

SYNTHESIS, SPECTROSCOPIC STUDY AND BIOLOGICAL ACTIVITY FOR Pd (II) COMPLEXES FROM MIXED LIGANDS

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ABSTRACT : Pd(II) complexes were synthesized from 2-(4-antipyrene azo)-4-nitroaniline (C₁₇H₁₆O₃N₆) as primary ligand, and (Oxalic acid, Malonic acid, sodium pyrophosphate) as secondary ligands using metal: ligand in (1:1) mole ratio with molecular formula [Pd(C₁₇H₁₆O₃N₆)Cl₂], [Pd(C₁₇H₁₆O₃N₆)(ox)], [Pd(C₁₇H₁₆O₃N₆)(ma)], [Pd(C₁₇H₁₆O₃N₆)pyph]. These complexes were characterized by spectral methods (FTIR, (U.V-Vis), (A.A), mass spectroscopy, (C.H.N), Magnetic moment, molar conductivity and melting point measurements. The complexes product gave square planer geometry. A fast, simple, sensitive and validated spectrophotometric approach was described for determining palladium(II) with the use of 2-(4-antipyrene azo)-4-nitroaniline. The complex product has been quantified at 595 nm length and the best conditions for interaction have been investigated and improved. Biological activity of the complexes were tested on three types of fungus *Aspergillus niger*, *Aspergillus parasiticus*, *Penicillium* sp., which showed high toxicity by measuring the diameters of the fungus used.

Key words : Palladium(II) complex, 2-(4-antipyrene azo)-4-nitroaniline, mixed ligands, spectrophotometry, biological activity.

INTRODUCTION

Many of the palladium complexes prepared, which compared the biological activity with the platinum complexes and gave higher activity from cisplatin (Ezzie *et al*, 2018; Popova *et al*, 2018). Palladium and platinum complexes have been worked against cancer cells and positive results and effects have been obtained (Dysz *et al*, 2019; Rahman *et al*, 2019). The chemistry of palladium with O, N, S donor ligands have been extensively studied to earn data about their mode of coordination, structural and spectral features, which suggest the structures of the prepared metal complexes square planar geometry for the Pd(II) complex (Manzano *et al*, 2017; Ahmad *et al*, 2017; Stojkoviæ *et al*, 2018; El-Sawaf *et al*, 2018). On the other hand, these ligands were used to determine of palladium spectrophotometric, which showed high recovery and sensitivity (Nagaraj *et al*, 2015; Tupys *et al*, 2017; Mohammed *et al*, 2018).

MATERIALS AND INSTRUMENTATION

Palladium (II) chloride PdCl₂, 2-(4-antipyrene azo)-4-nitroaniline was prepared Oxalic acid, Malonic acid, Tetra Sodium pyrophosphate, DMSO and ethanol were supplied by Aldrich and BDH company.

Melting points were measured with an electro thermal (Mettler Toledo MP90 melting points system). Infrared

spectra have been carried out with the use of a Shimadzu, FT-IR-8400S. The compounds' electronic spectra have been recorded with the use of a double-beam (U.V-Vis) spectrophotometer type U.V (Shimadzu-160A), Electrical conductivity measurements were recorder at (25°C) for (0.001M) solution of the samples in DMSO with the use of (HANNAEC214-Conductivitymeter), Elemental analysis recorded with the use of Euro Vector, model EA 3000, single V.3. Single, Magnetic moment measurements recorder by using Johnson Matthey, Mass spectra have been recorded with the use of the device LC-MS QP50A: shimadzu(E170Ev) spectrometer and Spectrophotometer measurements of the absorbance complexes were recorder by using Jenway 6405.

