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SYNTHESIS, SPECTRAL STUDIES AND ANTIOXIDANT STUDY OF METAL-COORDINATED AZO-DYE OF PYRIDINE AND ITS ANALYTICAL APPLICATION FOR SPECTROPHOTOMETRIC MICRO-DETERMINATION OF COPPER(II)

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ABSTRACT. A novel azo dye ligand namely (2-(pyridin-3-yldiazenyl)naphthalen-1-ol (HPYNA), was synthesized by the coupling reaction of diazonium salt of 3-aminopyridine with naphthol. The palladium(II) complex for HPYNA ligand was prepared by reacting palladium(II) ions with the HPYNA ligand. These synthesized compounds were characterized using different techniques, including mass, ^{1}H-NMR, infrared, and UV-Vis spectroscopy. The infrared results show that the azo ligand reacts as a bidentate via the oxygen atom of phenol and nitrogen atom of the azo group. The palladium(II) complex is square-planer with diamagnetic properties depending on the results of electronic transitions and magnetic sensitivity. The HPYNA ligand and palladium complex showed significant activity as antioxidants by DPPH method. Trace levels of copper in synthetic urine sample can be successfully determined using the validated method. And finally, the proposed method showed selectivity, in addition to have high accuracy and control.

KEY WORDS: Azo dye, Naphthol, DPPH, Palladium(II) complex, Synthetic urine

INTRODUCTION

Azo ligands are attention center of scientists and researchers due to azo compounds which are the most extensively used organic reagents, and differentiated by their important applications. These compounds showed high stability and quick interaction with diverse metal ions with exceptional sensitivity and selectivity, many assays used to surveil antioxidant activity of the compounds which happen under different mechanisms such as hydrogen atom transfer, reducing power, single electron transfer, and metal chelation [1-3].

Antioxidants play an important role to inhibit oxidation processes in food and human to get health promotion [4, 5]. The hydroxyl groups found in the phenolic compounds have been granted a crucial position in medicinal chemistry. Because they are responsible for anti-oxidant, and other applications [6]. Azo ligands and their complexes consider important antioxidant complexes of azo ligands demonstrated antimicrobial activity by diffusion technique on selected gram-positive and gram-negative bacteria with high zones of inhibition which indicates a much higher ability to stop the growth of the tested pathogens pyridine scaffolds, phenols and derivatives of azo moiety have co-relate the synergistic effect to create antioxidant potential [7]. Azo chromophores give brilliant colors for the azo dyes especially with push-pull groups. Attention to the preparation of azo dye based on pyridyl drugs started since long time ago due to their high biological activity compared to homogeneous azo dyes derived from aniline [8]. The heterocyclic systems, included in chromophore structures as hetrocyclic azo dyes have advantageous influence on nonlinear-

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*Corresponding authors. E-mail: hasan.sh.mohemmed@qu.edu.iq optical properties of polymers that increase the static hyperpolarizability and second-order hyperpolarizability which lead to large nonlinearity properties. Azo dyes has containing pyridine ring various advantages, including an intrinsic color-deepening effect and a compact molecular structure that leads to greater dye ability [9]. Because of the heterocyclic nature of the pyridine ring, the dyed fibers have exceptional sublimation fastness. Due to the low concentration of the heavy metals in the environmental and biological samples and interfering effects for this reason, a number of analytical techniques have been employed. For life, heavy metals are extremely important. Humans require certain of them, such copper. Others, like mercury, cadmium, and lead, are hazardous due to environmental and occupational [10, 11]. Therefore, we are interested in preparation and characterization new azo dye for pyridyl and its palladium complex and study their antioxidant activity as well as using the azo pyridyl ligand as reagent to determine the copper(II) ions.

EXPERIMENTAL

Materials and methods

The suppliers of all chemicals were from Aldrich Chemical Company. All substances used in this research were of analytical grade. ^{1}H-NMR spectra were acquired in DMSO-d6 on a Bruker 500 MHz spectrometer using TMS as an internal standard. The UV–Vis spectra were recorded using a UV-1650PCUV-Visible spectrophotometer. A Bruker spectrophotometer captured the FT-IR spectra on a KBr disc, covering in the range of 400–4000 cm^{-1}. Electro-thermal 9300 M.P. was used to determine the melting points of the synthesized compounds. The Mass AB sciex 3200 QTRAP instrument was used to record the mass spectra for the synthesized compounds. $CuSO_4$ was dissolved in double-distilled water, and a few drops of concentrated sulfuric acid were added to create a stock solution of copper (100 mg/L).

