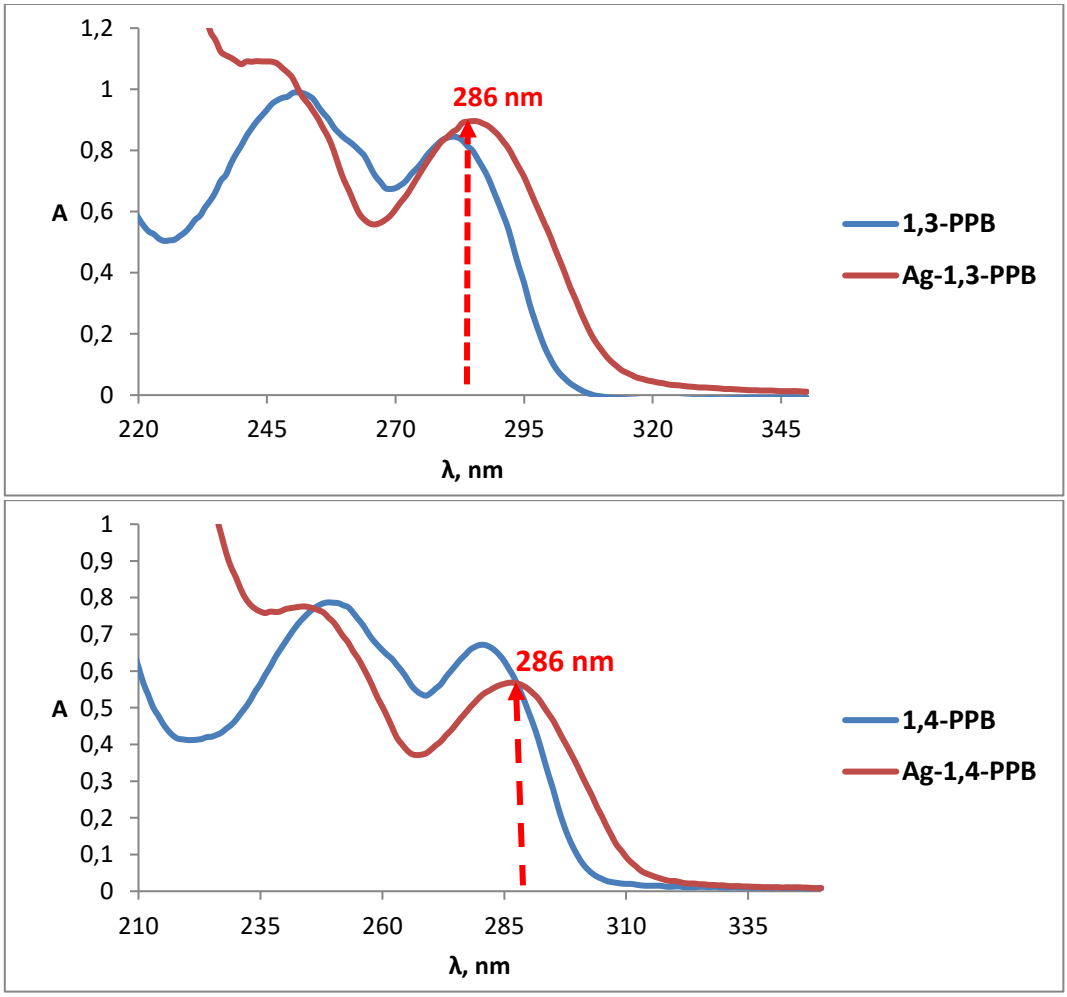

Fig. 2. The spectra of free 1,3-PPB, 1,4-PPB, and Ag(I) complexes in mixed solvent (1:1)

The absorption maximum around 280 nm is due to pyrazole-pyridyl system in the ligand which include π→ π* and n→ π* transitions. The energy levels n, π, π* are affected by complexation and therefore the absorption maximum has been altered [8, 9]. 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 will be investigated.

