Synthesis, spectroscopic study, and identification of Palladium Pd(II) complexes from blend in ligands

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Abstract
Palladium (Pd)(II) complexes resulted from 2-aminopyridine ($C_5H_6N_2$) as the main ligand and malonic acid and sodium pyrophosphate as minor bonds with a molar ratio of (1:1) [Pd($C_5H_5N_2$)(ma)] and [Pd ($C_5H_5N_2$)(pyph)] complexes were studied by melting point, magnetic moment elemental microscopic analysis, FT-IR spectroscopy, molar conductivity and UV-vis spectral. Aminopyridine, malonic acid, and sodium pyrophosphate form two bonds with the Pd(II) ion being binary ligands. The geometric structure suggested the values data for the studied measurements, also suggested that the reagent 2-aminopyridine could be used to determine micrograms of palladium ions using spectroscopy where colored solutions or precipitates possess absorption peaks within the titration curves for each ion.

INTRODUCTION

Palladium a metal element discovered by the scientist William Hyde and Lalaston in 1803 AD [1]He called it this name, and it is an element available in nature, and one of its characteristics is that it is a bright silvery white, and it is almost similar to the platinum element in terms of appearance and hardness, except that it is more flexible and malleable than the platinum element. [2]It has a privileged position in the group of metallic platinum, which consists of distinctive elements platinum, rhodium, ruthenium and iridium[3]. Palladium plays an active role in catalytic reactions and for this reason it is used extensively in these reactions [4], This distinctive catalytic property is used with high efficiency to convert more than 90% of the polluting gases emitted from factories and cars in the form of hydrocarbons, nitrogen dioxide and carbon monoxide into substances with a less harmful effect (converting them into nitrogen and carbon dioxide), carbon, and water fume [5,6].Palladium is also used in the field of dentistry and the field of electronic industries, and in the field of the pharmaceutical industry [7].It is used in hydrogen filtration technology, industrial fields, and the field of groundwater treatment and purification. It is also considered an important and vital part of living cell fuel, which plays the role of mediator in the interaction of hydrogen with oxygen to produce energy, heat, and water inside the cells[8].

MATERIALS AND METHODS

Materials and Instrumentation:

Gold(III) chloride trihydrate PdCl2, 2-aminopyridine, TetraSodiumpyrophosphate, Malonic acid, ethanol and DMSO (Aldrich, BDH, USA). Melting points were estimated with electro thermal melting point apparatus (Stuart). Infrared were determined (Shimadzu (FT-IR) _8400S, Japan) recorded with adouble-beam, Electricalconductivity of complexes were recorded at 25ºCf or 10-3 mole. L-1 in DMSO (Jenway, model 4070), elemental analysis (model EA-3000 single V.3.O Euro Vector), (U.V-Vis) spectrophotometer (U.V-160A-Shimadzu, Japan). magnetic moment (Johnson Matthey).

Creation of [Pd(C5H5N2) (ma)]complex.

Prepared from dissolving (0.09 g), 0.0005 mol PdCl$_2$ in 20 ml of deionized water and adding it to a solution (0.047 g), 0.0005 mol of 2-aminopyridine, dissolved in 30 ml of absolute ethanol with a stirring process and adjusting the pH values to 10 Then, the continuous stirring process took place for 30 minutes. at 30°C. Then (0.0528 g) 0.0005 mol of $C_3H_4O_4$ was added to the mixture whose pH was adjusted to 10, and then the new mixture was continuously stirred for 30 minutes at 30 °C with continuous stirring. Until a precipitate

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representing the manufactured complex was deposited, the process of filtering was carried out, then it was washed, and finally it was dried.

Creation of [Pd(C5H5N2) (pyph)]complex.

Prepared from dissolving (0.09 g), 0.0005 mol PdCl2 in 20 ml of deionized water and adding it to a solution (0.047 g), 0.0005 mol of 2-aminopyridine, dissolved in 30 ml of absolute ethanol with a stirring process and adjusting the pH values to 10 Then, the continuous stirring process took place for 30 minutes. at 30°C. Then (0.2264g), 0.0005mol of $Na_4P_2O_7$ was added to the mixture whose pH was adjusted to 10, and then the new mixture was continuously stirred for 30 minutes at 30 °C with continuous stirring. Until a precipitate representing the manufactured complex was deposited, the process of filtering was carried out, then it was washed, and finally it was dried.

Standard solutions

The standard solution was prepared at a concentration of 1.0 10-2 M from palladium (II) after dissolving 0.1773 g of PdCl2 in a container containing 100 ml of absolute ethanol. Also, a standard solution of the main ligand 2-aminopyridine $(1.0 \times 10\text{-}2)$ was prepared after dissolving 0.0941 g of 2-aminopyridine in a container containing 100 ml of absolute ethanol. Also, a series of buffer phosphate solutions were prepared that covered a wide range of pH

No	Compounds	H_2O	C_2H_5OH	CH_3COCH_3	DMF	DMSO
3	[Pd($C_5H_6N_2$)(ma)]	÷	+	+	+	+
4	[Pd($C_5H_6N_2$)(pyph)]	÷	+	+	+	+

ranging from 2.0 to 12.0 (0.1M KH2PO3 + 1M H3PO4) and a 0.1M NaOH solution was used to adjust the pH to the required number (10).