Synthesis of complexes

Synthesis of [Pd(C₁₇H₁₆O₃N₆)Cl₂] complex: About 0.0011 mol (0.2g) PdCl₂, dissolved in 30 mL distilled water and 2-3 drops 0.1 M HCl was mixed with 0.0011 mol (0.3972g) of 2-(4-antipyrene azo)-4-nitroaniline, dissolved in 30 mL acetone. The two solutions were mixed and the pH was adjusted to 8 and refluxed at 45°C for 12 h. The solution was cooled and the pH was adjusted to 6. The complex was precipitated. The precipitate has been filtered off, washed repeatedly by ethanol and then by dried ethyl ether.

Synthesis of [Pd(C17H16O3N6) (ox)]complex
: About 0.0011mol (0.2g) PdCl₂, dissolved in 30 mL distilled water and 2-3 drops 0.1 M HCl was mixed with 0.0011mol (0.3972g) of 2-(4-antipyrineazo)-4-nitroaniline, dissolved in 30 mL acetone, stirring and the pH was adjusted to 8 and the solution was refluxed for 3 h at 45°C. 0.0011mol (0.1421g) of C₂H₂O₄ has been added to the mix and the solution has been adjusted to pH 6 and refluxed for 12 h at 40°C under constant stirring. The complex was precipitated which has been separated by filtration. The produced complex has been washed thoroughly with ethanol, then with diethyl ether.

Synthesis of [Pd(C17H16O3N6) (ma)] complex
: About 0.0011 mol (0.2g) PdCl₂, dissolved in 30 mL distilled water and 2-3 drops 0.1 M HCl, was mixed with 0.0011 mol (0.3972g) of 2-(4-antipyrineazo)-4-nitroaniline, dissolved in 30 mL acetone, stirring and the pH was adjusted to 8 and the solution was refluxed for 3 h at 45°C. 0.0011mol (0.1173g) of C₃H₄O₄ has been added to the mix and the solution was adjusted to pH 6 and refluxed for 12 h at 40°C under constant stirring. The complex was precipitated, which has been separated by filtration. The produced complex has been washed thoroughly with ethanol, then with diethyl ether.

Synthesis of [Pd(C17H16O3N6) (pyph)] complex
: About 0.0011 mol (0.2g) PdCl₂, dissolved in 30 mL distilled water and 2-3 drops 0.1 M HCl was mixed with 0.0011 mol (0.3972g) of 2-(4-antipyrineazo)-4-nitroaniline, dissolved in 30 mL acetone, stirring and the pH was adjusted to 8 and the solution was refluxed for 3 h at 45°C. 0.0011mol (0.5031g) of Na₄P₂O₇ has been added to the mix and the solution has been adjusted to pH 6 and refluxed for 12 h at 40°C under constant stirring. The complex was precipitated which has been separated by filtration. The produced complex has been washed thoroughly with ethanol, then with diethyl ether.

Preparation of standard solutions : A 1.0×10^{-3} M Palladium (II) has been prepared via dissolving 0.0443g of PdCl₂ in 250 mL ethanol. A standard solution of 2-(4-antipyrineazo)-4-nitroaniline (1.0×10^{-3}) M has been prepared via dissolving 0.088 g of 2-(4-antipyrineazo)-4-nitroaniline in 250mL 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.

RESULTS AND DISCUSSION

Characterization of four Palladium(II) Complexes Solubility

Solubility of four prepared complexes has been tested in various solvents, show complete solubility at both

Table 1 : Some physical properties of Pd (II) complexes.

Complex	M-wt g/mol	Yield %	Color	m.p.°C
[Pd (C17H16O3N6)Cl ₂]	529	75	Dark brown	257
[Pd (C17H16O3N6)(ox)]	546	66	Blackish brown	>300
[Pd(C17H16O3N6)(ma)]	560	92	Blackish brown	>300
[Pd(C17H16O3N6)(pyph)]	678	79	Blackish brown	>300

(DMSO, DMF, CH₃OH, CH₃CH₂OH) and dissolve completely in distilled water.

