



Synthesis and Spectroscopic Study for Pt (IV) Complexes with 4-Aminoantipyridine and Sodium Pyrophosphate

Sattar R. Majeed*¹, Sajid M. Lateef², Hanaa A. Mohammed¹

¹Department of Chemistry, College of Science, University of Anbar, Anbar, Iraq

²Department of Chemistry, College of Education for Pure Science (Ibn Al-Haitham), University of Baghdad, Baghdad, Iraq

Abstract

Pt (IV) complexes were synthesized from 4-Aminoantipyridine (4-AAP) as a primary ligand, and sodium pyrophosphate as a secondary ligand using metal: ligand in (1:1) mole ratio with molecular formula [Pt (4-AAP)Cl₄], [Pt (4-AAP)(Pyph)Cl₂]. These complexes were characterized by elemental microanalysis (C.H.N), (A.A), [I.R, (U.V–Vis), mass spectroscopy], along with molar conductivity, chloride contents and melting point measurements. The ligands (4-AAP) and (Pyph) gave octahedral geometry with Pt (IV) rapid, simple, sensitive and validated spectrophotometric method has been described for the determination of platinum (IV) using 4-aminoantipyridine. The complex product was quantitatively measured at 385nm and the reaction conditions were studied and optimized.

Keywords: Platinum complex, 4-aminoantipyridine, Sodium pyrophosphate, Spectrophotometry.

تخليق ودراسة طيفية لمعقدات البلاتين الرباعي مع 4-أمينو أنتي بايرين وبايروفوسفات الصوديوم

ستار رجب مجيد^{1*}، ساجد محمود لطيف²، هناء عبدالرحمن محمد¹

¹قسم الكيمياء، كلية العلوم، جامعة الانبار، الانبار، العراق.

²قسم الكيمياء، كلية التربية للعلوم الصرفة ابن الهيثم، جامعة بغداد، بغداد، العراق.

الخلاصة

تم تحضير معقدات البلاتين الرباعي من تفاعل 4-أمينو أنتي بايرين كليند اولي وبايرو فوسفات الصوديوم كليند ثانوي باستخدام النسبة المولية (1:1) وفق الصيغ الجزيئية [Pt(4-AAP)Cl₂] و [Pt(4-AAP)Cl₂]. تم تشخيص المعقدين باستخدام تحليل العناصر المايكروبي (C.H.N) و (A.A) و R. او (U.V. Vis) وطيف الكتلة والتوصيلية المولارية ومحتوى الكلورايد وقياسات درجة الانصهار. واستنادا الى النتائج المستحصل عليها اقترح شكل ثماني السطوح لمعقدات البلاتين الرباعي. وقدمت الدراسة طريقة طيفية متوفرة سريعة وبسيطة وحساسة وذات مصداقية تم تطبيقها لتقدير البلاتين الرباعي باستخدام 4-أمينو أنتي بايرين. تم القياس الطيفي للمعقدات الناتجة عند الطول الموجي 385 (نانوميتر) وتم ضبط ودراسة امثل الظروف لتقدير الفلزات في الطرق المقترحة.

*Email: sat70tar@yahoo.com

1-Introduction

4-Aminoantipyrine, which is an antipyretic agent [1] is one of the pyrazole derivatives. Numerous synthetic compounds containing pyrazole moiety have been focused in the field of medicinal chemistry because of their pharmacological, photographic, catalytic and liquid crystals applications. 4-aminoantipyrine is a yellow powder, melting point about (107-109)° C, stable and sensitive for light [2]. The scientific name for 4-aminoantipyrine is (1-phenyl-2, 3-dimethyl-4-amino pyrazole-5-one), 4-Aminoantipyrine is a temperature reducing pyrazole derivatives, it is one of the synthetic drugs [3]. And it can be used as an intermediate for the synthesis of pharmaceuticals especially antipyretic and antianalgesic drugs. Its metal complexes have some applications in analytical and pharmacological areas. It also used in preparation of azo dyes and the 4-aminoantipyrine formylation derivate have biological activities like antimicrobial, antifungal, anti-inflammatory, antiviral, analgesic and antibacterial activities [4].

2- Experimental

2.1 Materials and Instrumentation

HydrogenhexachloroPlatinatate (IV) hexahydrate, 4-Aminoantipyrine, TetraSodiumpyrophosphate, DMSO and ethanol were supplied by Aldrich company.

Melting points of the prepared complexes were measured with an electro thermal (Stuart melting point apparatus). Infrared spectra were performed using a Shimadzu (FT-IR)-8400S. The electronic spectra of the compounds were recorded by using double-beam (U.V-Vis) spectrophotometer type U.V 160A (Shimadzu). Electrical conductivity measurements of the complexes were recorder at (25°C) for (10⁻³ mole L⁻¹) solution of the samples in DMSO by using (conductivity meter, Jew wary, model 4070). The Chloride contents were determined using (686-Titro processor-665. Dosimat Matron Swiss). Elemental analysis recorder by using

Euro Vector, model EA 3000 single V.3.Osinglein. Mass spectra were recorder by using the device GC-mass QP SO A: shima (170 eV) and Spectrophotometer measurements of the absorbance complexes were recorder by using UV-1100.

2.2. Synthesis of Complexes

2.2.1 Synthesis of [Pt (4-AAP) Cl₄] complex.

0.2 mmol (0.103 g) H₂PtCl₆.6H₂O, in 30 mL distilled water, mixed with 0.2 mmol (0.0406 g) 4-Aminoantipyrine, then dissolved in 20 mL ethanol. The two solutions were mixed, adjusted the pH to 8 and refluxed at 40 °C for 14 h. The solution was cooled and the pH was adjusted to 1. The complex was precipitated. The precipitate was filtered off, washed several times by ethanol and then by dried ethyl ether.

2.2.2 Synthesis of [Pt (4-AAP) (Na₂Pyph) Cl₂] complex.

0.2 mmol (0.103g) H₂PtCl₆.6H₂O, dissolved in 30 mL distilled water, mixed with 0.2 mmol (0.0406 g) of 4-AAP, then dissolved in 30 mL ethanol, with stirring, adjusted the pH to 8 and the solution was refluxed for 2 h at 40 °C. 0.2 mmol (0.053g) of Na₄ P₂O₇ was added to the mixture, adjusted the solution pH 1 and refluxed for 15 h at 40 °C under constant stirring. The complex was precipitated and separated by filtration. The produce complex was washed thoroughly with ethanol, then with diethyl ether.