RESULTS AND DISCUSSION

Solubility of complexes in solvents is shown in Table (1) .

Table 1. Solubility of Pd (II) complexes in solvents

Where: (+) = Soluble and (□) = sparingly soluble

Some physical feature and Elemental microanalysis

Physical feature are listed, Percentage of yield, elemental microanalysis (CHN),
Metal, Magnetic moment measurements,coincided with calculated significance s in Table (2) below.

Table 2. Physical properties ,Percentage of yield, Magnetic moment measurements, Micro elemental analysis and Mass spectral data of Pd (II) Complexes

N0.	Complex	M.wt (g.mol^{-1})	Yield %	m.p c°	μ_{eff} (B.M)	Micro elemental analysis			A.A
						C%	H%	N%	Pd%
3	[Pd($C_5H_5N_2$)(ma)]	299.56	76	170	0.87 Diamagnetic	32.08 (32.09)	1.68 (1.99)	9.35 (8.79)	35.53 (46.13)
4	[Pd($C_5H_5N_2$)(pyph)]	419.45	79	176	0.90 Diamagnetic	14.32 (14.31)	1.22 (1.05)	6.68 (6.93)	25.37 (24.88)

Molar conductance complexes.

The molar conductivities of [Pd(C5H5N2)(ma)] and [Pd(C5H5N2)(pyph)] complexes were measured in DMSO solvent and values of (10.4, 8.5) were given from S.cm2.mole-1, respectively. These values indicate that it behaves non-electrolytic behavior[9].

FTIR Spectroscopy data of Pd (II) complexes.

The infrared spectra recorded the prepared complexes and were compared with the infrared spectrum of the ligands in the pre-coordination ligands shown in Figures (1,2,3). Figures (4) and (5) show the infrared spectra of the prepared complexes, These figures showed absorption beams in the prepared palladium complexes at 3431-3342 cm-1 and 3438-3344 cm, respectively, which represent the amine group covalently bonded with palladium (II)[10]Also, the Figures for the prepared complexes gave bands at 1620 - 1623 cm -1, which are attributed to the group C = N. The ring is covalently bonded with the palladium (II) ion. When comparing the bands before and after coordination, it was found that they suffered from changes attributed to the occurrence of coordination, as they were shifted towards highest and lowest frequency. The change in the shape and position of the adsorption band due to the cycling rate of the amine group is evidence for coordination between the nitrogen atom of this group and the palladium(II) ion. Also, the Figures of the prepared complexes gave new distinct bands at 516-522 cm -1 as a result of the bond vibrations. M-N is attributed to the coordination of the palladium (II) ion with cyclic nitrogen.