Elemental microanalysis and some physical characteristics

Some of the physical characteristics have been listed in Table 1. Elemental microanalysis (C.H.N) and metal Table 2.

Molar conductance complexes : The molar conductance in DMSO solvent of complexes [Pd(C17H16O3N6)Cl₂], [Pd(C17H16O3N6) (ox)], [Pd(C17H16O3N6) (ma)] and [Pd(C17H16O3N6) (pyph)] lie in the (7.32, 6.88, 6.21, 5.40) S.cm².mole⁻¹ respectively, indicating their non-electrolytic behavior (Tupys *et al*, 2015).

FT-IR spectral data of Pd (II) Complexes : IR spectral data of four complexes [Pd(C17H16O3N6)Cl₂], [Pd(C17H16O3N6) (ox)], [Pd(C17H16O3N6) (ma)] and [Pd(C17H16O3N6) (pyph)] summarized in Table 3, Fig. 1.

The IR spectra of four prepared complexes have been compared to the prepared complexes of free ligand. The detected band at 3460 cm⁻¹ and 3425 cm⁻¹ that was assigned to the stretching frequency of amine group (ν_{asy} - NH₂) and (ν_{sy} - NH₂) of the free ligand(2-(4-antipyrineazo)-4-nitroaniline), this band was shifted to lower or higher frequency at (3456, 3456, 3456, 3456) cm⁻¹ and (3437, 3437, 3433, 3433) cm⁻¹ in spectra of four prepared complexes; this shift refers to coordination of NH₂ group via N atom with metal ions Pd(II). The band at 1400 cm⁻¹ stretching vibration that denotes $\delta_{N=N}$ for azo group of free ligand has been shifted to higher frequency at (1415, 1415, 1419, 1415 cm⁻¹) in the complexes' spectra, which shows that the coordination between nitrogen atom of azo group (N=N) and metal ions has occurred (Mohammed *et al*, 2018). In spectra of complexes [Pd(C17H15O3N6) (pyph)] the band shows two peaks due to consistency ν (P-O-P) appeared at 1284 cm⁻¹ and ν (P = O) appeared at 968 cm⁻¹ in spectrum of complex. The shifted in band of ν P-O-P and the change in intensity and shape of band (ν P=O) was attributed to coordination of pyrophosphate ion with metal ions Pd(II), via two O atoms (Armatas *et al*, 2008).