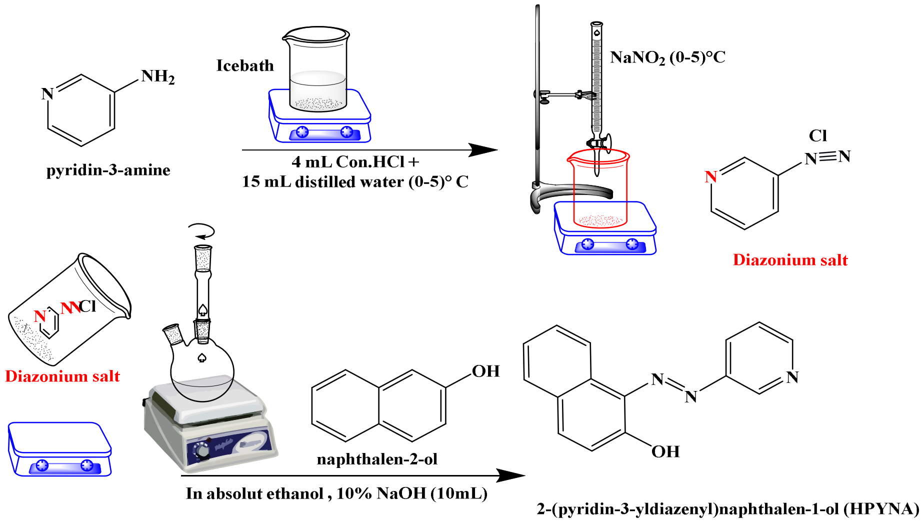
Synthesis of (HPYNA) ligand

The HPYNA ligand was prepared by dissolving 0.5 g, 0.005 mol of 3-aminopyridine in 15 mL of distilled water, then 4 mL of HCl (37%) was added to it and the mixture was cooled to zero degrees Celsius. Sodium nitrite $NaNO_2$ 0.34 g, 0.005 mol was dissolved in 10 mL of distilled water, then the solution was cooled to the zero degrees Celsius, then the sodium nitrite solution add gradually to the above-mentioned acid solution under cooling with stirring and keeping the temperature low, then leave it for 30 min to complete formation process of diazonium salt.

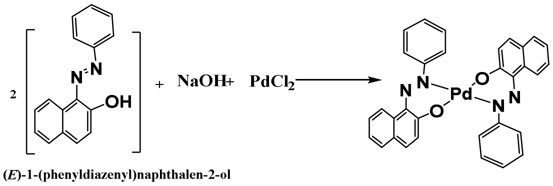
The diazonium salt solution was added drop by drop with continuous stirring to the coupling compound solution consisting of dissolving 0.8 gm, 0.005 mol of 2-naphthol with 15 mL of ethyl alcohol with (10 mL) sodium hydroxide solution (10%) as shown in Scheme 1(a). The solution was left to settle for 30 min. The solution was colored, then left overnight. The precipitate was filtered and washed several times with cold distilled water and recrystallized using an absolute ethanol solution. It was observed that an orange dark crystalline precipitate was formed. The precipitate was dried using a desiccator. The yield is 79% and melting point is 105 °C. The elemental analysis (C.H.N. %) for complex is C, 72.28 (theoretical 72.05); H, 4.45 (4.36); N, 16.86 (16.89).

Synthesis of palladium(II) complex

This complex was prepared as shown in Scheme 1(b), by gradually adding (0.25 g, 0.0009 mol) of the ligand dissolved in 20 mL of absolute ethanol with continuous stirring and heating to a temperature of 60 °C, which was gradually added to (0.1 g, 0.00045 mol) of palladium(II) chloride diluted in 10 mL distillated water (solution of $PdCl_2$ was mixed with little of HCl acid for dissolving then the solution was justified the acidity at pH = 7) with an acid pH of 7. Heated the mixture (under refluxing) for 120 min at 80 °C to finish the reaction, at which we noticed the production of reddish brown for palladium(II) precipitate. The precipitate of palladium(II) complex was filtered and washed many times with distilled water before being dried. The yield is 64% and the melting point is 193 °C to Pd(II) complex. The elemental analysis (C.H.N. %) for complex is C, 64.34 (theoretical 64.28); H, 3.60 (3.48); N, 15.01 (15.06).