The absorption spectra showed beams at 437-445-443 cm-1 due to the oscillations of the M-O bond (11), and their appearance is attributed to the coordination of the metal ion with the oxygen atom in the secondary ligands (Ma) and (Pyph), respectively. stomach complexes. The Figures of the prepared complexes also showed absorption at 1554 and 1226-1245 cm-1, which is attributed to the broadening vibration of the COO and COO groups of the secondary ligands (containing ions and malonato) [Pd (C5H5N2) (Ma)]. Also, the Figures of the complexes showed that the stomachs are absorption bands at 993 cm-1 and 1319 cm-1 belonging to the P=O and UPOP groups, respectively. [12,13] of the ligand (pyrophosphito[Pd(C5H5N2)(Pyph)].
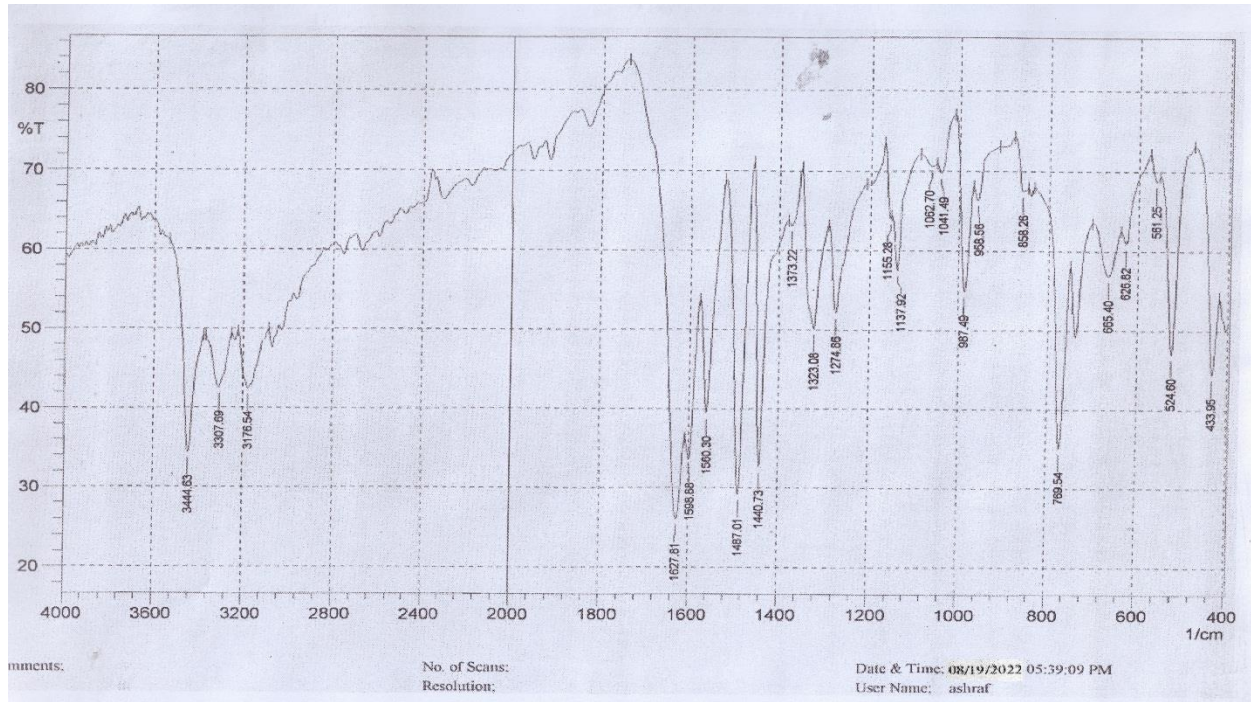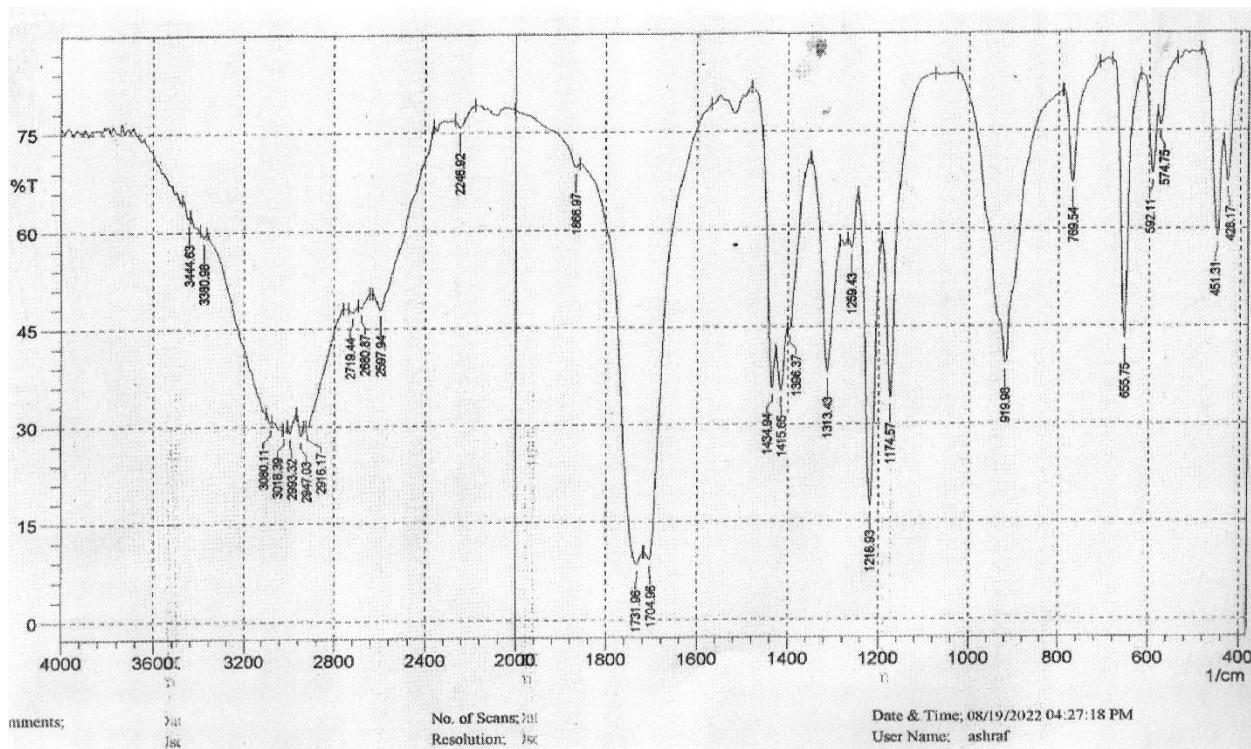
Figure 1 FT-IR spectrum of ($C_5H_5N_2$)
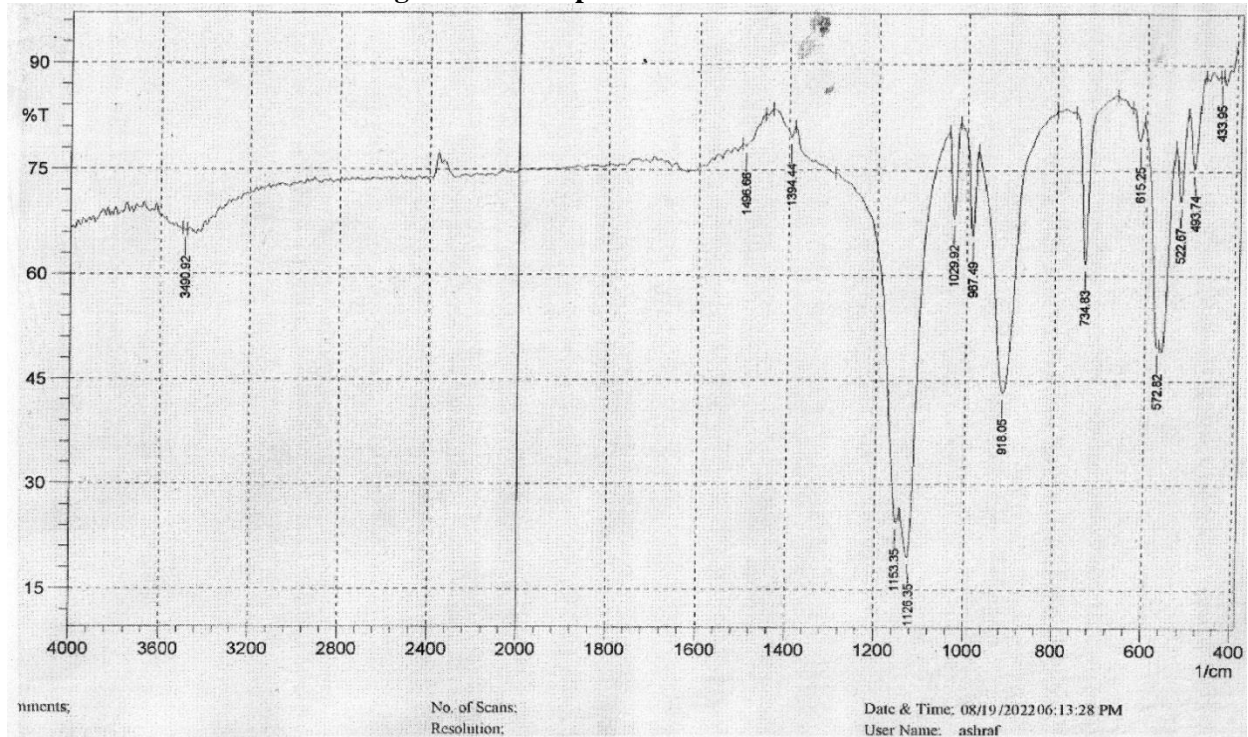
Figure 2 FT-IR spectrum of Malonic acid
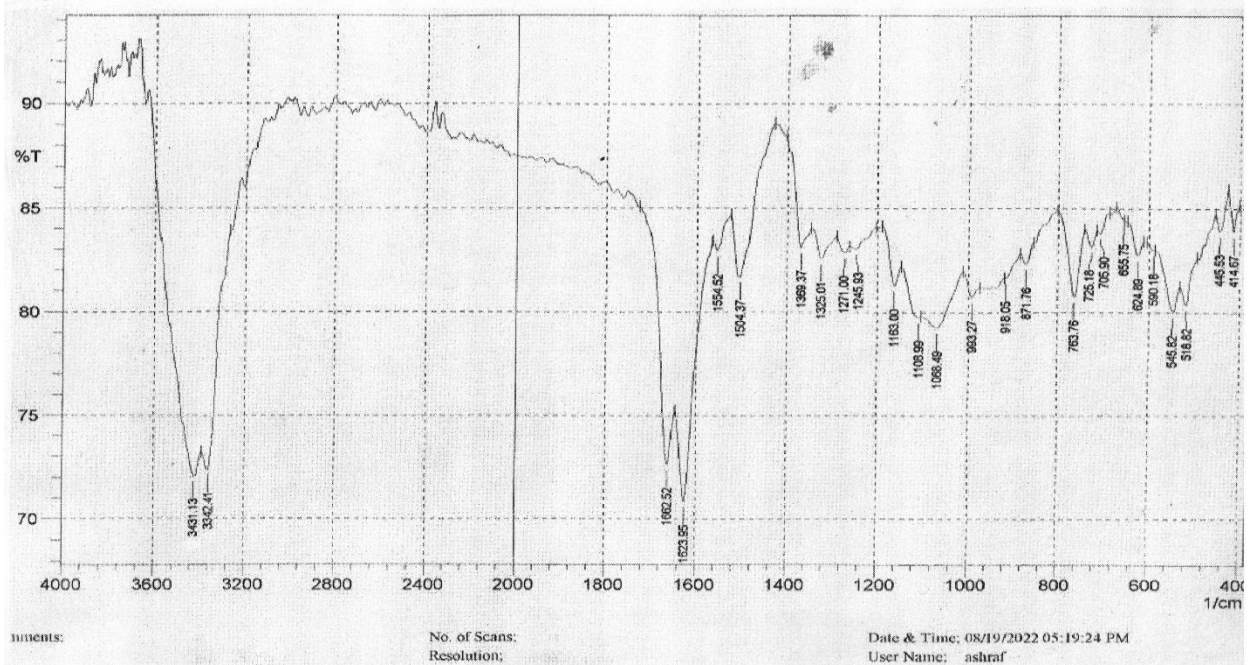