2.3. Preparation of standard solutions

1.0 × 10⁻³ M platinum (IV) was prepared by dissolving 0.026 g of H₂PtCl₆.6H₂O in 50 mL ethanol. A standard solution of 4-AAP (1.0 × 10⁻³) M was prepared by dissolving 0.01g of 4-AAP in 50mL ethanol. A series of phosphate buffer solution covering the pH range of 3.0 to 11.0 was prepared (0.1M KH₂PO₃ +1M H₃PO₄) or 0.1M NaOH to the desired pH [5].

3. Results and Discussion

3.1. Characterization of two Platinum (IV) Complexes.

3.1.1 Solubility

The solubility of the two prepared complexes were tested in different solvents. The results were listed in Table- 3-1.

3.1.2 Elemental microanalysis and some physical properties

Some physical properties were listed in Table-3-2. The elemental microanalysis (C.H.N), metal and chloride analysis Table -3-3, are in a good agreement with calculated values.

3.1.3 Molar conductance complexes.

The molar conductance in DMSO solvent of complexes [Pt(4-AAP)Cl₄] and [Pt(4-AAP)(Pyph)Cl₂] lie in the (20.3, 24.5) S.cm².mole⁻¹ respectively, indicating a non-electrolytic behavior [6].

3.1.4 FT-IR spectral data of Pt (IV) Complexes.

The IR spectral data of two complexes [Pt (4-AAP) Cl₄] Figure- 3-3 and [Pt(4-AAP)(Na₂Pyph)Cl₂] were summarized in Table- 3-4. The I.R spectra of the two prepared complexes were compared with that of free ligand. The detected bands at (3433) cm⁻¹ and (3325) cm⁻¹ were assigned to the stretching frequency of amine group ($\nu_{\text{asy. NH}_2}$) and ($\nu_{\text{sy. NH}_2}$) of the free ligand (4-AAP) [7], this band was shifted to lower or higher frequency at (3475, 3498) cm⁻¹ and (3429, 3410) cm⁻¹ in spectra of two prepared complexes; this shift refers to coordination of NH₂ group via N atom with metal ions Pt (IV). The coordination of the NH₂ group has been also confirmed from the shifts of its bending vibration found at (1647) cm⁻¹ in the spectra of the ligand which was shifted to lower frequency in the spectrum of complexes to (1616, 1620) cm⁻¹. The band at (1678) cm⁻¹ stretching vibration which refers to $\nu\text{C=O}$ for 4-AAP ring of the free ligand, was shifted to lower frequency at (1635,1648) cm⁻¹ in the spectra of complexes, showing that the coordination between oxygen atom of this group (C=O) and metal ions was happened [8, 9]. In spectra of complexes [Pt (4-AAP) (Pyph)], the bands show two peaks due to consistency $\nu(\text{P-O-P})$ appeared at (1118, 1149) cm⁻¹ and $\nu(\text{P=O})$ appeared at (910) cm⁻¹. In the spectrum of the ligand. The $\nu(\text{P-O-P})$ was shifted to a higher frequency at (1153) cm⁻¹. But the only band at (910) cm⁻¹ refers to $\nu\text{P=O}$, was found at the same position, change only in shape and intensity in the spectrum of complex. The shifted in band of $\nu\text{P-O-P}$ and the change in intensity and shape of band ($\nu\text{P=O}$) was attributed to coordination of pyrophosphate ion with metal ions Pt(IV), via two oxygen atoms [10,11]. The I.R spectra of Pt (IV) complexes exhibited new two bands which are not present in the spectrum of the free ligand, these bands are located at (524, 597) cm⁻¹ and at (435, 482) cm⁻¹ which are attributed to $\nu(\text{M-N})$ and $\nu(\text{M-O})$ respectively [12,13]. Other bands in the IR spectra of complexes were listed in Table- 3-4.

3.1.5 U.V-Vis spectral data of Pt (IV) complexes

The U.V-Vis spectral data of Pt (IV) complex [Pt(4-AAP)Cl₄] Figure-3-4 and [Pt(4-AAP)(pyph)Cl₂] were summarized in Table- 3-5, in each case the spectrum showed intense absorption peak in the U.V region at (275)nm (36364) cm⁻¹ ($\epsilon_{\text{max}}=2335$) l mol⁻¹.cm⁻¹ and (275)nm (36364)cm⁻¹ ($\epsilon_{\text{max}}= 1756$) l mol⁻¹.cm⁻¹ respectively refers to ($\pi \rightarrow \pi^*$) electronic transition for intra-ligand (4-AAP), which was shifted to lower frequency when it was compared with that peak at (280)nm of free ligand (4-AAP), this shifting can be assigned to coordination between ligand (4-AAP) with metal ion Pt(IV). The peak at (351)nm (28490) cm⁻¹ ($\epsilon_{\text{max}}=830$) l.mol⁻¹.cm⁻¹ and (346)nm (28902)cm⁻¹ ($\epsilon_{\text{max}}=1389$) l mol⁻¹.cm⁻¹ in spectra of Pt(4-AAP)Cl₄] and [Pt(4-AAP)(Pyph)Cl₂] complexes respectively refers to ($n \rightarrow \pi^*$) electronic transition of intra-ligand. The spectra of two Pt(IV) complexes Pt(4-AAP)Cl₄] and [Pt(4-AAP)(Pyph)Cl₂] displayed absorption peak at (362)nm (27624)cm⁻¹ ($\epsilon_{\text{max}}= 830$) l mol⁻¹.cm⁻¹ and (360)nm (27778) cm⁻¹ ($\epsilon_{\text{max}}=948$) l mol⁻¹.cm⁻¹ respectively, which may be attributed to LMCT, while the peak at (476)nm (21008) cm⁻¹ ($\epsilon_{\text{max}}= 346$) l mol⁻¹.cm⁻¹ and (485)nm (20619) cm⁻¹ ($\epsilon_{\text{max}}= 506$) l. mol⁻¹.cm⁻¹ in spectra of [Pt(4-AAP)Cl₄] and [Pt(4-AAP)(Pyph)Cl₂] complexes respectively, can be assigned to ($^1\text{A}_1\text{g} \rightarrow ^1\text{T}_1\text{g}$); respectively [14]. In the spectra of Pt(4-AAP)Cl₄] complex, the peak at (508)nm (19685)cm⁻¹ ($\epsilon_{\text{max}}= 261$) l.mol⁻¹.cm⁻¹ refers to spin-allowed (d-d) electronic transition type ($^1\text{A}_1\text{g} \rightarrow ^3\text{T}_2\text{g}$) [14]. The spectra of two complexes Pt(4-AAP)Cl₄] and [Pt(4-AAP)(Na₂Pyph)Cl₂] displayed two peaks at (824)nm (12136)cm⁻¹ ($\epsilon_{\text{max}}= 50$) l mol⁻¹.cm⁻¹ and [(618)nm (16181)cm⁻¹ ($\epsilon_{\text{max}}= 343$) l. mol⁻¹.cm⁻¹, (725)nm (13793) cm⁻¹ ($\epsilon_{\text{max}}= 264$) l mol⁻¹.cm⁻¹] Respectively, which can be attributed to spin-allowed and spin-forbbedin (d-d) electronic transition type ($^1\text{A}_1\text{g} \rightarrow ^3\text{T}_1\text{g}$) and ($^1\text{A}_1\text{g} \rightarrow ^3\text{T}_2\text{g}$), ($^1\text{A}_1\text{g} \rightarrow ^3\text{T}_1\text{g}$) respectively [15]. All (d-d) electronic transitions for two Pt(IV) complexes Pt(4-AAP)Cl₄] and [Pt(4-AAP)(Pyph)Cl₂] suggest low-spin octahedral geometry about center ion Pt(IV) (5d⁶- configuration) [14].