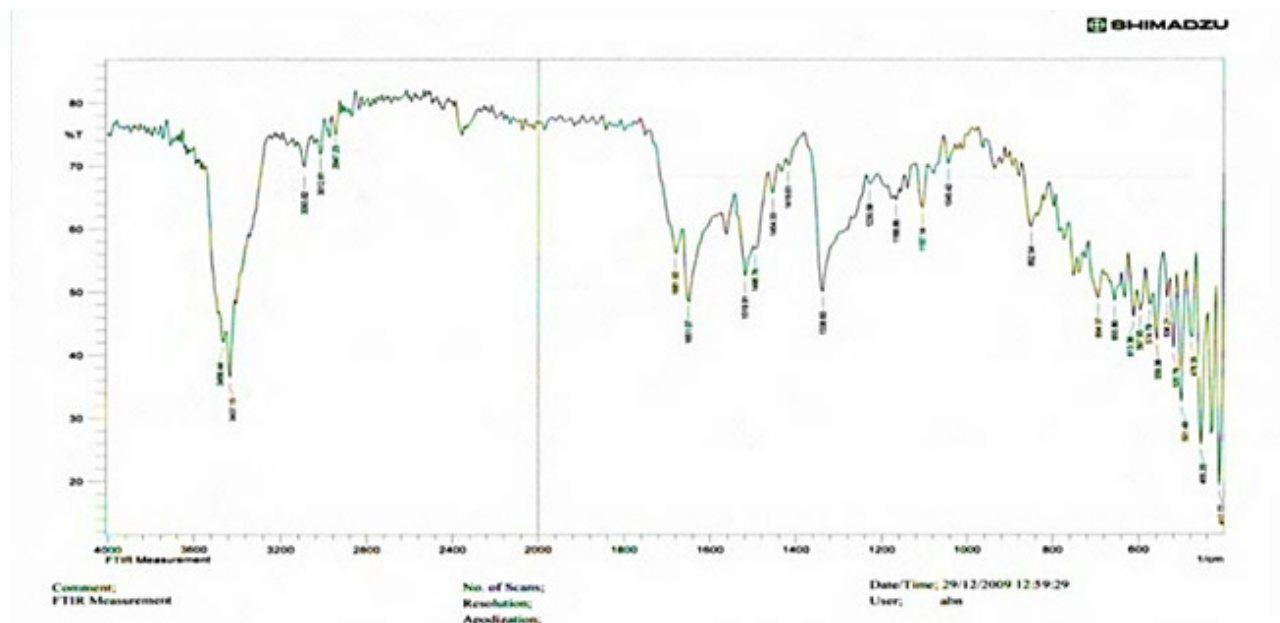


Fig. 1 : FT-IR spectrum of $[\text{Pd}(\text{C}_{17}\text{H}_{16}\text{O}_3\text{N}_6)\text{Cl}_2]$.

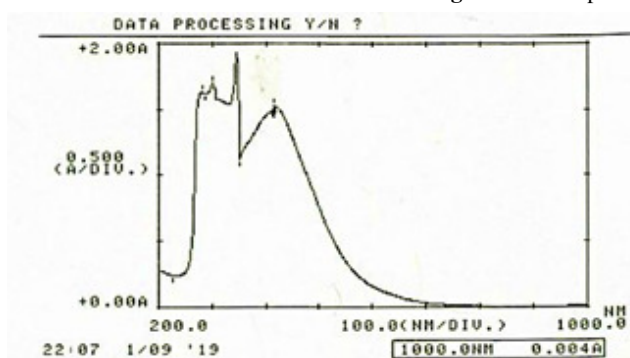


Fig. 2a : Electronic spectrum of ligand 2-(4-antipyrineazo)-4-nitroaniline.

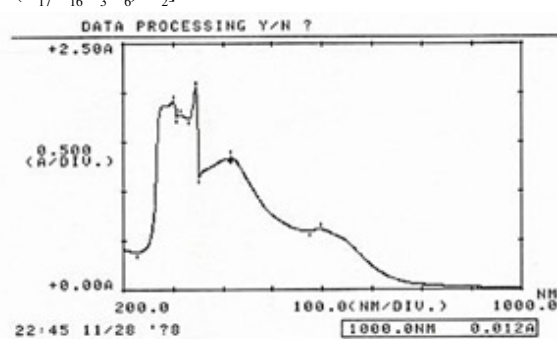


Fig. 2b : Electronic spectrum of $[\text{Pd}(\text{C}_{17}\text{H}_{16}\text{O}_3\text{N}_6)\text{Cl}_2]$.

Table 2 : Micro elemental analysis of Pd (II) complexes.

Empirical formula	Microanalysis found, (Calc.) %			AA
	C	H	N	
1 $[\text{Pd}(\text{C}_{17}\text{H}_{16}\text{O}_3\text{N}_6)\text{Cl}_2]$	38.58	3.04	15.88	20.10
	(39.21)	(4.31)	(16.08)	(21.32)
2 $[\text{Pd}(\text{C}_{17}\text{H}_{16}\text{O}_3\text{N}_6)(\text{ox})]$	41.75	2.95	15.39	36.06
	(40.98)	(3.05)	(16.84)	(37.45)
3 $[\text{Pd}(\text{C}_{17}\text{H}_{16}\text{O}_3\text{N}_6)(\text{ma})]$	42.89	3.23	15.00	35.16
	(43.21)	(4.26)	(16.19)	(36.67)
4 $[\text{Pd}(\text{C}_{17}\text{H}_{16}\text{O}_3\text{N}_6)(\text{pyph})]$	30.11	2.37	12.39	29.04
	(31.09)	(3.14)	(13.18)	(30.21)