Figure 3 FT-IR spectrum of TetraSodiumpyrophosphate
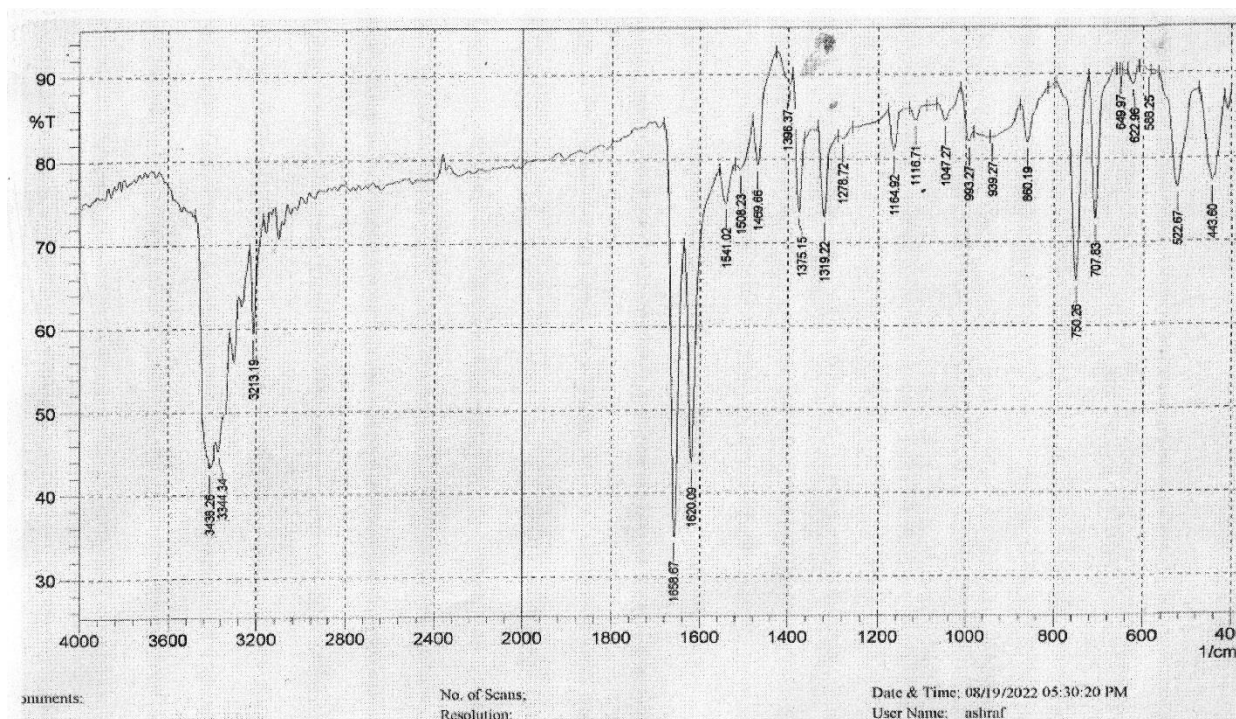