3.1.6. Mass spectra of Pt (IV) complexes.

Mass spectrum of [Pt (4-AAP)Cl₄]

The Mass spectrum of complex [Pt (4-AAP) Cl₂] is shown in Figure-3.5. The mass spectrum of this complex (M.wt 540.324 g mol⁻¹) gave a parent peak at m/z = 540 (M⁺), and a peak at m/z = 429.3 assigned to the [M⁺ - (3Cl+4H)].

Mass spectrum of [Pt (4-AAP) (Na₂Pyph)Cl₂]

The mass spectrum of this complex (M.wt 689.224 g mol⁻¹) gave a parent peak at m/z = 689.3 (M⁺), a peak at m/z = 430.3 assigned for the [M⁺ - (C₁₁H₁₂N₂O)Cl₂], a peak at m/z = 429.3 assigned for the [M⁺ - (C₁₁H₁₃N₂O)Cl₂] and a peak at m/z = 204.2 assigned for the [M⁺ - [Pt(Pyph) Cl₂]].

3.1.7 The suggested structural formula of prepared Pt(IV) Complexes

According to the results obtained from M. C, FT- IR, U.V-Vis, C. H. N, chloride content and Mass spectra, the suggested structural formula of complexes were shown in Figures- 3-1 and 3-2 as 3D drawing by using Ultra chem. Office program, 3Dx (2015).

3.1.8. Selection of the analytical wavelength

The analytical wavelength (λ_{max}) of the complex [Pt (4-AAP) Cl₄] was selected at (385)nm which refers to MLCT[14].

3.1.9. Effect of PH

The effect of pH on the formation of Pt (IV)- 4-AAP complex in aqueous solution was investigated over a PH range of (3-11). For this purpose, aliquots solutions of 2.0 mL of 1.0×10⁻³ 4-AAP was pipetted into 0.5 mL of 1.0×10⁻³ Pt (IV) in 10 ml volumetric flasks, the flask was made to 10.0 mL by phosphate buffer solution (pH range 3-11). The absorbance of the solutions was recorded at 385nm; Figure-3.6 that the maximum absorbance and hence the maximum formation of the Pt (IV)-4-AAP complex, was reached at pH= 9. This pH is fixed in the whole study.

3.1.10. Effect of time on the stability of Pt (IV)- 4-AAP Complex.

The stability of complex between 4-AAP and Pt (IV) was observed by measuring the absorbance, at the analytical wavelength (λ_{max} = 385 nm) and pH= 9, 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. The result is shown in Figure- 3.7.

3.1.11. Stoichiometry of Pt (IV)-4-AAP complex.

Under the optimum conditions, the stoichiometry of the formation of Pt (IV)-4-AAP complex was investigated by Job's method of continuous variation [16, 17].

❖ Job's method of continuous variation

The Job's method of continuous variation was applied as described by Yoe and Jones [16, 17]. Keeping the sum of the molar concentration of Pt (IV) and 4-AAP constant, the ratio of both Pt (IV) and 4- AAP was varied (see experimental section) and the absorbance of the resultant mixtures were recorded at 385nm and PH 9. The maximum absorbance corresponds to the stoichiometric ratio, this was found at 1:1(Pt (IV) : 4-AAP); Figure-3-8.

3.1.12. Validity of the method

I. Linear range

2.0 mL of 1.0 × 10⁻³ M 4-AAP was pipetted into each of ten 10-mL volumetric flask containing 0.1, 0.2, 0.3, 0.4, 0.5, 0.6, 0.7, 0.8, 0.9, 1.0 mL of Pt (IV) (1.0 × 10³M). The solutions were made up to 10 mL by phosphate buffer solution of pH (9). After 30 minutes, the absorbance of the solutions were measured at 385 nm and plotted against Pt (IV) concentration in $\mu\text{g mL}^{-1}$ Figure- 3-9.

II. Sensitivity of the Method

The sensitivity of the method was tested by evaluation of both the limit of detection (LOD), limit of quantification (LOQ) and Sandell's sensitivity [18, 19]. 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 uncertainty. LOD of a method is an important factor if quantitative measurements are to be made at concentrations close to it [18]. The LOD was calculated from the calibration graph of the Pt (IV)-4-AAP system where the intercept (y_B) can be calculated. The following equations were used:

$$SD = \frac{\sqrt{\sum[y_i - \hat{y}]^2}}{n-2} \quad (1)$$

$$LOD_{abs} = y_B + 3SD \quad (2)$$

LOD_{abs} was transferred to LOD value by the equation of the regression line.

$$LOD_{abs} = \text{slope (LOD)} + y_B \quad (3)$$

Where y_i and \hat{y} are the measured absorbance and the absorbance from the regression equation; respectively. SD is the standard deviation of absorbance from the regression line (equation 2), LOD_{abs}

is the limit of detection of the absorbance, y_B is the intercept of the calibration line and LOD is the detection limit expressed in concentration unit.