The infrared spectra of Pd(III) complexes showed new two bands that aren't present in the free ligand spectrum, those bands are located at 536, 563, 583, 547 cm^{-1} and at 435, 482, 462 cm^{-1} that are attributed to $\nu(\text{M}-\text{N})$ and $\nu(\text{M}-\text{O})$, respectively (John, 1978; Manjula and Antony, 2013). Other bands in the infrared Spectra of complexes

have been listed in Table 3.

U.V-Vis Spectral data of Pd (II) complexes :

The u.v-vis spectral data of Pd(II) complex $[\text{Pd}(\text{C}_{17}\text{H}_{16}\text{O}_3\text{N}_6)\text{Cl}_2]$, $[\text{Pd}(\text{C}_{17}\text{H}_{16}\text{O}_3\text{N}_6)(\text{ox})]$, $[\text{Pd}(\text{C}_{17}\text{H}_{16}\text{O}_3\text{N}_6)(\text{ma})]$ and $[\text{Pd}(\text{C}_{17}\text{H}_{16}\text{O}_3\text{N}_6)(\text{pyph})]$ were summarized in Table 4, Fig. 2a,b. In each case the spectrum showed intense absorption peak in the u.v region at (280)nm and (301)nm refers to ($\delta \rightarrow \delta^*$) electronic transition for intra-ligand, at 340 nm and (416) refers to ($n^* \rightarrow \delta$) electronic transition. The spectra of complexes displayed absorption peak at (416)nm (24038) cm^{-1} , (416 nm) (24038 cm^{-1}) (416nm) (24038 cm^{-1}), (416nm) (24038 cm^{-1}), respectively, which may be attributed to LMCT, while the peak at (595)nm (16806) cm^{-1} , (597)nm (16750) cm^{-1} , (599 nm) (16694 cm^{-1}), (590)nm (16949) cm^{-1} in spectra of $[\text{Pd}(\text{C}_{17}\text{H}_{16}\text{O}_3\text{N}_6)\text{Cl}_2]$, $[\text{Pd}(\text{C}_{17}\text{H}_{16}\text{O}_3\text{N}_6)(\text{ox})]$,

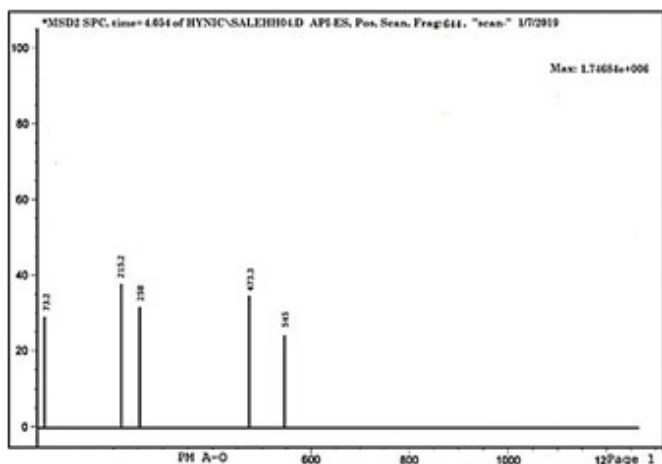


Fig. 3-3a : Mass spectrum of [Pd(C17H16O3N6)(ox)]

