Synthesis and Spectroscopic Study of Palladium Pd (II) Complexes from Mixed Ligands

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Abstract

Palladium (II) (Pd) complexes were synthesized from[(1-Naphthyl) ethylenediamine dihydrochloride]($C_{12}H_{14}N_2$. 2HCl) asprimary ligand, and malonic acid, oxalic acid and sodium pyrophosphateas secondary ligands with (1:1) mole ratio [Pd($C_{12}H_{14}N_2$) Cl_2], [Pd($C_{12}H_{14}N_2$)(ox)],[Pd($C_{12}H_{14}N_2$)(ma)] and [Pd($C_{12}H_{14}N_2$))(pyph]. The complexes were identified by mass spectroscopy ,elemental microanalysis, Chloride Contents ,molar conductivity and melting point. The complex products had square plane geometry quantitatively measured at 410 nm at optimal reaction. Results suggested that [1-Naphthyl) ethylenediamine dihydrochloride] oxalic and malonic acids and sodium pyrophosphate behave as bidentate ligands with Pd (II) ion. Geometrical structure was based on data from previous techniques. We find that [(1-Naphthyl) ethylenediamine dihydrochloride] detector can beused in spectral analysis to estimate micrograms of palladium ions as it complexes with colored solutions or sediments resulting in super absorbent peaks within calibration curves for each ion.

INTRODUCTION

Palladium was discovered by the scientist William Hyde Wollaston in 1803⁽¹⁾.

Palladium (II) chemistry and its closely related platinum (II) are always consideredtogether because they share the same outermost shell electronic configuration d8⁽²⁾. Infact, they have the same oxidation states from 0 to +4 and also have the samegeometrical configuration⁽³⁾.Palladium is used in catalytic reactions for conversion⁽⁴⁾. These reactions are responsible for converting more than 90% ofharmful gases emitted from cars and factories (in the form of hydrocarbons, carbonmonoxide CO, and NO2) to less harmful substances (convert them into N_2 nitrogenand CO_2 carbon dioxide, And H_2O Water $Steam^{(5)}$. Palladium is also used inelectronic industries (6), in the dental industry, in medicine (7), in hydrogenpurification, in chemical applications, and in component in living cell fuel, whichinteracts with hydrogen groundwater treatment⁽⁸⁾, Palladium (II) complexes are prepared to perform the kinetic studies and understand the mechanism of substitution of the Platinum complexes with DNA constituents. This is because of the fact that the substitution of Pd(II) analogs of most cisplatin-related complexes with DNA constituents follows the same apparent substitution process, but at very high reactivities (10⁴-10⁵) times higher). For kinetic and mechanistic investigations of the mechanism of action of platinum basedantitumor compounds, their palladium analogs are most suitable model compounds as their structural and equilibrium behavior is similar⁽⁹⁻¹¹⁾.

MATERIALS AND METHODS

Materials and Instrumentation:

Palladium(II)chlorid PdCl₂ ,[1-Naphthyl) ethylenediamine dihydrochloride], Oxalic-acid, Malonic acid, TetraSodiumpyrophosphate, DMSO and ethanol (Aldrich, BDH, USA). Melting points were measured with electro thermal melting point apparatus (Stuart). Infrared spectra were determined (Shimadzu (FT–IR)–8400S, Japan) recorded with adouble-beam (U.V-Vis) spectrophotometer (U.V 160A, Shimadzu, Japan). Electrical conductivity of complexes were recorded at 25°Cf or 10⁻³ mole. L⁻¹ in DMSO (Jenway, model 4070), elemental analysis (Euro Vector, model EA 3000 single V.3.O), magnetic moment (Johnson Matthey, mass spectra by LC-mass QP SO A: shima 170ev) and spectrophotometric absorbance (Jenway 6405).

Synthesis of $[Pd(C_{12}H_{14}N_2)Cl_2]$ complex.

(0.1773g), 0.001 mol $PdCl_2$ was dissolved in 30 mL ethanol and add drops of concentrated hydrochloric acid HCl to complete dissolution with stirring and heating ,and it was mixed with (0.259g), 0.001 mol of [1-Naphthyl) ethylenediamine dihydrochloride] dissolved in 10 mL ethanol. When the two solutions were mixed the pH was adjusted to 6 and refluxed at 50 °C for 8 hours. The solution was cooled. The complex was precipitated and precipitate filtered off and washed several times by ethanol and dried with ethyl ether .