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 generally useful parameter than LOD. The LOQ is relevant only in trace analytical methods when measurements are being at concentrations close to that limit. 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:

$$\text{LOQ} = y_B + 10\text{SD} \quad (4)$$

or calculated directly from the LOD: [18]

$$\text{LOQ} = 3.3 \times \text{LOD} \quad (5)$$

Sensitivity of the proposed methods is also determined by calculating Sandell's sensitivity ($\mu\text{g}/\text{cm}^2/0.001 \text{ Abs unit}$), which can be defined as a smallest weight of substance that can be detected in column of unit cross section [19]. The values of LOD, LOQ and Sandell's sensitivity are given in Table- (3-6).

III. Accuracy and Precision

Accuracy is the main requirement of the determination methods. It can be described as the closeness of agreement between the value that adopted, either as a conventional, true or accepted reference value and the value found. The accuracy in this study is represented and determined by recovery studies. Accuracy of the method is indicated by the closeness of the 100% recovery value [18, 19]. The % recovery ($(\text{found}/\text{taken}) \times 100$) and the percent error ($\%Er = (\text{found}-\text{taken}/\text{taken}) \times 100$) were evaluated to indicate the accuracy of the proposed method. On the other hand, precision describes as the degree of agreement among individual test results when the procedure is applied repeatedly to multiple samplings of homogeneous sample[19].The repeatability (intra-day) and reproducibility precision (inter-day) were applied to the proposed method to indicate the precision. Repeatability were performed by analyzing four synthetic Pt (IV) samples whose concentrations cover the linear range of the method, each 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 performed over two weeks (inter-day) [18]. All the results such as the RSD% values which are an indication of the precision given in Table- (3-7).

3.1.13. Method analytical features.

The red brown color of Pt (IV)-4-AAP complex obeyed Beer's law in the concentration range of 1.95 -19.5 $\mu\text{g mL}^{-1}$ with a molar absorptivity value ($1.816 \times 10^3 \text{ L mol}^{-1} \text{ cm}^{-1}$) at 385 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 ($0.028 \mu\text{g mL}^{-1}$), LOQ ($0.092 \mu\text{g mL}^{-1}$) and Sandell's sensitivity ($0.358 \mu\text{g.cm}^{-2}$).The proposed method showed high accuracy as indicated by the percentage recovery (99.9%-100.0 5%) and %Er (-0.0009%-0.0011 %) values. The precision of the method was found to be also high as indicated from the very small values of the RSD% (0.092 -0.495 %) indicating reasonable repeatability and reproducibility of the proposed method Table-(3-7).The method is comparable with the other reported methods, Table-(3-8).

4. Conclusion

According to the characterization data for new complexes Pt (IV) with 4-Aminoantipyrine by FT-IR, U.V-Vis, atomic absorption, molar conductivity, elemental microanalysis, chloride content along with melting point, we found that:

1-The ligands 4-AAP and sodium pyrophosphate behave as bidentate ligands on coordination with Pt (IV) ion.

2-The geometrical octahedral structure was suggested for prepared complexes based on the characterization data using all previous techniques.

3-The results obtained from the research showed that the 4-Aminoantipyrine detector can be used in spectral analysis to estimate the micrograms of Platinum ions. As it have complex with (colored solutions or colored sediments). These complexes have super absorbent peaks in which these ions can be quantitatively for concentrations within the calibration curve for each ion.

Table 3-1- Solubility of the complexes Pt (IV) in different solvents.

NO	compounds	H ₂ O	DMSO	DMF	CH ₃ OH	C ₂ H ₅ OH
1	[Pt(4-AAP)Cl ₄]	÷	+	+	+	+
2	[Pt(4-AAP)(Na ₂ Pyph)Cl ₂]	+	+	+	+	+

Where: (+) = Soluble and (÷) = sparingly soluble.

Table 3-2- Some physical properties of Pt (IV) Complexes.

Complexes	M-wt g/mol	Yield%	Colour	m.p. °C
[Pt (4-AAP)Cl ₄]	540.324	52	Red brown	Over 250
[Pt (4-AAP)(Na ₂ PyPh)Cl ₂]	689.224	61	Black brown	Over 250

Table 3-3- Micro elemental analysis of Pt (IV) complexes.

Empirical formula	Microanalysis found, (Calc.) %			A.A	Cl
	C	H	N		
1 [Pt(AAP)Cl ₄]	24.43	2.41	7.77	19.69	26.28
	23.68	1.98	8.02	18.94	25.64
2 [Pt(AAP)(Pyph)Cl ₂]	19.15	1.89	6.09	28.30	10.30
	18.76	2.04	7.12	28.06	9.74

Table 3-4- Important IR spectral data of complexes (cm⁻¹).

Compound	$\nu_{\text{asy.}}\text{NH}_2$	$\nu_{\text{sy.}}\text{NH}_2$	$\nu_{\text{C=O}}$	$\delta\text{N-H}$	$\nu_{\text{P-O-P}}$	$\nu_{\text{P=O}}$	$\nu_{\text{M-N}}$	$\nu_{\text{M-O}}$
4-AAP	3433	3325	1678	1647				
[Pt (4-AAP)Cl ₄]	3475	3429	1635	1616	-	-	524	435
[Pt(4-AAP)(Pyph)Cl ₂]	3498	3410	1648	1620	1153	910	597	482

Table 3-5- Electronic spectral data of Pt (IV) complexes.

No	Compound	Wave length (nm)	Wave number (cm ⁻¹)	ϵ_{\max} 1 mol ⁻¹ cm ⁻¹	Assignment	Suggested structure
1	4-AAP	280	35714	2413	($\pi \rightarrow \pi^*$)	
2	[Pt(4-AAP) Cl ₄]	275	36364	2335	Intra-ligand ($\pi \rightarrow \pi^*$)	Octahedral
		351	28490	1106	Intra-ligand (n $\rightarrow \pi^*$)	
		362	27624	830	LMCT	
		476	21008	346	¹ A _{1g} → ¹ T _{1g}	
		508	19685	261	¹ A _{1g} → ³ T _{2g}	
		824	12136	50	¹ A _{1g} → ³ T _{1g}	
3	[Pt (4AAP(Pyph)Cl ₂)]	275	36364	1756	Intra-ligand ($\pi \rightarrow \pi^*$)	Octahedral
		346	28902	1389	Intra-ligand (n $\rightarrow \pi^*$)	
		360	27778	948	LMC	
		485	20619	506	¹ A _{1g} → ¹ T _{1g}	
		618	16181	343	¹ A _{1g} → ³ T _{2g}	
		725	13793	264	¹ A _{1g} → ³ T _{1g}	

Table 3-6- Analytical parameters (Using 4-AAP-Reagent).