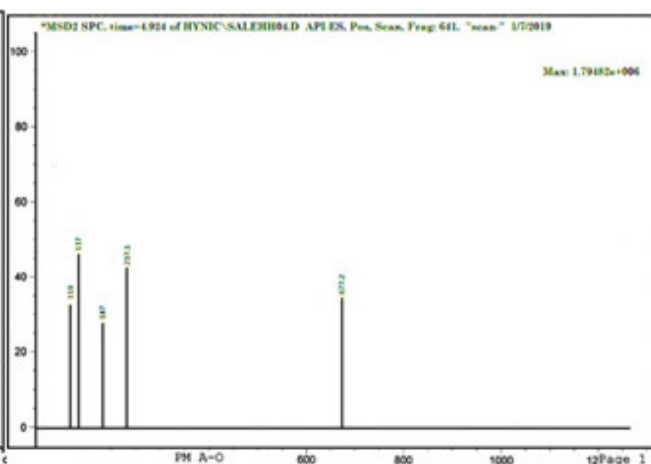


Fig. 3-3b : Mass spectrum of [Pd(C17H16O3N6)(pyph)]

Table 3 : Important IR spectral data of complexes.

No	NH2 Uasy	NH2 Uasy	C=O	N=N	COO Uasy	COO Uasy	P=O	O-P- O	M-N	M- O
L	3460	3425	1670	1400	-----	-----	-----	-----	-----	-----
1	3456	3437	1681	1419	-----	-----	-----	-----	536	-----
2	3456	3437	1681	1415	1554	1230	-----	-----	563	435
3	3456	3433	1647	1419	1562	1230	-----	-----	583	482
4	3456	3433	1678	1415	-----	-----	968	1284	547	462

[Pd(C17H16O3N6) (ma)] and [Pd(C17H16O3N6) (pyph)] complexes respectively, can be assigned to (1A1g→1B1g) (Lever, 1984) respectively. All (d-d) electronic transitions for four Pd(II) complexes [Pd(C17H16O3N6)Cl2], [Pd(C17H16O3N6) (ox)], [Pd(C17H16O3N6) (ma)] and [Pd(C17H16O3N6) (pyph)] suggest low-spin Square planer geometry about center ion Pd(II) (4d8-configuration).

Magnetic moment measurements : Magnetic moment results of Pd(II) complexes is shown that all palladium complexes were Diamagnetic.

Mass spectra of Pd(II) complexes : Mass spectrum of complex [Pd(C17H16O3N6) (ox)] is shown in Fig. 3 a. Mass spectrum of this complex (molecular weight equals 546.6) gave a parent peak at $m/z = 545$ (M+).

Mass spectrum of complex [Pd(C17H16O3N6)(ma)] is shown in Fig. 3 b. Mass spectrum of this complex (molecular weight equals 678.6) gave a parent peak at $m/z = 677.2$ (M+).

The suggested structural formula of prepared Pd(II) complexes

According to the results obtained from M. C, FT-IR, U.V-Vis, C. H. N and Lc-Mass, the suggested structural formula of complexes were shown in Fig. 5.

Selection of the analytical wavelength

The analytical wavelength (λ_{max}) of the complex [Pd(C17H16O3N6)Cl2] was selected at (595 nm), which refers to (1A1g→1B1g).

Impact of PH : The impact of pH on the formation of Pd (II) complex in aqueous solution has been researched within a PH range (2-11). Therefore, aliquots solutions of 1.0 mL of 1.0×10^{-3} was pipetted into 1.0 mL of 1.0×10^{-3} Pd (II) in 10 ml volumetric flasks, the flask was made to 10.0 mL by phosphate buffer solution (pH range 2-11). The absorbance of the solutions was recorded at 595nm, record the highest absorption at pH = 11.

Effect of time on the stability of Pd (II) Complex : The stability of complex between 2-(4-antipyrineazo)-4-nitroaniline and Pd (II) was observed by measuring the absorbance, at the analytical wavelength ($\lambda_{max} = 595$ nm) and pH = 11, every five minutes over a period of 1 hours. The complex attained stable absorbance values after 60 minutes for the subsequent 24 hours. This increased the reliability of the method as well the applicability for large number of sample, Complexity showed high stability.