Synthesis of $[Pd(C_{12}H_{14}N_2)(ox)]$ complex.

(0.1773g), 0.001 mol $PdCl_2$ was dissolved in 30 mL ethanol and add drops of concentrated hydrochloric acid HCl to complete dissolution with stirring and heating and it was mixed with (0.259g), 0.001 mol of [1-Naphthyl) ethylenediamine dihydrochloride], dissolved in 10 mL ethanol by stirring and pH adjusted to 6, The solution was refluxed for 30 min. at 50 °C. and (0.126g) 0.001 mol of $C_2H_2O_4$ in 10 ml distilled waterwas added to the mixture adjusted to pH 6 and refluxed for 8 hours at 50 °C under constant stirring. As described above, the complex was precipitated, filtered, washed and dry.

Synthesis of $[Pd(C_{12}H_{14}N_2)]$ (ma)]complex.

(0.1773g), 0.001 mol $PdCl_2$ was dissolved in 30 mL ethanol and add drops of concentrated hydrochloric acid HCl to complete dissolution with stirring and heating and it was mixed with (0.259g),0.001mol of [1-Naphthyl) ethylenediamine dihydrochloride], dissolved in 10 mL ethanol by stirring and pH adjusted to 6, The solution was refluxed for 30 min. at 50 °C. and (0.104g) 0.001 mol of $C_3H_4O_4$ in 10 ml distilled water was added to the mixture adjusted to pH 6 and refluxed for 8 hours at 50 °C under constant stirring. As described above, the complex was precipitated, filtered, washed and dry.

Synthesis of $[Pd(C_{12}H_{14}N_2) (phph)]$ complex.

(0.1773g), 0.001 mol PdCl₂ was dissolved in 30 mL ethanol and add drops of concentrated hydrochloric acid HCl to complete dissolution with stirring and heating and it was mixed with (0.259g), 0.001 mol of [1-Naphthyl) ethylenediamine dihydrochloride], dissolved in 10 mL ethanol by stirring and pH adjusted to 6, The solution was refluxed for 30 min. at 50 °C. and (0.446g) 0.001 mol of Na₄P₂O₇ in 10 ml distilled water was added to the mixture adjusted to pH 6 and refluxed for 8 hours at 50 °C under constant stirring. As described above, the complex was precipitated, filtered, washed and dry.

Standard solutions

 $1.0\times10^{\text{-3}}$ M palladium(II) was prepared by dissolving 0.0177g PdCl $_2$ in 100 mL ethanol. A standard solution of [1-Naphthyl) ethylenediamine dihydrochloride (1.0× $10^{\text{-3}}$) M was prepared by dissolving 0.0259 g of [1-Naphthyl) ethylenediamine dihydrochloride in 100 mL ethanol. A series of phosphate buffer solution covering the pH range 2.0 to 11.0 was prepared (0.1M KH2PO3 +1M H3PO4) or 0.1M NaOH to the desired pH(5).

RESULTS AND DISCUSSION

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

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

No	Compounds	H ₂ O	C ₂ H ₅ OH	CH ₃ COOH	DMF	DMSO
1	$[\operatorname{Pd}(C_{12}H_{14}N_2)Cl_2]$	÷	÷	÷	÷	+
2	$[\operatorname{Pd}(C_{12}H_{14}N_2)(ox)]$	+	÷	÷	÷	+
3	$[\operatorname{Pd}(C_{12}H_{14}N_2)(ma)]$	÷	÷	÷	÷	+
4	$[\operatorname{Pd}(C_{12}H_{14}N_2)(phph)]$	÷	÷	÷	÷	+

Where : (+) soluble (÷) slightly soluble

Elemental microanalysis and some physical properties.

Physical properties and elemental micro analysis (CHNO) and metal coincided with calculated values are listed in Table (2) below.