3.1. Solvent Effect

The effect of water on the stability of the complexes was studied using different ratios of ethanol and water. The higher the percentage of water in the mixture the lower the absorbance of the two complexes as shown in Fig. 3. This can be attributed to several reasons: firstly, the solubility of the complex decreases in the aqueous medium, and secondly, the water molecules are considered to be competitive ligands for the complexation with the metal ion. Finally, 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. The effect of last reason explained the Fig. 4 where a blue shift is observed with an increase in the proportion of water in the mixture (about 2 nm).

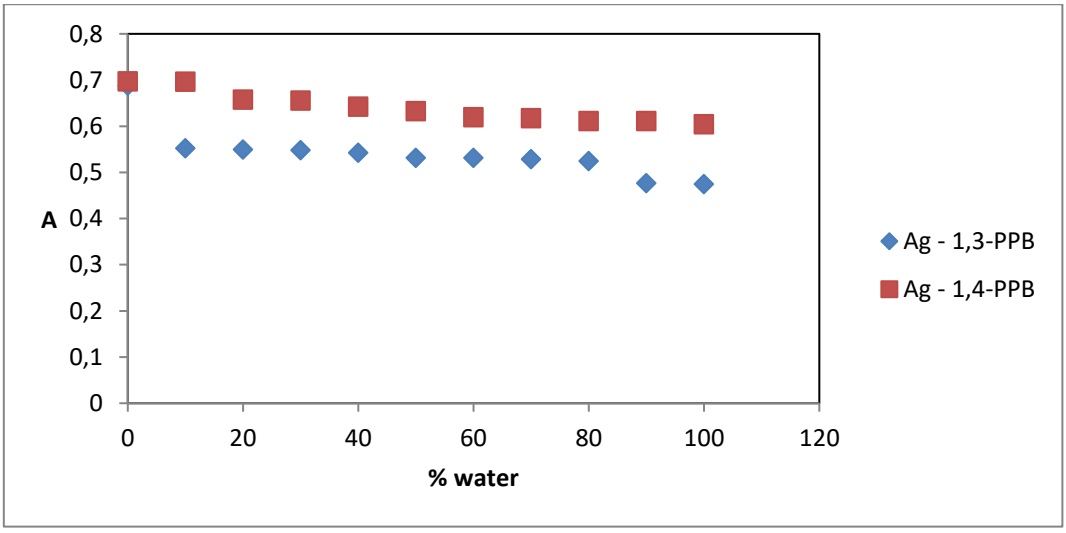

Fig. 3. Effect of water fraction on absorption maxima of Ag(I) complexes

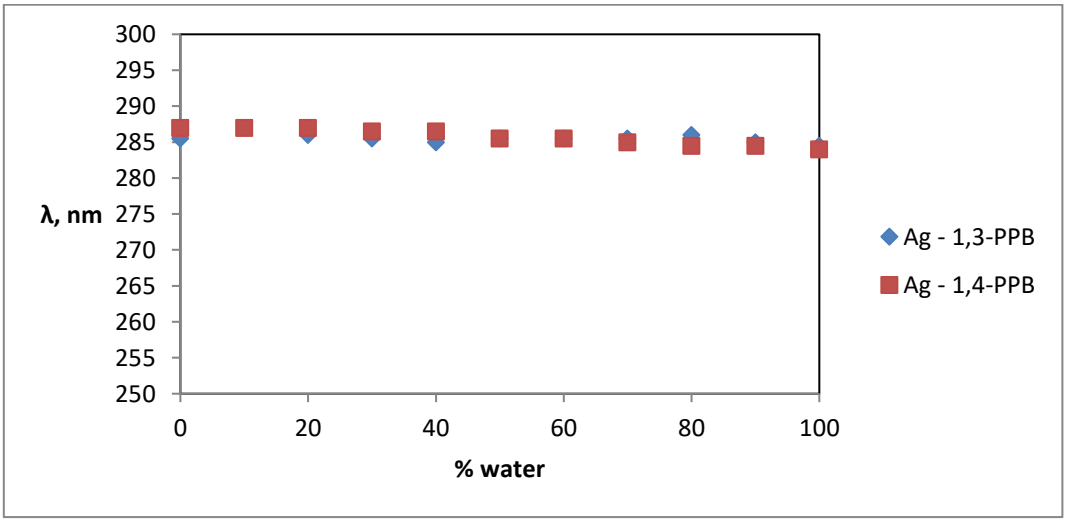

Fig. 4. Variation of λ_{max} with water fraction for Ag(I) complexes

3.2. 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. To examine whether the complex being dissociated or still created with time, the absorption of the complex is measured each 15 min and till 180 min as shown in Fig. 5. It is observed that the absorption of both complexes increases with time until approximately 30 minutes, while a relative stability occurs, indicating that the two reactions have reached their equilibrium state. Dissolution of the two complexes also does not occur until the end of the studied period of time, which indicates the relative stability of the formed complexes.