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Figure 4 FT-IR spectrum of [Pd(C$_5$H$_5$N$_2$)(ma)]

Figure 5 FT-IR spectrum of [Pd(C$_5$H$_5$N$_2$)(pyph)]

Table (3) FT-IR spectral data of Pd(II) complexes

No	NH$_2$ asy$\mho$	NH$_2$ sy$\mho$	NH	C=N ring	COO asy$\mho$	COO sy$\mho$	P=O	O-P-O	M-N	M-O
2-Ap	3444	3307	-----	1598	------	------	-----	-------	------	-----
3	3431	3342	-----	1623	1554	1245	-----	-------	518	445
4	3438	3344	-----	1620	-----	-----	993	1319	522	443

UV-Vis Spectral data of Pd (II) complexes.

UV-vis spectra were measured for the prepared complexes [Pd (C$_5$H$_5$N$_2$) (ma)] and [Pd (C$_5$H$_5$N$_2$) (pyph)] and Table (4) shows the obtained values and Figure (6). Showing the UV-vis spectra of the metal ion, the ligand and the as-prepared complexes, we found intense UV-vis absorption peaks at 204 and 202 nm which indicate the $\pi \to \pi^*$trans electron transitions on the internal ligand at 221 nm. We also found intense UV absorption peaks at 315 and 310 nm,attributed to

$n \to \pi^*$ electronic transitions on an internal ligand at 340 nm. In respect of all spectra of complexes, we observed absorption peaks at 595 and 595 nm which can be assigned to the (d–d) electronic transition type

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(^{1}A1g → ^{1}B1g) [14]. All (d d) electronic transitions of the Pd(II) complexes [Pd(C$_5$H$_5$N$_2$)(ma)] and [Pd(C$_5$H$_5$N$_2$)(pyph)] lead us to propose a low-spin square diagram geometry around a central Pd(II) ion[15,16].