Stoichiometry of Pd(II)-2-(4-antipyrineazo)-4-nitroaniline complex : In the optimal conditions, the stoichiometry of the formation of Pd (II)-2-(4-

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

No.	Compounds	λ_{max} nm	Wave number	Transition Assignment
1	Ligand	280 301 340 416	35714 33222 29411 24038	$\pi \rightarrow \pi^*$ $\pi \rightarrow \pi^*$ $n \rightarrow \pi^*$ $n \rightarrow \pi^*$
2	[Pd(C17H16O3N6)Cl2]	277 301 314 345 416 595	36101 33222 31847 28985 24038 16806	$\pi \rightarrow \pi^*$ $\pi \rightarrow \pi^*$ $n \rightarrow \pi^*$ $n \rightarrow \pi^*$ C.T 1A1g \rightarrow 1B1g
3	[Pd(C17H16O3N6)(ox)]	277 306 340 416 597	36101 32679 29411 24038 16750	$\pi \rightarrow \pi^*$ $\pi \rightarrow \pi^*$ $n \rightarrow \pi^*$ C.T 1A1g \rightarrow 1B1g
4	[Pd(C17H16O3N6)(ma)]	279 304 346 358 416 599	35842 32894 28901 27932 24038 16694	$\pi \rightarrow \pi^*$ $\pi \rightarrow \pi^*$ $n \rightarrow \pi^*$ $n \rightarrow \pi^*$ C.T 1A1g \rightarrow 1B1g
5	[Pd(C17H16O3N6)(pyph)]	271 302 313 345 416 590	36900 33112 31948 28985 24038 16949	$\pi \rightarrow \pi^*$ $\pi \rightarrow \pi^*$ $n \rightarrow \pi^*$ $n \rightarrow \pi^*$ C.T 1A1g \rightarrow 1B1g

antipyreneazo)-4-nitroaniline complex has been studied by Molar ratio and Job's approach of continuous variation (Yoe and Jones, 1944).

Molar ratio and Job's approach of continuous variation : The ratio of ligand to metal was determined using the Job method and the molar ratios, the ratio of both Pd (II) and 2-(4-antipyreneazo)-4-nitroaniline has been varied and the absorbance of the resulting mixtures have been recorded at 595nm and pH 11. This was found at 1:1 Pd (II): 2-(4-antipyreneazo)-4-nitroaniline).

Validity of the method

I. Linear range : about 1.0 mL of 1.0×10^{-3} M 2-(4-antipyreneazo)-4-nitroaniline has been pipetted into every ten 10-mL volumetric flask that contains 0.1-1.0 mL of Pd(II) (1.0×10^{-3} M). The solutions have been made up to 10 mL by a solution of phosphate buffer that has a pH value equal to (11). After 120 minutes, the absorbance of the solutions have been measured at 595 nanometer and plotted against Pd(II) concentration in $\mu\text{g mL}^{-1}$.

II. Sensitivity of the Method : The method's sensitivity has been expressed by calculating the detection limit, the quantitative limit and Sandell's

Table 5 : The suggested structural formula of prepared Pd (II) Complexes.

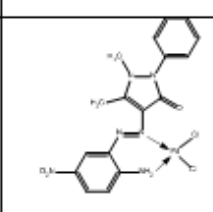
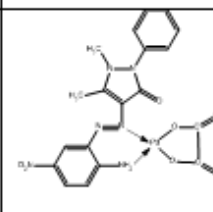
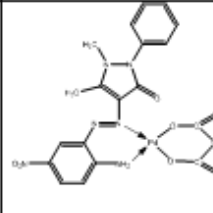
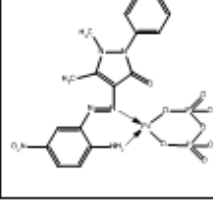
No.	Complexes molecular formula	The molecular structure
1	[Pd(C17H16O3N6)Cl2] (dichloro(2-(4-antipyrene azo)-4-nitro aniline)) palladium(II)	
2	[Pd(C17H16O3N6)(ox)] (oxalato(2-(4-antipyrene azo)-4-nitro aniline)) palladium(II)	
3	[Pd(C17H16O3N6)(ma)] (malonato(2-(4-antipyrene azo)-4-nitro aniline)) palladium(II)	
4	[Pd(C17H16O3N6)(pyph)] (pyrophospheto(2-(4- antipyrene az)-4-nitro aniline)) palladium(II)	