Table 2. Physical properties ,Micro elemental analysis and Mass spectral data of Pd (II) Complexes

Complexes	Colour	M.wt (g.mol	m/z	Yiel	m.p	Micro elemental analysis					A.A
Complexes	Colour	(g.mor m/2 d%)		d%	c°	С%	Н%	N%	Ο%	Cl%	Pd%
$[\operatorname{Pd}(\mathcal{C}_{12}H_{14}N_2)\mathcal{C}l_2]$	Dark Brown	363.6	362	85.3	245- 248	39.64 (41.87)	3.88 (2.89)	7.70 (8.98)	-	19.50 (18.08)	29.27 (31.11)
$[\operatorname{Pd}(C_{12}H_{14}N_2)(ox)]$	Blackish brown	380.7	381	66.5	>250	(42.68)	3.71 (2.98)	7.36 (8.99)	16.81 (15.87)	-	27.95 (29.87)
$[\operatorname{Pd}(\mathcal{C}_{12}H_{14}N_2)(ma)]$	Blackish brown	394.3	394	76	>250	45.64 (44.08)	4.09 (3.05)	7.10 (9.54)	16.21 (15.00)	-	26.96 (28.54)
$[\mathrm{Pd}(C_{12}H_{14}N_2)(\mathrm{phph})]$	Blackish brown	512.6	512	61	>250	28.12 26.54	2.75 (3.33)	5.46 (7.54)	21.85 (24.11)	-	20.76 (23.10)

Molar conductance complexes.

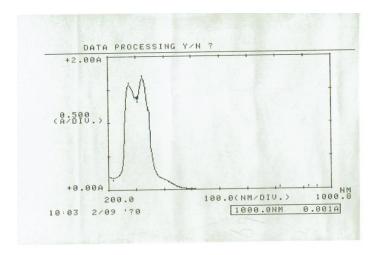
The molar conductance in DMSO solvent of complexes $[Pd(C_{12}H_{14}N_2)Cl_2]$, $[Pd(C_{12}H_{14}N_2)(ox)]$, $[Pd(C_{12}H_{14}N_2)(ma)]$ and $[Pd(C_{12}H_{14}N_2)$ (pyph)] lie in the (12, 24, 10, 9) S.cm².mole⁻¹ respectively, indicating their non-electrolytic behavior⁽¹²⁾.

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

The absorption $[Pd(C_{12}H_{14}N_2)Cl_2]$, $[Pd(C_{12}H_{14}N_2)(ox)]$, spectrum for $[Pd(C_{12}H_{14}N_2)(ma)]$, $[Pd(C_{12}H_{14}N_2)(phph)]$ are summarized in Table (3) and Figure(1) we found intense UV absorption peaks at (272,272, 274,263)nmFor the above complexes, respectively, suggesting an $\pi \to \pi^*$ electronic transition the intra ligand transitions (IL). Also we found intense UV absorption peaks at(340,342,345,346)nm respectively, suggesting an n $\rightarrow \pi^*$ electronic transition the intra ligand transitions (IL), which was shifted to higher frequency when it comparison with that of free ligand (NEDA.2HCl) at (260)nm and (333)nm. this shifting confirm the coordination of the ligand (NEDA.2HCl) with centeral metal ion Pd(II). The spectrum showed peaks in the visible region at (410, 412, 414, 413) nm respectively, which may be attributed to charge transfer transition from ligand to palladium ion (LMCT). The d-d transitions in the complexes were very weak, while the charge transfer peaks were very strong, so the d-d transitions were not observed (13). All electronic transitions for the four Pd (II)complexes suggest low-spin Square planner geometry round a central ion Pd (II) (4d⁸- configuration).

Table (3) Electronic spectral data of Pd (II) complexes

No.	Compounds	λ _{max} nm	Wave Number	Transition Assignment	
1	NED A QUO	260	38461	(π→π*)	
1	NEDA.2HCl	333	30030	(n→π*)	
		272	45454	(π→π*)	
2	$[\operatorname{Pd}(C_{12}H_{14}N_2)Cl_2]$	340	29411	(n→π*)	
		410	24390	LMCT	
		272	45454	(π→π*)	
3	$[\operatorname{Pd}(C_{12}H_{14}N_2)(ox)]$	342	29239	(n→π*)	
		412	24271	LMCT	
		274	36496	(π→π*)	
4	$[\operatorname{Pd}(C_{12}H_{14}N_2)(ma)$		(n→π*)		
		414	24154	LMCT	
		263	38022	(π→π*)	
5	$[\operatorname{Pd}(C_{12}H_{14}N_2)(phph)]$	346	28901	(n→π*)	
		413	24213	LMCT	