Parameter	Value
λ_{\max} nm	385
Beer's Law Limit ($\mu\text{g mL}^{-1}$)	1.95 -19.5
Molar Absorptivity (Lmol ⁻¹ cm ⁻¹)	1.816 x10 ³
Limit of Detection ($\mu\text{g mL}^{-1}$)	0.028
Limit of Quantification ($\mu\text{g mL}^{-1}$)	0.092
PH	9.0
Slope (mL $\mu\text{g}^{-1}\text{cm}^{-1}$)	0.00279
Intercept	0.02626
Correlation Coefficient (R ²)	0.998
Sandell's Sensitivity ($\mu\text{g cm}^{-2}$)	0.35829
% RSD	0.092 -0.495
% Recovery	99.9-100.0 5%
% Er	-0.0009-0.0011%

Table 3-7- Evaluation of accuracy and precision (intra-and inter-day) of the spectrophotometric determination for Platinum with 4-AAP.

Complex sample			Intra-day				Inter-day				
No	Take n (µg)	Found (µg)	Recovery (%)	SD	%RSD	%Er	Found (µg)	Recovery (%)	SD	%RSD	%Er
1	1.95	1.94	99.99	0.009	0.495	-0.0007	1.94	99.98	0.0058	0.3	-0.001
2	3.9	3.89	99.99	0.01	0.259	-0.0007	3.89	99.94	0.0050	0.129	-0.005
3	5.85	5.84	100.01	0.007	0.129	0.0012	5.84	99.9	0.0053	0.092	-0.0009
4	7.8	7.8	100.05	0.008	0.107	0.00045	7.39	100.0	0.005	0.064	0.0007
			100.01	0.009	0.247	5×10^{-5}		99.95	0.0053	0.146	-0.002

Table 3-8- Comparison of the 4-AAP method for the determination of Pt (IV) with other reported methods.

Parameter	This method	[20]ref	[21]ref	[22]ref
λ_{max} (nm)	385	440	403	680
Beer's Law Limit ($\mu\text{g. mL}^{-1}$)	1.95 -19.5	4-14		1.0-7.0
Molar Absorptivity ($\text{Lmol}^{-1}\text{cm}^{-1}$)	1.816×10^3	1.03×10^4	4.9×10^5	2.40×10^4
Limit of Detection ($\mu\text{g mL}^{-1}$)	0.028	-	-	-
Limit of Quantification ($\mu\text{g mL}^{-1}$)	0.092	-	-	-
PH	9	7	6-10	2.2-6
Slope ($\text{mL.}\mu\text{g.}^{-1}\text{cm}^{-1}$)	0.00279	-0.10877		
Intercept	0.02626	-	-	-
Correlation Coefficient (R^2)	0.998	-	-	-
Sandell's Sensitivity ($\mu\text{g cm}^{-2}$)	0.35829	0.0189	0.0078	0.008
% RSD	0.092 -0.495	0.22	-	0.65

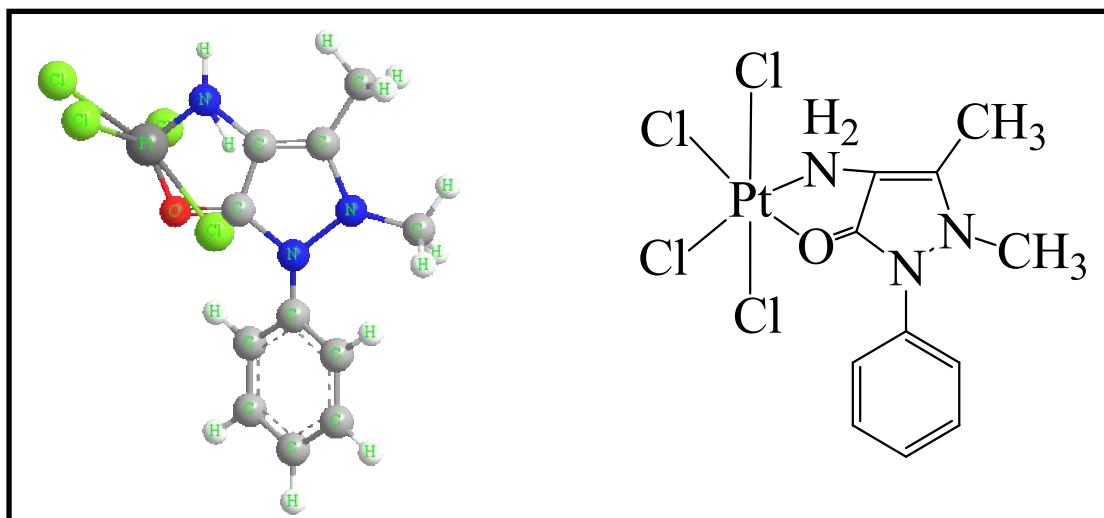


Figure 3-1- The molecular structure of [Pt (4-AAP)Cl₄].

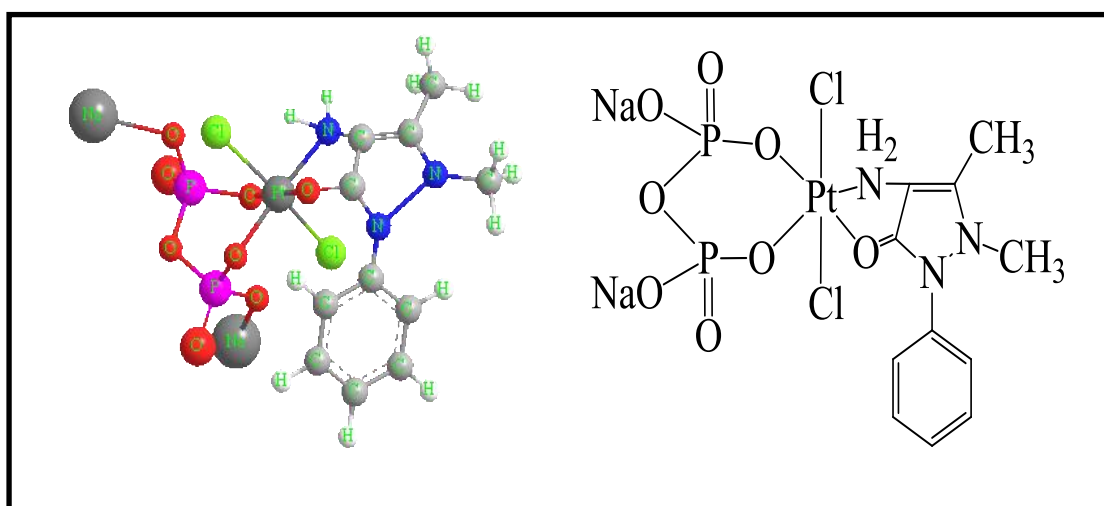


Figure 3-2- The molecular structure of [Pt(4-AAP)(Na₂Pyph)Cl₂].