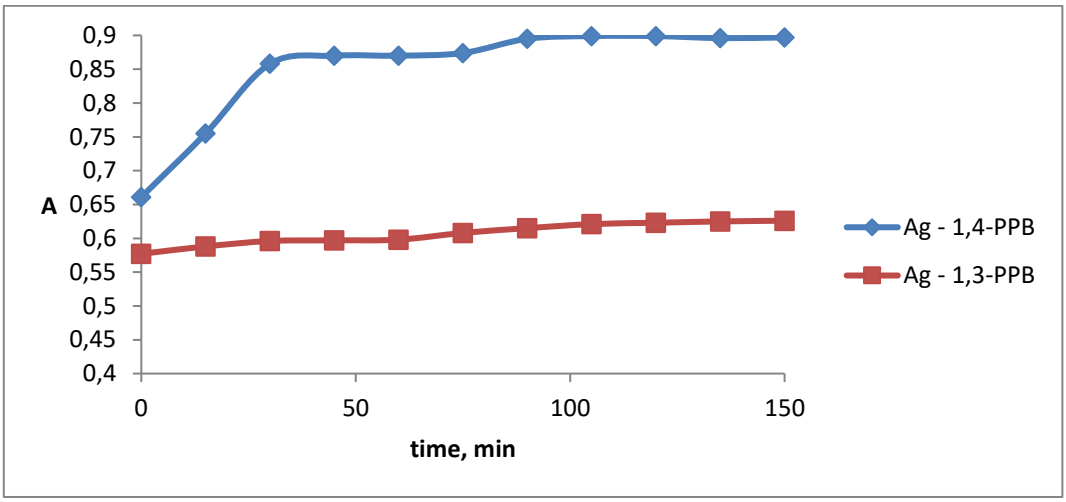

Fig. 5. Effect of time on absorption maxima of Ag(I) complexes

3.3. Ionic Strength Effect

To study the effect of ionic strength on the stability of the complex, different concentrations of NaCl solution were used, (from 0.005 – 1.0 M). The absorption of the complex is measured with each ionic strength and shown in Fig. 6. It can be shown that the absorption of the complex decreased by 40% with the highest concentration of NaCl (0.5 M). This means that the complex is slightly affected by the ionic strength of the solution and as the ionic strength increases the absorption decreases. It is also observed that the absorption peak gets a red shift with an increase in the ionic strength.

3.4. Effect of pH

The spectra of silver complexes were detailed at various pH values (from 2-10). pH values were altered using 0.1 M HCl and 0.1 M NaOH solutions. The pH is an essential consideration 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 ligands (1,3-PPB and 1,4-PPB) is considered to be a weak base [6, 7] 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. Thus, the complex formation equilibria might be influenced by pH value of the solution.