(a) Preparation of 2-(pyridin-3-yldiazenyl)naphthalen-1-ol (HPYNA)



(b) Preparation of palladium complex for 2-(pyridin-3-yldiazenyl)naphthalen-1-ol (HPYNA)

Scheme 1. Synthesis of HPYNA ligand and pallaium(II) complex.

Analytical procedures

After mixing appropriate amounts (1:2) of Cu(II) and HPYNA, 3 mL of DDW were added, and the pH was brought to the ideal level of 7.0. After that, the solution was quantitatively moved to a UV-Vis Cuvettes and mixed with ethanol to reach 3.5 mL. To guarantee full complexation, the cell was taken for direct spectrophotometric measurement of Cu(II) at 644 nm at 25 °C, against reagent blank prepared in the same manner but containing no Cu(II) salt.

Calibration graph

Under the chosen experimental conditions, a calibration graph for Cu(II) ion was constructed by plotting absorbance change as a function of analyte concentration and were constructed in the

Figure 1, and some analytical parameters of the proposed method are summarized in Table 1. Using absolute ethanol as the solvent, a range of metal ion concentrations from 1.0 to 10.0 mg/L were prepared, with a constant ligand concentration of 38 mg/L. The results demonstrated that the calibration curve adheres to Lambert Beer's law for a range of concentrations from 1.0 to 8.5 mg/L. The limit of detection and quantification were calculated according to the equation 3σ/m and 10σ/m where σ = standard deviation of the signal obtained from the blank from 5 replicates and m is the slope of the calibration curve. The limits of quantitation (LOQ) and detection (LOD) were 0.89 mg/L and 0.27 mg/L, respectively. This demonstrates that, under ideal reaction circumstances, the technique is extremely sensitive and capable of identifying Cu with low concentrations with respectable accuracy and precision.

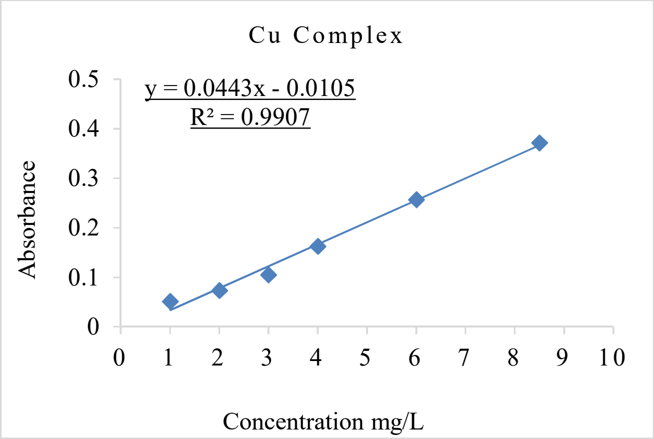


Figure 1. Calibration curve for the complex of HPYNA-Cu.

Table 1. Analytic parameters of Cu calibration plot using UV- method.

Analytical parameter	Proposed method
Regression equation	y = 0.0443x - 0.0105
Slope	0.04
Correlation coefficient	0.99
Linear range (mg/L)	1.0-8.5
Limit of detection(LOD) (mg/L)	0.27
Limit of quantification(LOQ) (mg/L)	0.89

RESULTS AND DISCUSSION

The mass spectra of (HPYNA) ligand and its palladium complex

The mass of HPYNA and palladium complex are 249.2 and 603.5 m/z respectively as shown in Figure 2. The results of mass and elemental analysis are in agreement with expecting formula $C_{15}H_{11}N_3O$ and $C_{30}H_{20}N_6O_2Pd$ for ligand and palladium(II) complex, respectively.

Electronic spectra of HPYNA ligand and its palladium(II) complex

The electronic spectra of the HPYNA azo ligand and its Pd(II) complex were done in DMSO solvent (10^{-5} M). The electronic spectrum of HPYNA showed two types of transitions. The bands at 271, 324 and 369 nm can be assigned to π→π* transition [12-14]. The second type of electronic transition at 473 nm is assigned to n→π* [15-17]. The electronic spectrum of palladium(II) complex for HPYNA ligand showed many absorption bands at different wavelengths. The band detected at 524 nm represents the electronic transition of ${}^1A_{1g}\rightarrow{}^1A_{2g}$ [18-20].While the other bands at 275 nm and 330 nm are related to the intra ligand [21].