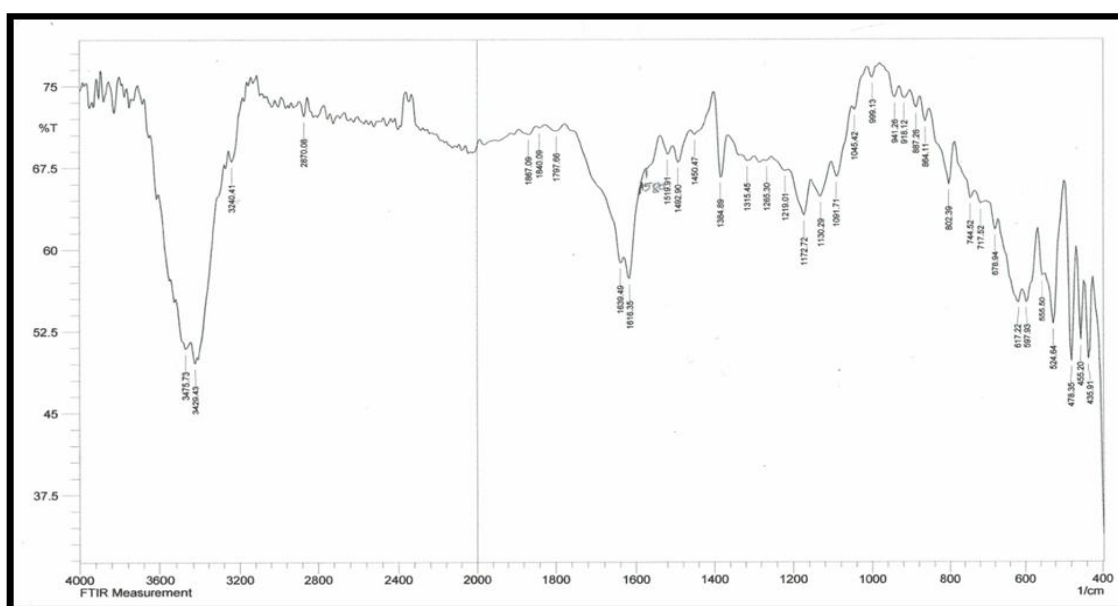


Figure 3-3- FT-IR spectrum of [Pt (4-AAP) Cl₄].

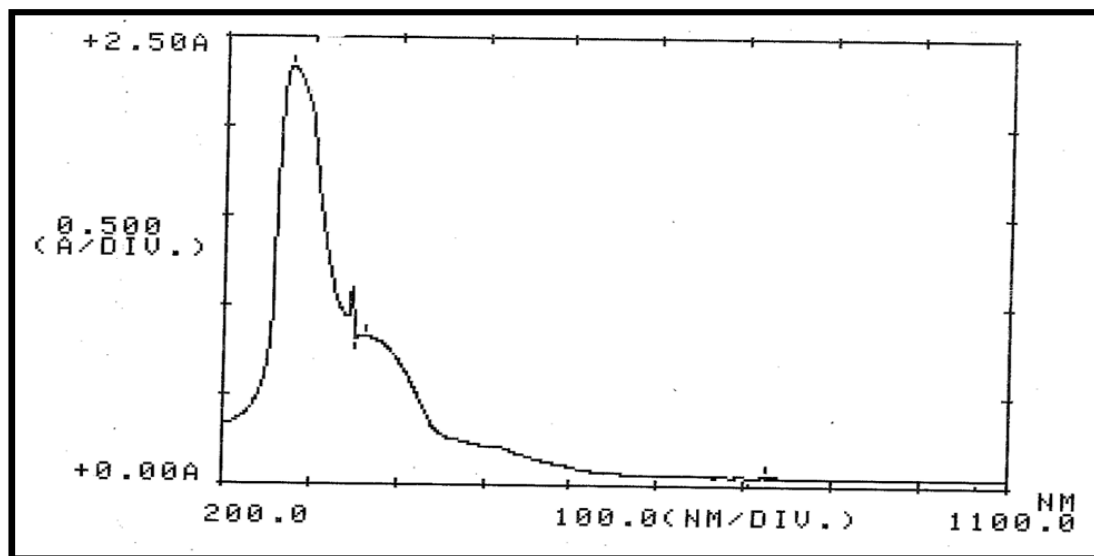


Figure 3-4- Electronic spectrum of [Pt (4-AAP)Cl₄].

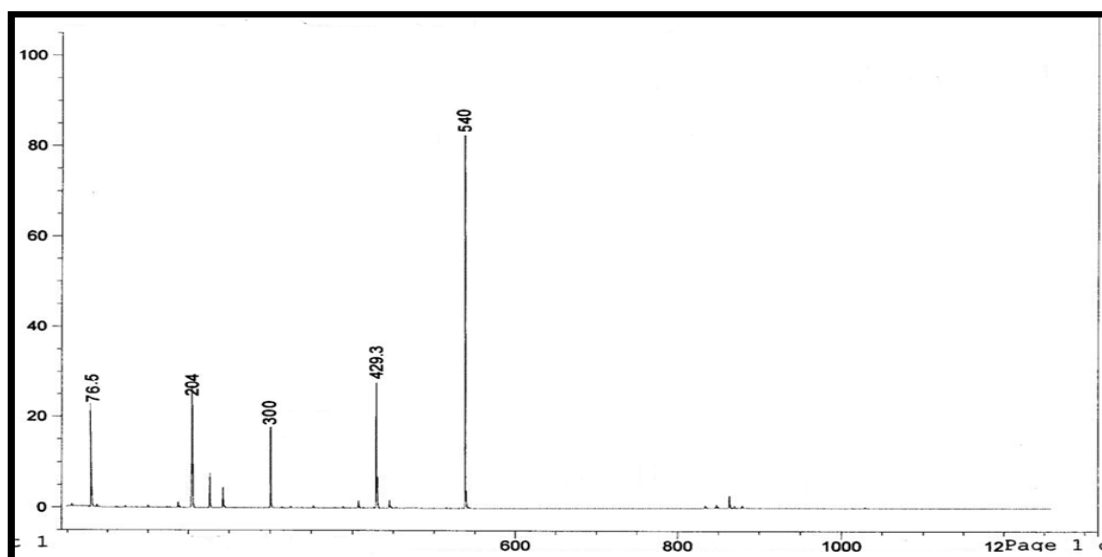


Figure 3-5- Mass spectrum of [Pt (4-AAP)Cl₄].