Table (4) Electronic spectral data of Pd(II) complexes

No.	Compounds	Λmax Nm	Transition Assignment
1	2-AP	221 340	π→π* n→π*
4	[Pd(C$_5$H$_5$N$_2$)(ma)]	204 315 595	π→π* n →π* ^{1}A1g→^{1}B1g
5	[Pd(C$_5$H$_5$N$_2$)(pyph)]	202 310 595	π→π* n→π*^{1}A1g→^{1}B1g
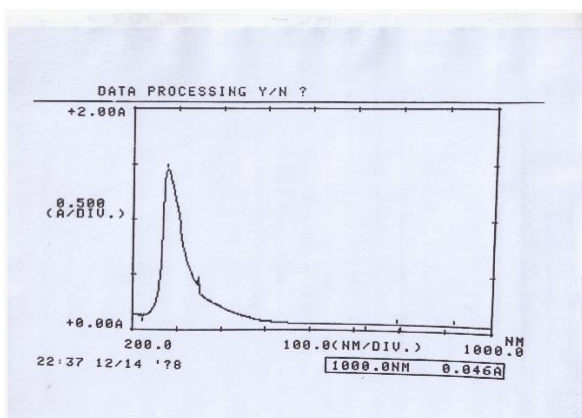
Figure 6a Uv-Vis of Palladium (II)
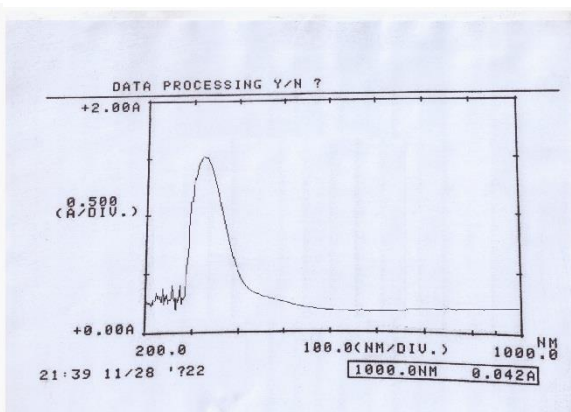
Figure 6b Uv-Vis of (C$_5$H$_5$N$_2$)
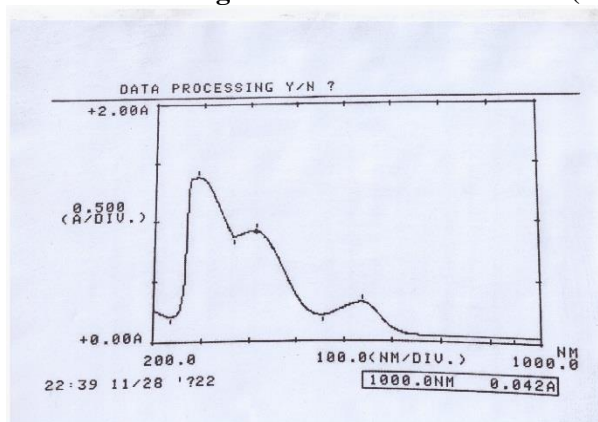
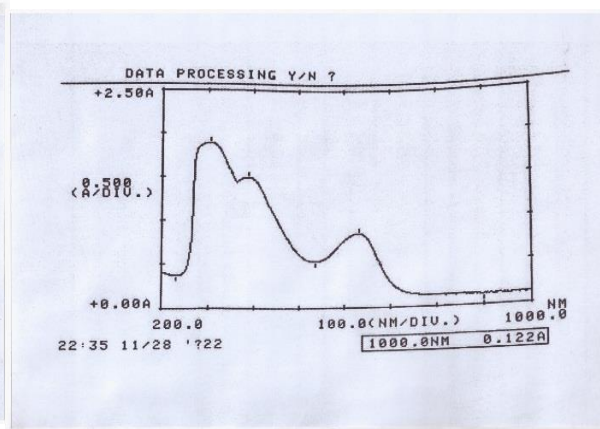**Figure 6e Uv-Vis of [Pd(C$_5$H$_5$N$_2$)(ma)] Figure 6f Uv-Vis of [Pd(C$_5$H$_5$N$_2$)(pyph)]**

Structure of Pd(II) Complexes

As determined by CHN ,MC, UV-Vis,FT-IR suggested molecular structures are shown in Figure (5).

Figure (5). The molecular structure of Pd(II) complexes

No.	Complexes	The molecular structure
3	[Pd(C$_5$H$_5$N$_2$)(ma)] (malonato(2-aminopyridine)) Palladium(II)	
4	[Pd(C$_5$H$_5$N$_2$)(pyph)] (pyrophospheto (2-aminopyridine)) Palladium(II)	

Determination of analytical wavelength

The analytical wavelength (λmax) of the as-prepared complex [Pd(C$_5$H$_5$N$_2$)ma] 595 nm was chosen for $^1A1g \rightarrow {}^1B1g$.