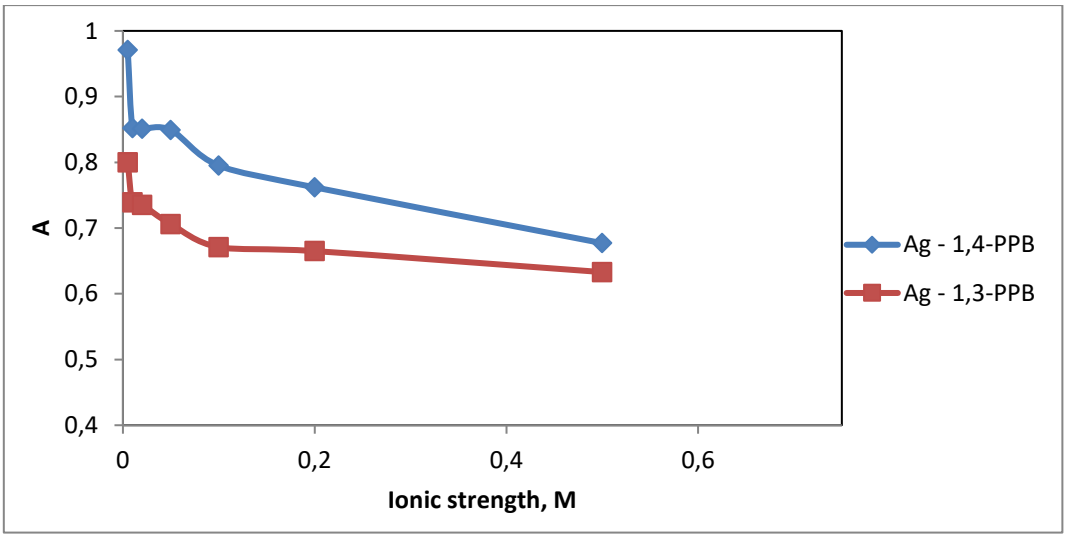

Fig. 6. Effect of ionic strength on absorption maxima of Ag(I) complexes

The optimum value for complexation of our ligands with Ag(I), as shown in Fig. 7, was between pH=4 and pH=7. Also, a second factor that control the optimum pH for complexation is the precipitation of metal ion as hydroxide at higher pH (in this study was at pH > 9. The values of optimum pH values are given in Table 1.

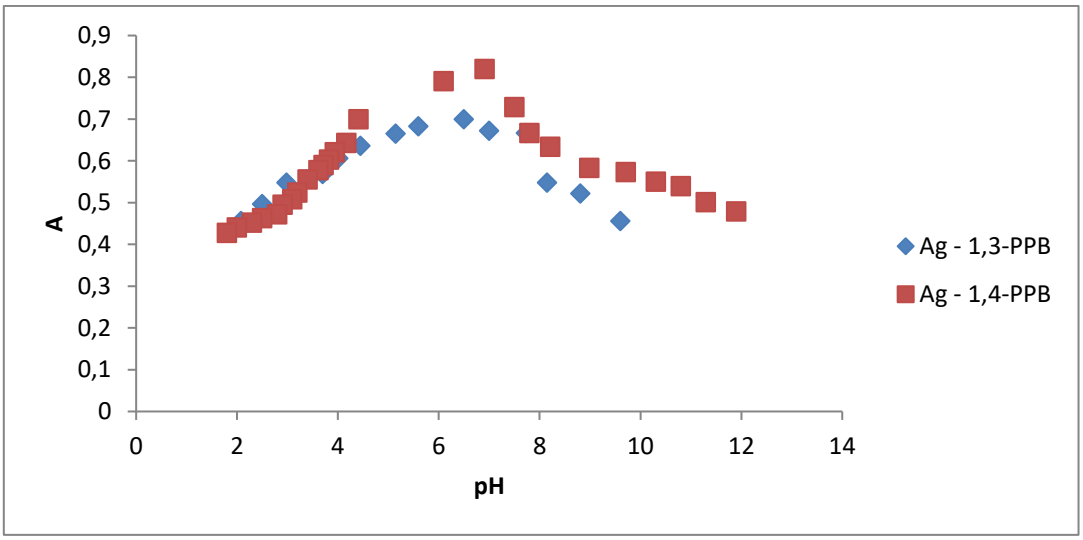

Fig. 7. Effect of pH on absorption maxima of Ag(I) complexes

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

The composition of Ag(I) complexes with PPB ligands was determined by mole ratio method. The absorbance of complexes prepared by mixing different metal to ligand ratios were measured at 286 nm. These absorbance values for each mixture were plotted against ligand to metal mole ratio (Fig. 8 and

Fig. 9) and the stoichiometry of each complex was determined. Also, the formation constant of each complex was determined by mole ration plot.