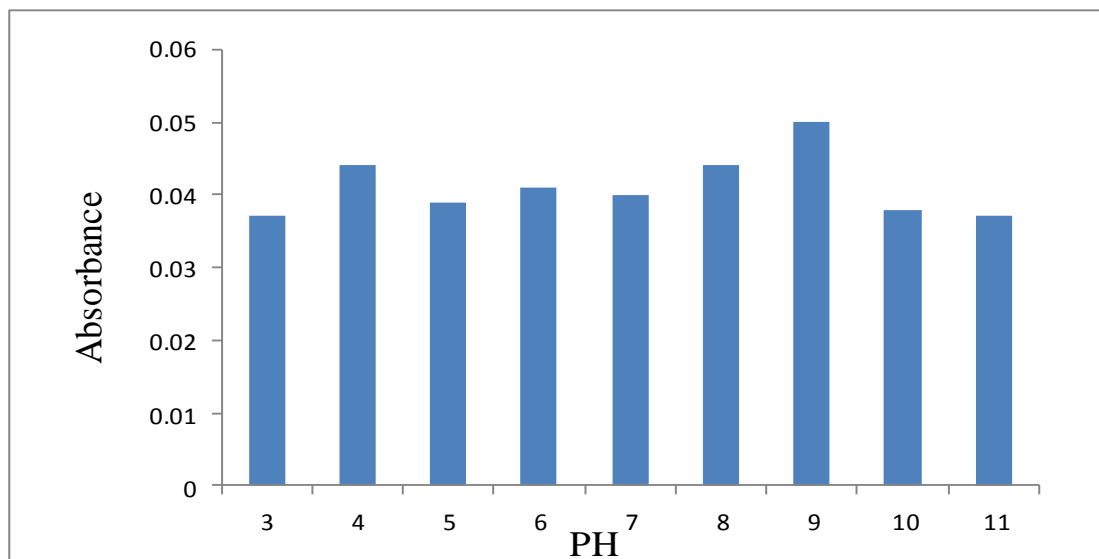


Figure 3-6- Effect of pH on the formation of Pt (IV)-4-AAP complex.

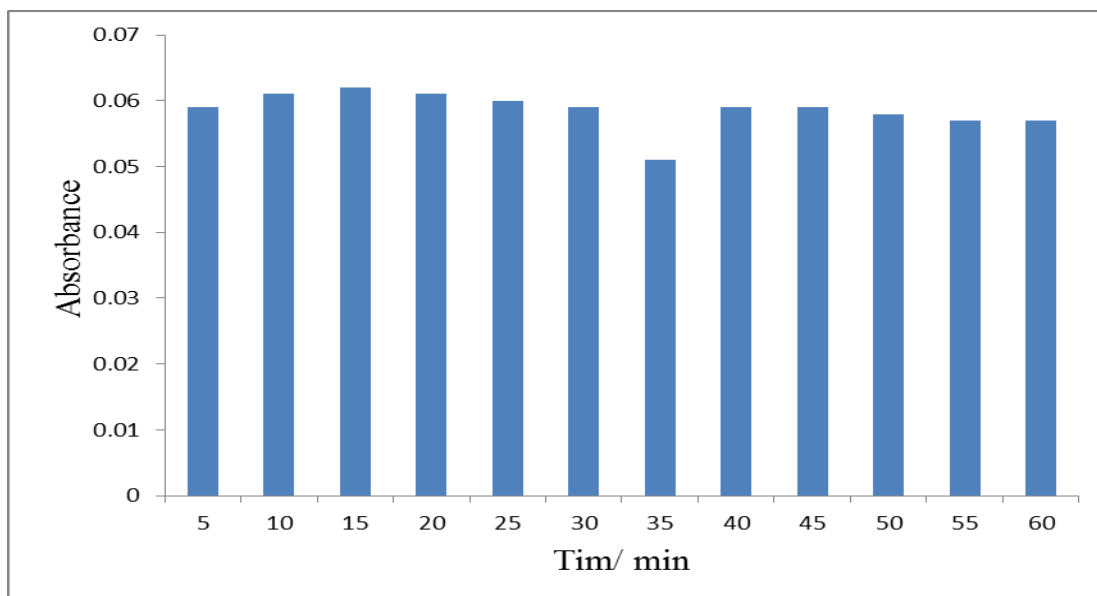


Figure 3-7- Effect of time of the formation of Pt-4-AAP complex.

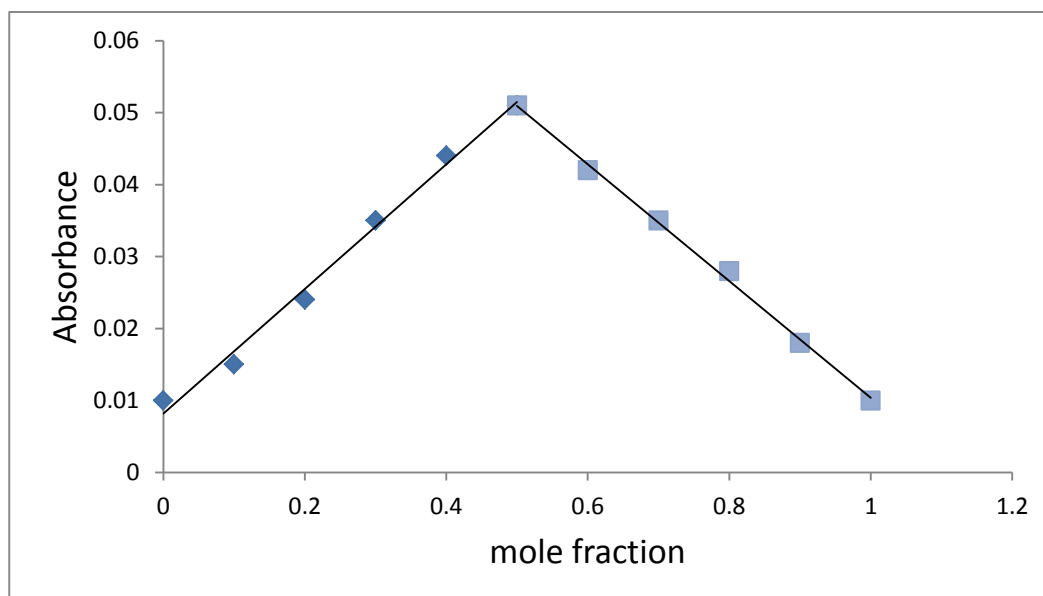


Figure 3-8- Job's plot of complex Pt (IV) – 4-AAP at PH 9.