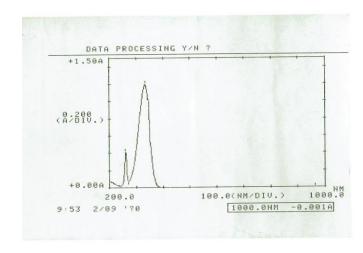
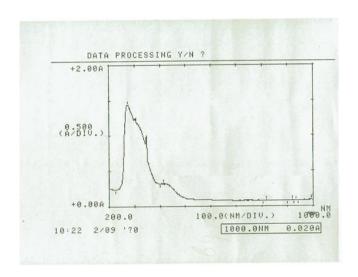


Figure 1a Electronic spectrum of palladium (II)

Figure 1b Electronic spectrum of $(C_{12}H_{14}N_2.2HCl)$



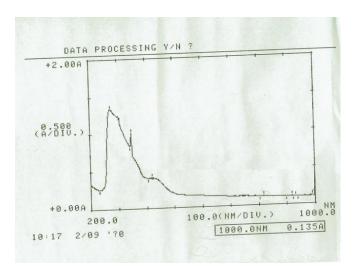


Figure 1c Electronic spectrum of $[Pd(C_{12}H_{14}N_2)Cl_2]$

Figure 1d Electronic spectrum of $[Pd(C_{12}H_{14}N_2)(ox)]$

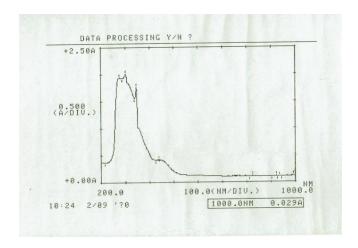


Figure 1e Electronic spectrum of $[Pd(C_{12}H_{14}N_2)(ma)]$

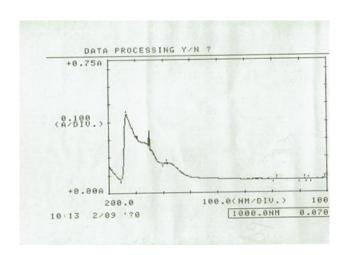


Figure 1f Electronic spectrum of $[Pd(C_{12}H_{14}N_2)(pyph)]$

Mass spectra of Pd(II) complexes:

Mass spectrum of complex $[Pd(C_{12}H_{14}N_2)Cl_2]$ is shown in Fig.(2a). Mass spectrum of this complex (molecular weight equals 363.6) gave a parent peak at m/z=362(M+).

Mass spectrum of complex $[Pd(C_{12}H_{14}N_2)(ox)]$ is shown in Fig.(2b). Mass spectrum of this complex (molecular weight equals 380.7) gave a parent peak at m/z=381 (M+).

Mass spectrum of complex $[Pd(C_{12}H_{14}N_2)(ma)]$ is shown in Fig.(2c). Mass spectrum of this complex (molecular weight equals 394.7) gave a parent peak at m/z=394 (M+).

Mass spectrum of complex $[Pd(C_{12}H_{14}N_2)(phph)]$ is shown in Fig.(d). Mass spectrum of this complex (molecular weight equals 512.6) gave a parent peak at m/z=512 (M+).

The Mass spectra for $[Pd(C_{12}H_{14}N_2)Cl_2]$, $[Pd(C_{12}H_{14}N_2)(ox)]$, $[Pd(C_{12}H_{14}N_2)(ma)]$ and $[Pd(C_{12}H_{14}N_2)$ (pyph)] are summarized in Table Figure (2).