Table 1. Metal ion complexes stoichiometry and formation constant values

Metal complex	m:n	pK_f	ε $l.mol^{-1}.cm^{-1}$	R^2	pH	Sensitivity $mg.l^{-1}$
Ag – 1,3-PPB	1:1	5.85	5039	0.994	5.5 – 6.5	0.045
Ag – 1,4-PPB	1:1	5.99	6320	0.995	6.0 – 7.0	0.055

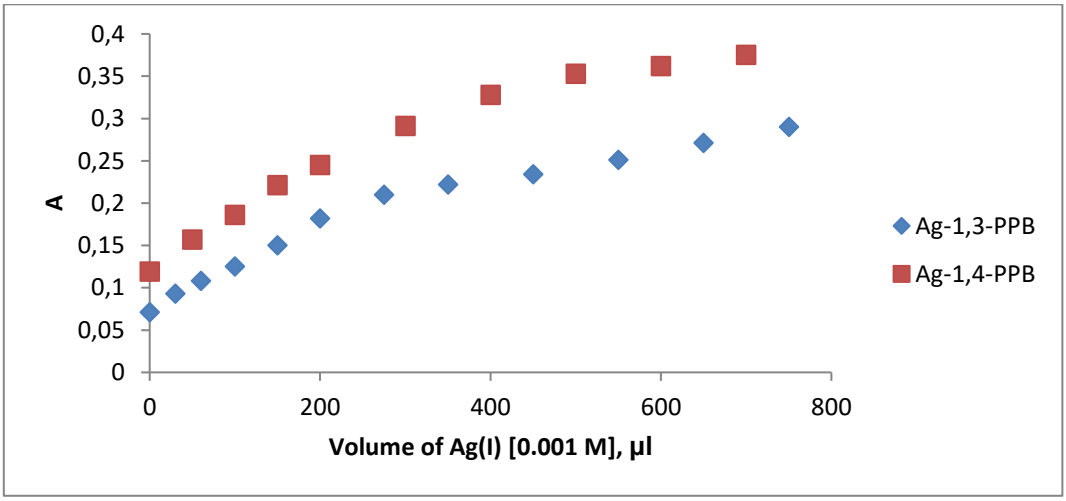

Fig. 8. Titration of ligand solution [$1.02X10^{-3}$ M] with Ag(I) [$1.00X10^{-3}$ M]