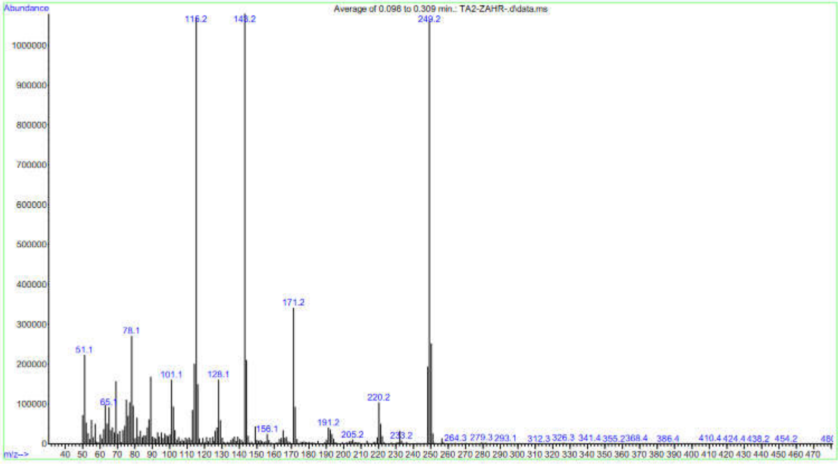


Figure 2. The azo ligand's mass spectrum (HPYNA).

^{1}H-NMR spectra for the pyridyl azo ligand (HPYNA) and its palladium(II) complex

The ^{1}H-NMR spectra of HPYNA ligand and its palladium(II) complex were recorded in a DMSO-d_6 solvent. The signal corresponding to the amino group in 3-aminopyridine disappeared in the HPYNA ligand spectrum as shown in Figure 3, indicating that the start material underwent a reaction and changed into azo dye. At a large chemical shift, the protons aromatic on the carbon atoms beside nitrogen atom in the pyridine ring other than the protons. At 7.9 ppm and 8.56 ppm, respectively, these signals appeared as singlet and doublet signals, as observed in the Figure 5. Chemical shifts (ppm) of ^{1}H-NMR for ligand are 10.80 (s, 1H), 9.07 (s, 1H), 8.94 (d, 1H), 8.54 (m, 1H), 8.13 (d, 1H), 7.88 (d, 1H), 7.61 (m, 2H), 7.41 (m, 2H), 7.25 (d, 1H).

The ^{1}H-NMR of the Pd(II) complex in DMSO-d_6 showed remarkable changes in the chemical shifts of active sites, including the absence of OH due to coordination of the lone pairs of OH and -N=N- groups with Pd(II). The chemical shift of Ar-H and pyridine ring protons were at (8.50-6.94) ppm which indicates to the formation of Pd complex.

The infrared spectra of HPYNA ligand and its palladium(II) complex

The infrared spectra of the (HPYNA) ligand and its palladium complex were recorded in the KBr pellets. The spectrum of the Pd(II) complex was compared with the free ligand to determine the coordination sites that may be involved in chelation. A comparison of the infrared spectra of the free ligand and azo complex gives proof for the complexation of the ligand to metal ion. The characteristic vibration band at 3466 cm^{-1} is due to the OH group of the HPYNA ligand, which disappeared in the infrared spectrum of the Pd complex. That means that the coordination has occurred with the oxygen atom under deportation with the metal ion. The C-O in ligand appeared at 1186 cm^{-1} while, it was at 1159 cm^{-1} in the Pd(II) complex. This shift supports the coordination of oxygen atom to the palladium in the complex [22].