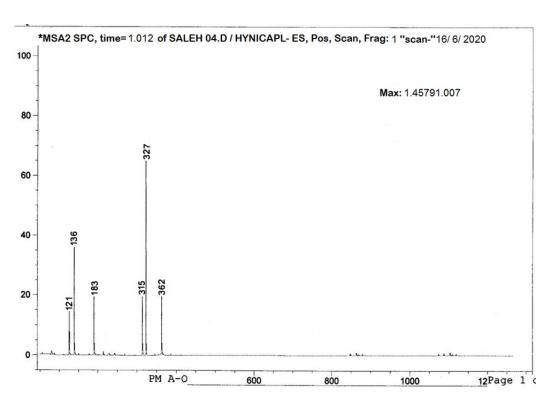
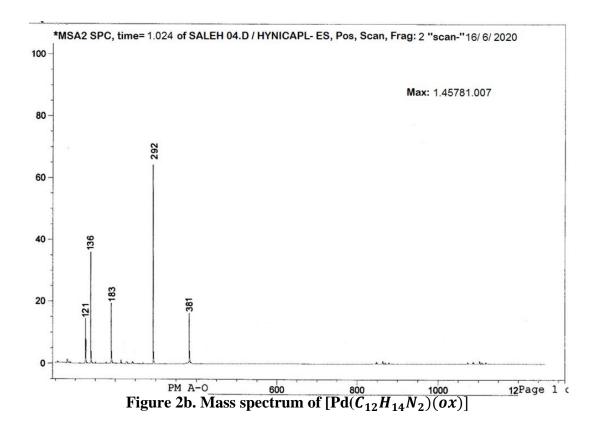
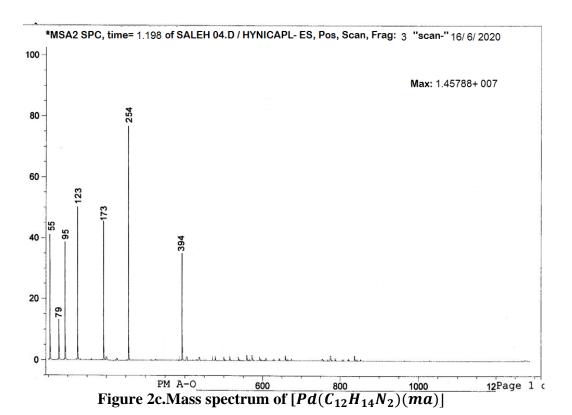
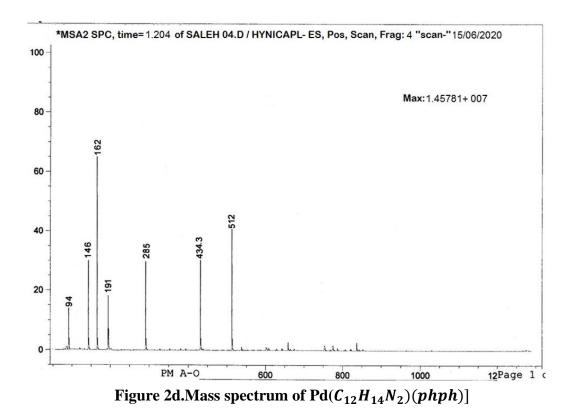


Figure 2a. Mass spectrum of $[(Pd(C_{12}H_{14}N_2)Cl_2]$







Structure of Pd(II) Complexes

As determined by CHNO, MC, UV-Vis, and Mass spectra, suggested molecular structures are shown in Figure (4).

Figure (4). The molecular structure of Pd(II) complexes

No	Complexes	The molecular structure
1	$[Pd(C_{12}H_{14}N_2)Cl_2]$ (dichloro(Naphthylethylenediamine)) $palladium(II)$	
2	$[Pd(C_{12}H_{14}N_2)(ox)]$ (Oxalato(Naphthylethylenediamine)) palladium(II)	
3	$[(Pd(C_{12}H_{14}N_2)(ma)]$ (Malonato(Naphthylethylenediamine)) $palladium(II)$	
4	$[Pd(C_{12}H_{14}N_2)(Phph)]$ (Pyrophospheto(Naphthylethylenediamine) palladium(II)	

Selection of the analytical wavelength.

The analytical wavelength (λ max) of the complex [Pd($C_{12}H_{14}N_2$) Cl_2] was 410nm.

Effect of PH and best concentrations

The effect ofpH of the mixing solutions was studied by mixing 1 ml of ligand solution with a concentration 10^{-3} M with 1 mL of palladium(II) solution at a concentration of 10^{-3} M and placed in volumetric flask 10 mL and complete the volume with Buffer solution and adjust for a wide range of acidic function (1-12) As the absorbance of the prepared solutions was measured at 410 nm wavelength and the pH with the highest absorbance was chosen,A varied range of concentrations of mixing solutions between $(10^{-3}_10^{-6})$ M at pH = 5 was also studied.Concentrations within range(10^{-5}) M were selected to work with them because their solutions are clear and colors are clear and easy to measure spectrally and undergo to the law of Beer-Lambert. The Effect pH and best concentrations shown in Table (5).