Effect of PH and the best concentrations

The pH has a clear effect on the formation of Pd(II) metal ion complexes in aqueous solution

Where extensively explored PH range from 2-12. To determine the best pH value, solutions of 1.0 mL of5×10^{-4} was dripped into 1.0 ml of 5×10^{-4} Pd(II) in 5 ml volumetric containers, bringing the final volume of the vial to 5.0 ml with phosphate buffer (pH range 2–12). The complex absorption peak was not present in the bonding absorption spectrum. A variety of concentrations of mixing solutions prepared in medium (10^{-2}_10^{-6}) molar at pH value = 10 were studied. Concentrations in the range (10^{-5}) mole were chosen to complete the work because their solutions are clear and the colors are clear and transparent. It is considered easy to measure spectrophotometrically and is subject to Beer-Lambert's law. The effect of pH values and the range of the best concentrations are reviewed in Table 6.

Table (6) Effect pH and best concentrations

pH for 5×10^{-4}	Absorbance at (λ_{max})nm	[Pd]$\times 10^{-5}$	Absorbance at (λ_{max})nm
2	0.047	1	0.016
3	0.048	2	0.035
4	0.084	3	0.049
5	0.083	4	0.072
6	0.185	5	0.087
7	0.180	6	0.106
8	0.188	7	0.119
9	0.195	8	0.135
10	0.247	9	0.158
11	0.180	10	0.178
12	0.172		

Stability of Pd(II) compounds with time.

The stability of the complex between 2-aminopyridine and the metal ion Pd (II) was studied by measuring the absorbance of the complex, at the analytical wavelength (λmax = 595 nm) and at the pH value = 10, and the absorbance was measured every five minutes for one hour. The absorption values of the complex were constant and after 60 minutes the absorption was measured for a subsequent 24 hours. This measurement magnified the reliability of the method as well as the applicability to a large number of the sample. The result is presented in Table 7 below.

Table (7) Effectiveness of time on the stability of Pd (II)Complex

Time/min	Absorbance at (λ_{max})nm
5	0.087
10	0.086
15	0.086
20	0.087
25	0.088
30	0.087
35	0.088
40	0.087
45	0.087
50	0.087
55	0.086
60	0.087

Determination of its stability constant and Stoichiometry of Pd(II)- 2-aminopyridine complex .

Under optimal conditions, the stoichiometry of the Pd(II)-2-aminopyridine complex was determined by Job's method defined by continuous change [17,18] and the molar ratio method [19]. Job's knowledge of continuous change method and molar ratio instrumental method were described by Yoe and Jones (1944). Where the total molar concentration of the metal ion Pd (II) and the ligand 2-aminopyridine were kept constant, the ratio of each of Pd (II) and 2-aminopyridine varied and the absorption record of the resulting mixtures at the analytical wavelength of 595 nm and the pH value of 10 corresponded to the maximum for absorption with the stoichiometric ratio, which is found in 1:1 (Pd(II):2-aminopyridine as reviewed in Figure (7,8) below.

The following equations were adopted to calculate the stability constant of 2-aminopyridine based on Job's method defined by continuous change [20-21].

$$k = \frac{[ML]}{[M][L]} \qquad \text{......... (1)}$$

$$k = \frac{\left(\frac{A2}{A1}\right)}{\left[1-\frac{A2}{A1}\right]\left[CL-CM\left(\frac{A2}{A1}\right)\right]} \qquad \text{......... (2)}$$

represents, A1 = absorption at breaking point, represents A2 = actual absorption, represents
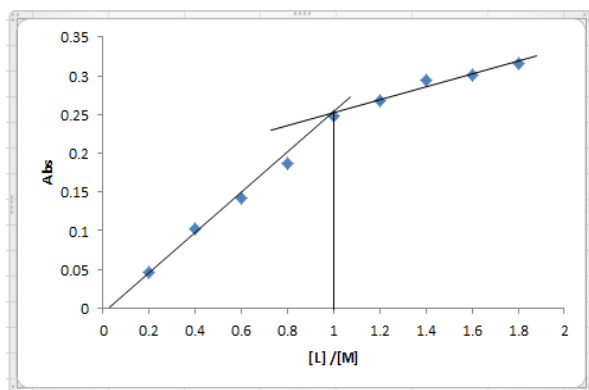   CL = ligand concentration, and CM = metal ion concentration at equilibrium.