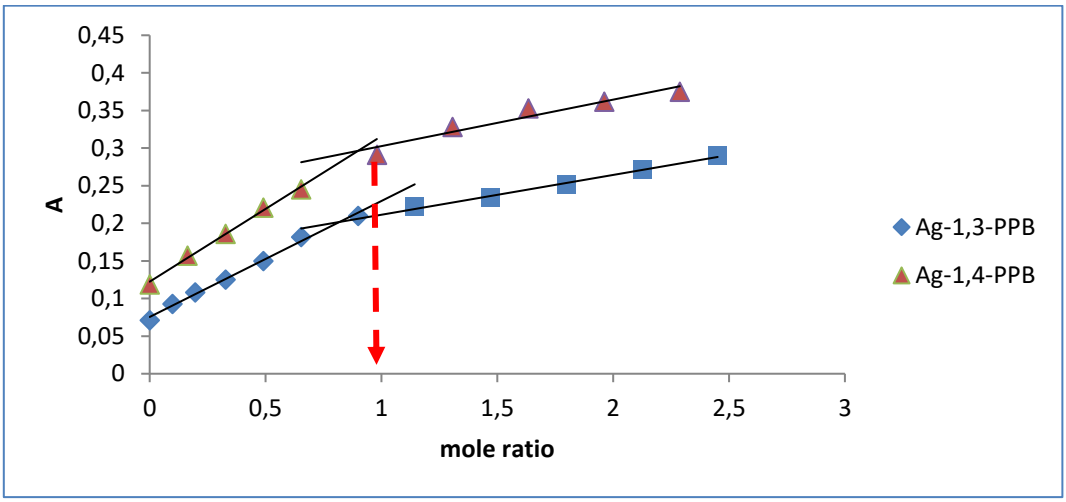

Fig. 9. Stoichiometry of Ag(I) complexes by mole ratio method

The molar absorptivity ε of the complex can also be determined by calculating the concentrations of the complex at each point and plotting the concentration against the absorbance as shown in Fig. 10. The complex stoichiometry, stability constants, and molar absorptivity values are given in Table 1. The sensitivity of the spectral method, if the silver ion was estimated using these ligands, was estimated by

plotting the relationship between the silver ion concentration against the absorption of the complex, as shown in Fig. 11, and the obtained values are shown in Table 1.