Table (5) Effect of time on the stability and effect pH and best concentrations

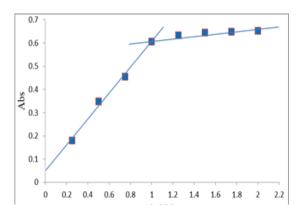
Time/min	Absorbance at 410 nm	pН	Absorbance at (\lambdamax)nm	[Pd]×10 ⁻⁵ M	Absorbance at 410 nm
5	0.077	1	0.20	1	0.012
10	0.076	2	0.23	2	0.031
15	0.077	3	0.21	3	0.058
20	0.076	4	0.20	4	0.077
25	0.076	5	0.26	5	0.097
30	0.077	6	0.23	6	0.104
35	0.077	7	0.20	7	0.119
40	0.078	8	0.23	8	0.130
45	0.078	9	0.19	9	0.149
50	0.076	10	0.20	10	0.165
55	0.077	11	0.18		
60	0.077	12	0.20		

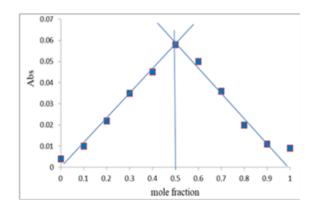
Effect of time on the stability of Pd (II)Complex.

The stability of complex between NEDA.2HCl and pd(II) was observed by measuring the absorbance, at the analytical wavelength (λ max=410 nm) and pH= 5, every five minutes over a epoch of 1 hours. The complex got stable absorbance values after 60 minutes for the subsequent 24 hours. This amplified the reliability of the method as well the applicability for great number of sample. The result is shown in Table(5) above.

Stoichiometry of Pd (II)- NEDA.2HCl complex

Under best conditions, the stoichiometry of Pd(II) –NEDA.2HCl complex was determined by Job's method of continuous variation and Mole ratio (14,15,16). Job's method of continuous variation and mole ratio was useful as described by Yoe and Jones (1944). Keeping the sum of the molar concentration of Pd(II) and NEDA.2HCl constant, the ratio of both Pd (II) and NEDA.2HCl varied and the absorbance of the resulting mixtures were recorded at 410nm and PH 5 The maximum absorbance corresponds to the stoichiometric ratio, this was found at 1:1 Pd (II): NEDA.2HCl as shown in Figure 3,4 below.





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Figure 3 Mole ratio of complex Pd(II)-NEDA.2HCl at pH 5

Figure 4 Job's plot of complexPd(II)-NEDA.2HCl at pH 5

Linear range

1.0 mL of 10×10^{-5} M NEDA.2HCl was pipetted into each of ten 5-mL volumetric flask containing 1.0 mL of $(1, 2, 3, 4, 5, 6, 7, 8, 9, 10) \times 10^{-5}$ M of Pd (II). The solutions were made up to 5 mL by phosphate buffer solution of pH (5). After 60 minutes, the absorbance of the solutions were measured at 410 nm and plotted against Pd (II) concentration $\times 10^{-5}$ M (Figures5)

Figure 5. Correlation of absorbance of complex between Pd (II) and NEDA.2HCl

[Pd]*10-5

Sensitivity

The sensitivity of the method was tested by evaluation of both the limit of detection (LOD), limit of quantification (LOQ) and Sandell's sensitivity⁽¹⁷⁻¹⁸⁾ The limit of detection (LOD) is the lowest amount of the investigated compound in a sample that can be detected, but not necessarily quantified with an acceptable uncertainly. LOD of a method is an important factor if quantitative measurements are to be made at concentrations close to it .The LOD was calculated from the calibration graph of the metal- ligand where the intercept (yb) can be calculated. The following equations were used:

$$SD = \frac{\sqrt{(Xi - X)2}}{n - 1}$$

LOD=yb +3SD

Where, Xi is the measured absorbance, X is the mean, SD is the standard deviation, LOD is the detection limit, and yb is the intersection point of the calibration curve.