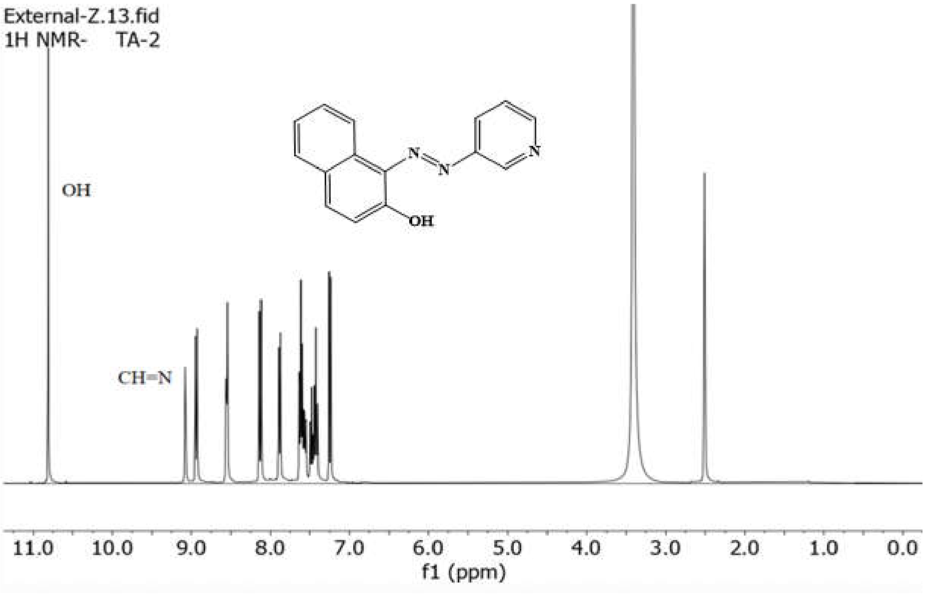


Figure 3. HPYNA ligand's ^{1}H-NMR spectrum.

Upon complexation, the N=N stretching vibrations shifted from 1489 cm^{-1} to the lower frequency in the complex which was at 1465 cm^{-1} in the complex [23]. This shift was due to the donation of electron density from the ligand to the metal center. New vibration bands, which are not present in the spectrum of the HPYNA ligand, appeared around 567-523 cm^{-1}, corresponding to M-N and M-O vibrations supporting the involvement of N and O atoms in coordination with the metal center [1].

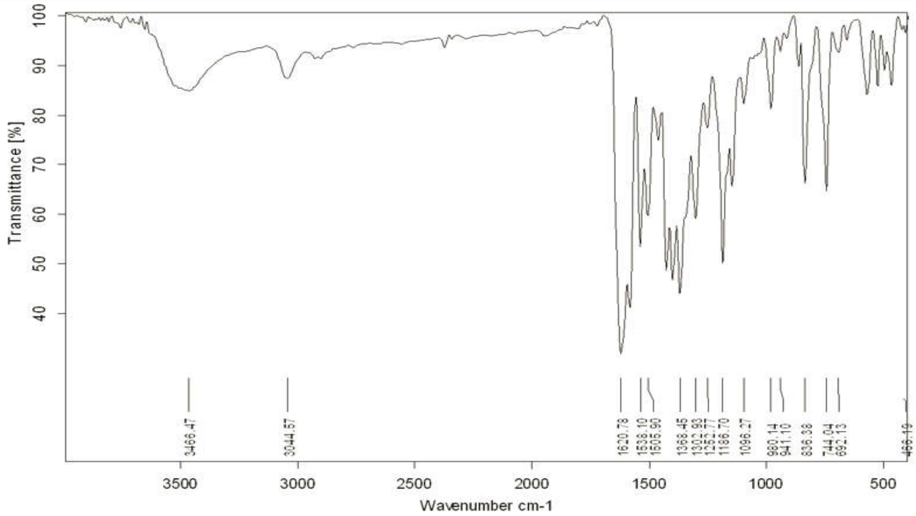


Figure 4. Infrared spectra of the azo ligand (HPYNA).

Evaluation of antioxidant activity of ligand (HPYNA) ligand and its palladium complex

Pyridine is an important heterocyclic compound and is consider a part of various natural products and drugs, which are available in the market to combat different human diseases [24]. Azo dyes and their complexes are the most important chemical compounds having common features in most of the essential compounds and active medicinal agents. These compounds have a broad range of biological activity as antioxidant [25]. The antioxidant activity of the HPYNA ligand and palladium complex was determined by using the 1,1-diphenyl-2-picrylhydrazyl (DPPH) free radical scavenging activity. The palladium complex showed a higher DPPH radical-scavenging activity comparing to the ascorbic acid and the HPYNA ligand as shown in Figures 5. We conclude that the palladium complex is useful source as antioxidants, which confer significant protection against free radical damage [26, 27]. The palladium complex showed higher antioxidant activity than ascorbic acid in all the used concentrations. The antioxidant activity at 12.5 µg/mL was 18.05, 39.85, 36.23% and the results at 200 µg/mL were 61.57, 78.97 and 79.7% for HPYNA ligand, palladium complex and ascorbic acid respectively as shown in Table 2. These results of synthesized compounds are better than many compounds of pyridyl derivatives, azo dyes, and their complexes [28], due to incorporation all in our synthesized compound as well az hydroxy group as phenol. Where the IC_{50} using DPPH inhibition was in the range 172-365 µg mL^{-1} for pyridyl derivative [29]. That means that, heterocyclic pyridyl azo ligands containing nitrogen and oxygen can enhance the antioxidant activity by enhanced the lipophilicity which may increase the antioxidant behavior.