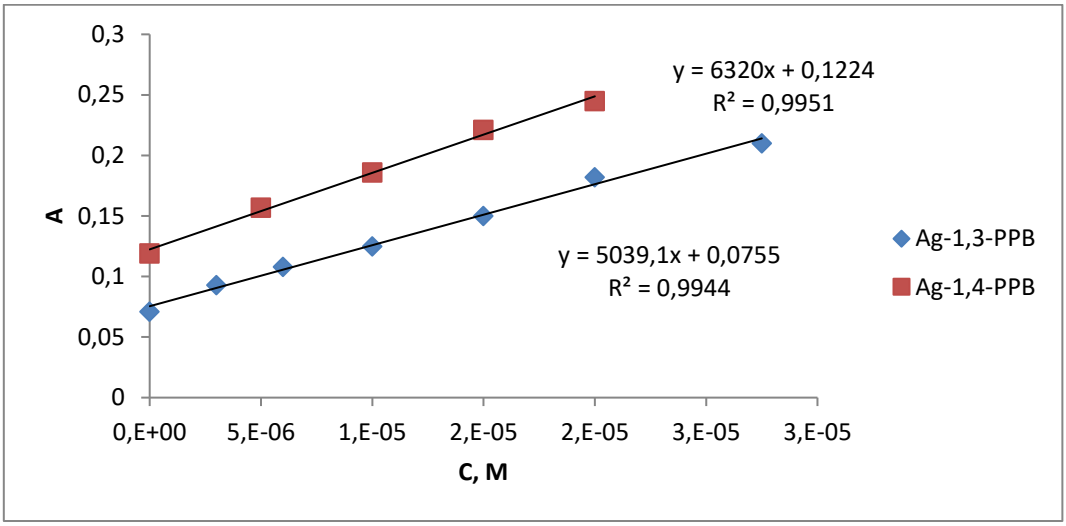

Fig. 10. Calibration curve for Ag(I) complexes

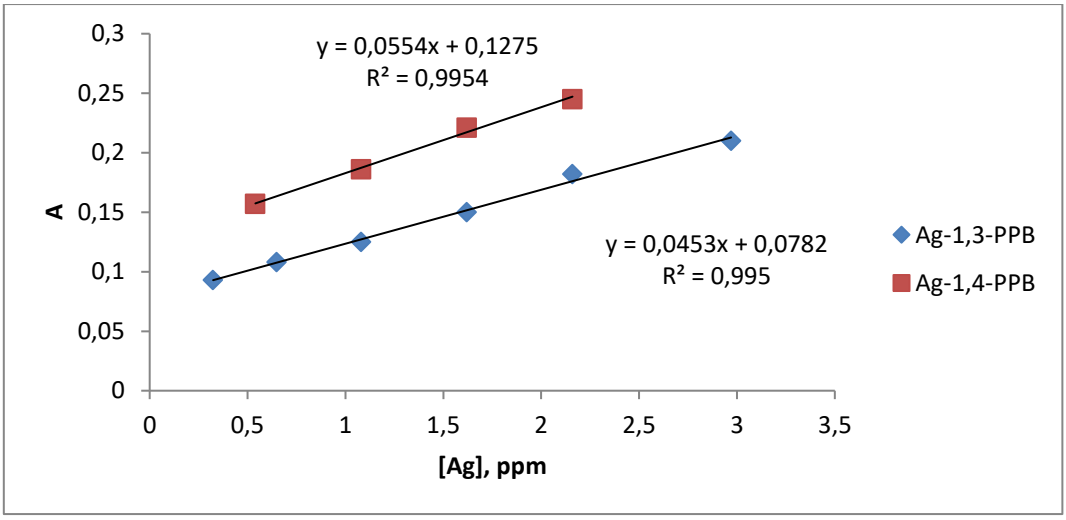

Fig. 11. Calibration curve for Ag(I) ions

Conclusion

The present study reports spectrophotometric study of the metal complex of Ag(I) with 1,3-PPB and 1,4-PPB ligands. All studied complexes under optimum conditions were stable for at least 3 hours. Stability constants for studied complexes have been found to be in the order: Ag-1,4-PPB > Ag-1,3-PPB, this could be due to steric effects, and the values determined were as follows: $7.1x10^5$ and $9.7x10^5$, respectively. The stability is strongly depended on pH of the solution. The stoichiometric studies showed that the formation of 1:1 metal to ligand in the two complexes. The complexes just formed could be used for spectrophotometric determination of Ag(I) in aqueous solutions.

Conflict of Interest-The authors declare that the research was conducted in the absence of any commercial or financial relationships that could be construed as a potential conflict of interest.
Acknowledgments-We would like to acknowledge the Research Center at Misurata University for providing all facilities to complete this research.

References

[1] E. Gondek, I. V. Kityk, A. Danel, A. Wisla, J. Sanetra, Blue electroluminescence in 1H-pyrazoloquinoline derivatives. *Synthetic Metals*, 156, 21-24: 1348-1354 (2006).

[2] F. Bellina, S. Cauteruccio, R. Rossi, Synthesis and biological activity of vicinal diaryl-substituted 1H-imidazoles. *Tetrahedron* 63, 22: 4571-4624 (2007).

[3] S. Park, O. H. Kwon, S. Kim, S. Park, M. G. Choi, M. Cha, S. Y. Park, D. J. Jang, Imidazole-Based Excited-State Intramolecular Proton-Transfer Materials: Synthesis and Amplified Spontaneous Emission from a Large Single Crystal. *Journal of the American Chemical Society*, 127, 28: 10070-10074 (2005).

[4] L. A. Summers, The Bipyridines. *Advances in Heterocyclic Chemistry*, 35: 281-374 (1984).

[5] R. Mukherjee, Coordination chemistry with pyrazole-based chelating ligands: molecular structural aspects. *Coordination Chemistry Reviews*, 203, 1: 151-218 (2000)

[6] K. M. Elsherif, A. Najar, and H. Shuwat, and E. Bazina, Solvent And pH Effects On Uv Absorption Spectrum Of 1,3-bis[(3-(2-pyridyl) pyrazol-1 ylmethyl)] benzene (1,3-PPB), *Journal of Applied Chemical Science International*, 7, 3: 181-192 (2016)

[7] K. M. Elsherif, A. Najar, and H. Shuwat, Spectral Study of 1,4-bis(3-(2-pyridyl)pyrazol-1-ylmethyl) benzene (PPB): UV-VIS Absorption Spectra Investigation in Single and Binary Solvents and Spectrophotometric Determination of the Dissociation Constant (pK_b), *Eurasian Journal Analytical Chemistry*, 12, 1 : 67-82 (2017)

[8] K. M. Elsherif, A. Zubi, A. Najar, E. Bazina, 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-H_2O), *To Chemistry Journal*, 1, 2: 214-223 (2018)