Figure 7. Molar ratio of complex Pd(II)- 2-aminopyridine at pH 10

Figure 8: Job's plot of complex Pd(II)- 2-aminopyridine at pH 10

Linear range

Add 1.0 ml of the ligand-2-aminopyridine solution at a concentration of 10×10^{-4} M to each 5 ml volumetric container pre-containing 1.0 ml of the Pd(II) metal ion solution in concentrations (1, 2, 3, 4, 5, 6, 7, 8, 9, 10) x 10^{-5} m. I supplemented the volume of the solutions to 5 mL by adding a phosphate solution having a pH of (10). Then, 60 minutes later, she measured the absorbance of the solutions at an analytical wavelength of 595 nm, and then plotted the absorbance values against the metal concentration the metal ion Pd (II) $\times 10^{-5}$ M, and the results of the plot were presented in Figure 9.
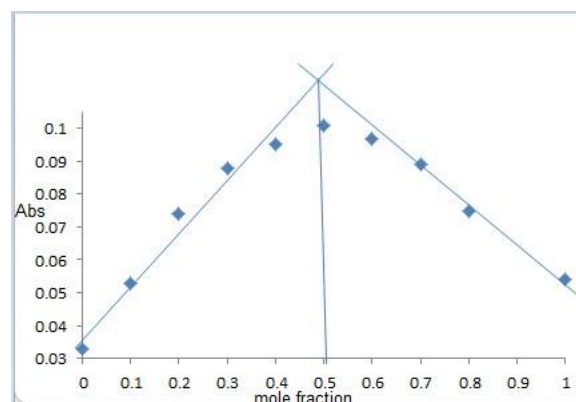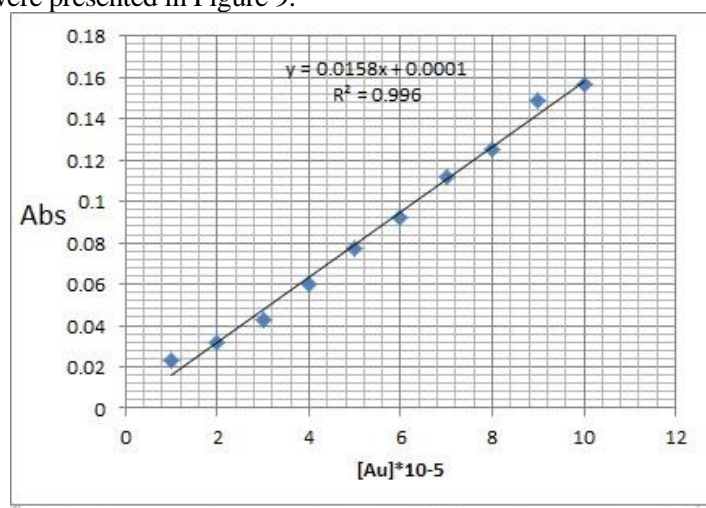

Figure 9. Correlation of absorbance of complex amidst Pd (II) and 2-aminopyridine

Sensitivity.

To test the sensitivity of this analytical method, I evaluated the limit of detection (LOD).

Then followed by evaluating the limit of quantification (LOQ) and finally I evaluated Sandell's sensitivity (22,23). And based on the titration scheme for the Pd(II)-2-aminopyridine system. The LOD, LOQ, and Sandell sensitivity values were adopted

Accuracy and Precision

The accuracy of the method was determined by a significance recovery close to 100% [24] .

Regeneration was done by studying three synthetic Pd(II) tasters they had

Concentrations were subject to the linear range of the procedure, often at any one 3 intervals in the same day (intraday). In the same way, the regeneration test is carried out, as measurements were taken only during one week (between today). All results are reported where the significance of %RSD was set as an indicator of accuracy as shown in Table (8).

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Table 8. Accuracy and precision (intra-and inter-day) ofspectrophotometric

No	Intra-day						Inter-day					
	Taken (µg)	Found (µg)	SD	R_{ec}%	R.S.D%	Er%	Taken (µg)	Found (µg)	SD	R_{ec}%	R.S.D%	Er%
1	5.91	5.88	0.09	99.49	1.5	0.51	1.97	2.10	0.04	99.05	1.9	0.95
2	7.88	7.85	0.11	99.61	1.4	0.64	7.88	7.83	0.12	99.36	1.5	0.64
3	9.85	9.83	0.14	99.79	1.4	0.17	11.82	11.80	0.17	99.83	1.4	0.17

Analytical features.

The results indicated that the major ligand 2-aminopyridine and secondary ligands of malonic acid and sodium pyrophosphate ligand form bidirectional bonds in coordination with the Pd(II) metal ion. The proposed engineering structure of the complexes was adopted depending on the results of the technologies used. We found that the reagent 2-aminopyridine can be used in spectroscopy to determine micrograms of palladium ions because it forms colored solutions, and also the precipitated complexes have superior absorption peaks. These characteristic parameters listed in Table 9 indicate the accuracy and sensitivity of the method used that can be adopted.

Table 9. Analytical parameters (Using -2-aminopyridine Reagent).

Parameter	Significance
λmax nm	595
Molar Absorptivity ($Lmol^{-1}cm^{-1}$)	2205
Log K	4.411
Beer's Law Limit ($\mu g\ mL^{-1}$)	1.97-19.7
pH	10
Limit of Detection ($\mu g\ mL^{-1}$)	0.007
Limit of Quantification ($\mu g\ mL^{-1}$)	0.024
Correlation Coefficient (R^2	0.998
Slope ($mL\mu g^{-1}cm^{-1}$)	0.0202
Intercept	0.0032
Stability constant (K)	2.57×10^4
Sandell's Sensitivity ($\mu g\ cm^{-2}$)	0.005
% Recovery	99.05% - 99.83%
% Er	0.05% - 0.95%
% RSD	0.17% - 0.95%

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