The limit of quantification (LOQ) is the lowest concentration of compound that can be measured in a sample matrix at an acceptable level of accuracy and precision. The LOQ is always higher than the LOD and is often taken as fixed multiple of the LOD

(usually triple times higher than LOD value). The LOQ is determined by the same way as LOD:

$$LOQ = yB + 10SD$$

or calculated directly from the LOD:

$$LOQ = 3.3 \times LOD$$

Sensitivity of the proposed methods is also determined by calculating Sandell's sensitivity $(\mu g/cm^2)$, which can be defined as smallest weight of substance that can be detected

Where:

 $\varepsilon = a \times M.wt$

As:

 $\varepsilon = \text{molar absorptivity (L. mol}^{-1}.\text{cm}^{-1})$

a = a specific absorbance (L.g.cm⁻¹)

M.wt = molecular weight of the substance to be estimated (g.mol⁻¹).

By calculating the specific absorption coefficient (a), the sensitivity of Sandell's was calculated

 $a = \varepsilon / wt \times 1000$

S = 0.001 / a

Accuracy and Precision

Accuracy of the manner is indicated by the closeness of the 100% recovery value ⁽¹⁹⁾. Repeatability were made by studying four synthetic Pd (II) samples whose Concentrations undergo the linear range of the method, each one was repeatedly measured 6 times in the same day (intra-day). The reproducibility is tested by the same way as the repeatability but the measurements were made over one weeks (inter-day). All the outcomes are reported as the RSD% values as pointer of the precision are given in Table (6).

Table 6. Accuracy and precision (intra-and inter-day) of spectrophotometric

No.			Intra	-day				Inter-day					
	Taken (μg)	Found (μg)	SD	R _{ec} %	RSD %	Er%	Taken (μg)	Found (µg)	SD	R _{ec} %	RSD %	Er%	
1	3.19	3.18	0.066	99.68	2.07	0.31	3.19	3.17	0.057	99.37	1.79	0.6	
2	4.25	4.23	0.048	99.53	1.13	0.47	4.25	4.225	0.08	99.41	1.89	0.59	
3	5.32	5.29	0.057	99.44	1.07	0.56	5.32	5.29	0.057	99.44	1.08	0.56	

Analytical features.

The Dark Brown color of Pd (II)- NEDA.2HCl complex undergo Beer's law in the concentration range (1.06 -10.6) μg mL $^{-1}$ when a molar absorptivity value of 1.96×10^3 Lmol $^{-1} {\rm cm}^{-1}$ at 410nm. The linearity is pointer from the high correlation coefficient (R 2 =0.9995). The manner is sensitive as indicated from the low values of LOD (0.0068 $\mu g m L^{-1}$), LOQ (0.0157 $\mu g m L^{-1}$) and Sandell's sensitivity (0.054 $\mu g m C^{-2}$). The proposed manner showed high accuracy as listed by the percentage recovery (99.37%-99.68%) and %Er (0.31% -0.6%) values. The exactitude of the manner was found to be also high as shown from the small values of the RSD% (1.07%-2.07%) indicating equitable repeatability and reproducibility of the suggested manner. (Table 7).

Table7.Analytical parameters (Using NEDA.2HCl-Reagent)

Parameter	Value
አ _{max} nm	410
Beer's Law Limit (μg mL ⁻¹)	1.06-10.6
Molar Absorptivity (Lmol ⁻¹ cm ⁻¹)	1.96×10 ³
Limit of Detection (μg mL ⁻¹)	0.0068
Limit of Quantification (µg mL ⁻¹)	0.0157
рН	5
Slope (mLµg ⁻¹ cm ⁻¹)	0.0185
Intercept	0.003
Correlation Coefficient (r ²)	0.9995
Sandell's Sensitivity (μg cm ⁻²)	0.054
% RSD	1.07-2.07
% Recovery	99.37-99.68
% Er	0.31-0.6

Our outcomes suggest that the ligands NEDA.2HCl and oxalic acid, malonic acid and sodium pyrophosphate work as bidentate ligands in coordination with Pd(II) ion. The proposed geometrical structure of the complexes was depended on former techniques. We find that NEDA.2HCl detector can be used in spectral analysis to estimation micrograms of Palladium ions as it complexes with tinted solutions or deposits which have super absorbent peaks.

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