[9] K.M. Elsherif, A. Zubi, A Najar, E. Bazina, UV-VIS Absorption Spectral Studies of Complexation of 1,3-bis (3-(2-pyridyl) pyrazol-1-ylmethyl) benzene (1,3-PPB) with Cu (II), Co (II), Ni (II) in EtOH-H_2O Mixed Solvent, Special Issue for The 2nd Annual Conference on Theories and Applications of Basic and Biosciences, September, 1st: 730-738 (2018)

[10] Ž. K. Jaćimović, G. A. Bogdanović, B. Holló, V. M. Leovac, and K. M. Szécsényi, Transition metal complexes with pyrazole-based ligands Part 29. Reactions of zinc(II) and mercury(II) thiocyanate with 4-acetyl-3-amino-5-methylpyrazole, *Journal of the Serbian Chemical Society*, 74, 11: 1259–1271 (2009).

[11] H. S. Seleem, B. A. El-Shetary, S. M. E. Khalil, and M. Shebl, Potentiometric and spectrophotometric studies of the complexation of Schiff-base hydrazones containing the pyrimidine moiety, *Journal of the Serbian Chemical Society*, 68, 10: 729–748 (2003).

[12] E. Reisner, V. B. Arion, B. K. Keppler, and A. J. L. Pombeiro, Electron-transfer activated metal-based anticancer drugs, *Inorganica Chimica Acta*, 361, 6: 1569-1583 (2008)

[13] F. P. Pruchnik, P. Jakimowicz, Z. Ciunik, J. Zakrzewska-Czerwińska, A. Opolski, J. Wietrzyk, E. Wojdat, Rhodium(III) complexes with polypyridyls and pyrazole and their antitumor activity, *Inorganica Chimica Acta*, 334, 1: 59-66 (2002).

[14] G. Lemaire, W. Mnif, J.-M. Pascussi, A. Pillon, F. Rabenoelina, H. Fenet, E. G. C. Casellas, J.-C. Nicolas, V. Cavaillès, M.-J. Duchesne, and P. Balaguer, *Toxicological Sciences*, 91, 2: 501-509 (2006)

[15] C. B. Vicentini, D. Mares, A. Tartari, M. Manfrini, and G. Forlani, Synthesis of Pyrazole Derivatives and Their Evaluation as Photosynthetic Electron Transport Inhibitors. *Journal of Agricultural and Food Chemistry*, 52, 7: 1898-1906 (2004)

[16] S. Baluja, K. Nandha and P. Ramavat, Potentiometric Determination of Acidity Constants of Some Pyrimidine Derivatives in Organic-Water Media. *Journal of Chemistry and Materials Research*, 5, 2: 32-38 (2016).

[17] M. B. Ibrahim and A. Moyosore, Spectrophotometric Study of Stability Constants of Co(II), Ni(II) and Cu(II) Complexes of 2, 2– Bipyridine at Different Temperatures. *ChemSearch Journal*, 5, 1: 51 – 55 (2014).

[18] E. S. Reza, Synthesis and Determination of Stability Constants of Bis –1,2,4– triazole Ligand for Complexation with Zn (II), Ni (II) and Cu (II) in Acetonitrile Medium. *American Journal of Analytical Chemistry*, 3, 6: 437–442 (2012).

[19] Z. R. Bell, L. P. Harding, M. D. Ward, Self-assembly of a molecular M_8L_{12} cube having S_6 symmetry. *Chemical Communications*, 19: 2432-2433 (2003).

[20] S. P. Argent, H. Adams, L. P. Harding, & M. D. Ward, A closed molecular cube and an open book: two different products from assembly of the same metal salt and bridging ligand. *Dalton Transactions*, 4: 542-544 (2006).

[21] P. Quezel, S. Santa, 1963. Nouvelle flore de L'Algérie et des régions désertiques méridionales. *Editions du Centre National de la recherche scientifique.* Tome II (1963).