Table 6 : Values of inhibition diameter of fungus.

	Control	1	2	3	4
<i>Aspergillus niger</i>	55mm	-	-	-	-
<i>Aspergillus parasiticus</i>	37mm	-	-	-	-
<i>Penicillium sp.</i>	26mm	8mm	8mm	5mm	7mm
	Control	1	2	3	4
<i>Aspergillus niger</i>	55mm	-	-	-	-
<i>Aspergillus parasiticus</i>	37mm	-	-	-	-
<i>Penicillium sp.</i>	26mm	8mm	8mm	5mm	7mm

sensitivity (Miller and Miller, 2006; Gouda *et al*, 2008). The LOD has been computed from the calibration graph of the Pd(II)-2-(4-antipyreneazo)-4-nitroaniline system.

III. Accuracy and Precision : The accuracy of the analytical approach has been tested by taking samples for different concentrations and measuring absorption during the day (intra-day) and each day for one week (intraday).

Method analytical features : The dark brown color of Pd (II)-2-(4-antipyrineazo)-4-nitroaniline complex obeyed Beer's law in the concentration ranging from 1.06 to 10.6 $\mu\text{g mL}^{-1}$ with a molar absorptivity value of 2021 $\text{L mol}^{-1} \text{cm}^{-1}$ at 595 nm. The linearity is indicated from the high correlation coefficient ($R^2 = 0.998$). The method is sensitive as indicated from the low values of LOD ($0.007 \mu\text{g mL}^{-1}$), LOQ ($0.03 \mu\text{g mL}^{-1}$) and Sandell's sensitivity ($0.005 \mu\text{g cm}^{-2}$). The proposed method showed high accuracy as indicated by the percentage recovery (97.16%-100.15%) and % Er(-2.84%-0.15%) values. The precision of the method was found to be also high as indicated from the small values of the RSD% (1.09-2.8%) indicating reasonable repeatability and reproducibility of the proposed method.

Biological activity

All the Pd(II) complexes showed good activity against *Aspergillus niger*, *Aspergillus parasiticus*, *Penicillium* sp. The inhibitory diameter of the fungus was measured before and after each palladium complex was added. The results in Table 4 revealed that the synthesized compounds have a good inhibitor impact on the growth of fungi.

CONCLUSION

Based on the characterization data for new complexes Pd(II) with 2-(4-antipyrineazo)-4-nitroaniline by FT-IR, U.V-Vis, atomic absorption, molar conductivity, elemental microanalysis, Magnetic moment measurements, mass spectrum with melting point and biological activity, we found that :

1. The ligands 2-(4-antipyrineazo)-4-nitroaniline and Oxalic acid, Malonic acid, sodium pyrophosphate behave as bidentate ligands on coordination with Pd (II) ion.
2. The square planer shape of all complexes prepared were suggested according to the characterization data using all previous techniques
3. The results obtained from the research showed that the 2-(4-antipyrineazo)-4-nitroaniline detector can be used in spectral analysis to estimate the micrograms of Palladium ions. All complexes have super absorbent peaks in which these ions can be quantitatively for concentrations within the calibration curve for each ion.
4. The synthesized compounds have a good inhibitor effect on the growth of fungi, by measuring its inhibition diameter
5. Improve the solubility process of the prepared complexes compared with the primary ligand.

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