Table 2. The data of antioxidant activity of HPYNA ligand and its palladium(II) complex.

	Ascorbic acid		HPYNA		Pd complex of HPYNA	
Conc. µg mL^{-1}	Mean (%)	SD (%)	Mean (%)	SD (%)	Mean (%)	SD (%)
200	79.7	2.09	61.57	1.73	78.97	3.97
100	74.07	1.01	52.43	4.74	73.07	1.04
50	64.27	4.15	42.28	1.53	63.66	2.61
25	54.67	5.77	29.94	3.07	55.75	2.47
12.5	36.23	4.87	18.06	2.74	39.85	2.72

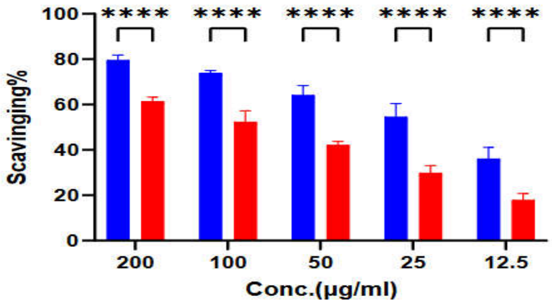


Figure 5. Antioxidant activity of HPYNA ligand (red color) comparing with ascorbic acid (blue color).

Analytical application studies

To evaluate the practical performance of proposed method, this analytical method was applied for determination of Cu(II) in synthetic urine samples. The preparation of samples and procedure for their analysis, salt-free samples were reserved in sterilized plastic containers. 10 mL of the samples was filtered using Whatman filter paper (0.45 µm pore size).The sample was analyzed using the standard addition method without any prior treatment or separation. Measurements were made in triplicate. The synthetic urine sample was prepared according to reference [30]. The synthetic urine was used immediately after its preparation. Synthetic urine samples were doped with three different concentrations of Cu(II): 3, 6 and 7 mg/L, respectively. From Table 3, we can observe the UV-Vis method can be widely used in the determination of copper in urine as shown in Figure 6 in different models with precision, selectivity and high sensitivity.

Table 3. Determination of Cu in synthetic urine samples.

Sample	Cu (mg/L)		Recovery (%)
	Added	Found	
A	3	3.09	103.00
B	6	5.96	99.33
C	7	6.93	99.00

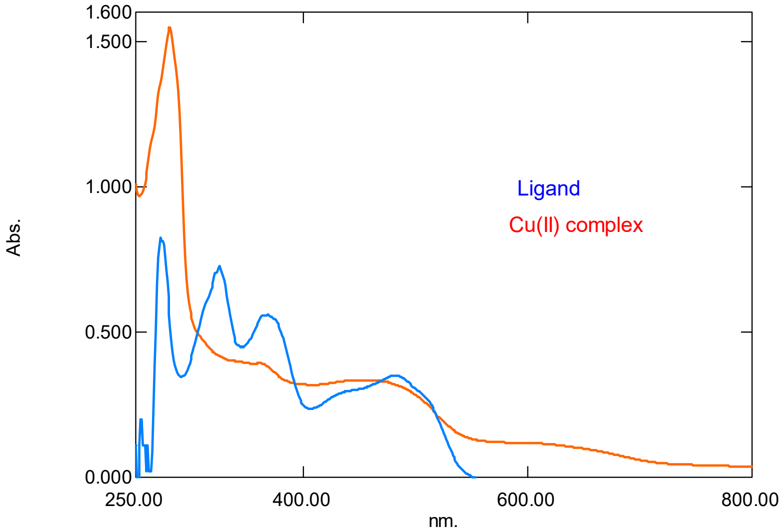


Figure 6. UV-Visible spectra of HPYNA reagent and HPYNA reagent with Copper(II) ions

CONCLUSION

We discussed the design, synthesis, and characterization of (2-(pyridin-3-yldiazenyl)naphthalen-1-ol (HPYNA), which was prepared by coupling diazonium salts of 3-aminopyridine with naphthol. The HPYNA ligand is bidentate, coordinating with the palladium ion through N and O atoms. Compound of Pd(II) with HPYNA ligand was prepared. The palladium complex was created as [Pd(HPYNA)$_2$] based on the results of FT-IR, NMR, and mass spectra, as well as electronic transitions. Its shape is square planar. The UV-Vis method can be widely used in the determination of copper in urine models by HPYNA with precision, selectivity and high sensitivity.

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