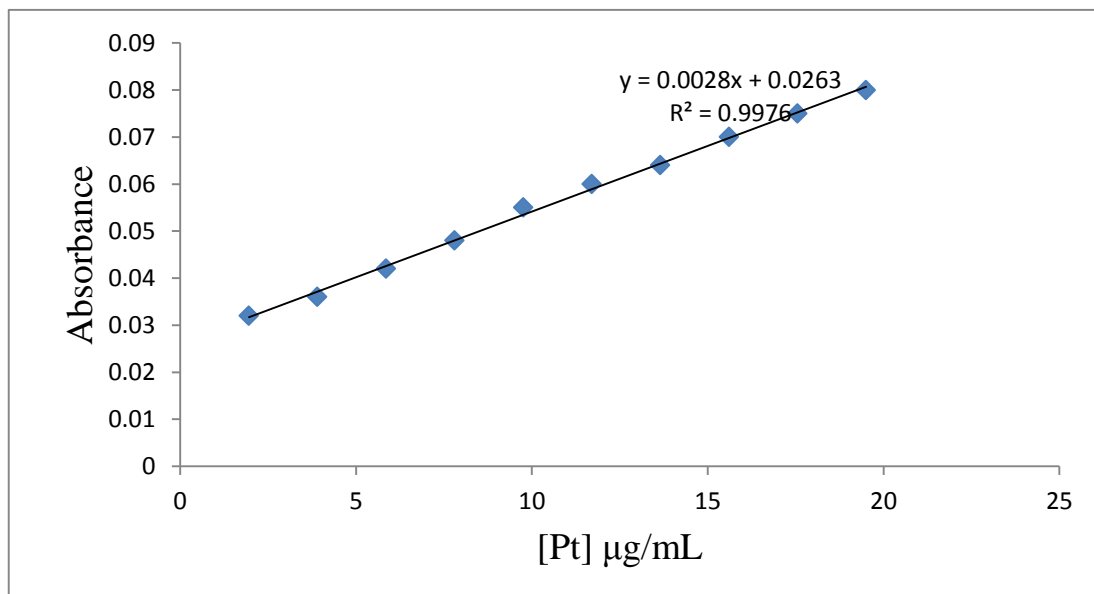


Figure 3-9- Relationship of the absorbance of complex between Pt (IV) and 4-AAP by increasing concentration of Pt (IV) in excess 4-AAP solution.

References

1. Acheson, R. M. **2009**. *Introduction to Heterocyclic Compounds*. 4th, Ed. John Wiley and Sons, New York.
2. Trivedi, G. S. and Desai. **1992**. N-C.Synthesis and Antimicrobial Activity of Some 4-Thiazolidinones. *Indian. J. Chem.* **31**(6): 366-369.
3. Manjula, B. and Arul, A. S. **2013**. Preparation Characterization Antimicrobial Activities & DNA Cleavage Studies of Schiff base Complexes Derived From 4-Aminoantipyrine. *Biochem. Pharma. Res.* **3**(1): 168-178.
4. Raman, N., Sakthivel, A. and Rajasekaran, K. *Mycobiolog.* **2007**. Synthesis and Spectral Characterization of Antifungal Sensitive Schiff Base Transition Metal Complexes. *Mycobiology.* **35**(3): 150- 153.
5. Alzahrani, Z. **2009-2010**. Preparation of buffer solutions. BCH 233, 2nd, Semester, KSU-College of Science-Department of Biochemistry.
6. Tupys, A. and Tymoshuk, O. **2015**. 1-(5-Benzylthiazol-2 yl) Azonaphthalen-2-ol -a New Reagent for The Determination of Pd (II). *Acta. Chimica. Slovaca*, **8**(1): 59-64
7. Kohout, J., Hvastijova, M., Diaz, J. G., et al. **1999**. Cyanamidonitrate-Copper (II) Complexes of Imidazole Ligands: X-ray Crystallography and Physical Investigation. *Inorg. Chim. Acta.* **287**(2) : 186-192.
8. Contreras-Celedón, C. A., Mendoza-Rayó D. and Rincón-Medina, J. A. A. **2014**. Novel 4-Aminoantipyrine-Pd(II) Complex Catalyzes Suzuki–Miyaura Cross-Coupling Reactions of Aryl Halides, *Beilstein J. Org. Chem*, **10**: 2821–2826
9. Shankar, G., Premkumar, R. R. and Ramalingam, S. K. **1986**. 4-Aminoantipyrine Schiff-Base Complexes of Lanthanide and Uranyl Ions. *Polyhedron*, **5**(4): 991-994.
10. Essehli, R., El Bali, B., Lachkar, M., et al. **2006**. Bis (Ethylenediammonium) Diaquabis [Hydrogendiphosphato (3-)] Nickelate (II): Structure and Vibrational Spectroscopy. *Acta Cryst.* **62**(3): 538-541
11. Armatas, N. G., Allis, G. D., Prosvirin, A., et al. **2008**. Molybdophosphonate Clusters as Building Blocks in the Oxomolybdate-Organodiphosphonate/Cobalt(II)–Organoimine System: Structural Influences of Secondary Metal Coordination Preferences and Diphosphonate Tether Lengths. *Inorg. Chem*, **47**(3): 832-854
12. Kazuo, N. **1978**. *Infrared and Raman Spectra of Inorganic and Coordination Compounds*. 3rd Ed., John Wiley and Sons, New York.

13. Manjula, B. and Antony. S. A. **2013**. Arsenic Induced Biochemical Changes in *Perna viridis* as Potential Biomarkers in Metal Pollution. *Asian J. of biochem. And Pharm. Res.* **3**(1): pp. 168-178.
14. Lever, A.B.P. **1984**. *Inorganic Electronic Spectroscopy*. 2nd ed, New work, Elsevier, Amsterdam.
15. Clark, R. J. H. and Turtle, P. C. **1977**. Advances in Photochemistry. *J. Chem. Soc. Dalto*, **16**: 2142
16. Job, P. **1936**. About The Bivalent Cobalt, Copper and Nickel Salts in Hydrochloric and Hydrobromic Acids. pages: 140,153,156,265. *Ann.chim.(Paris)* **6**: 97-144.
17. Yoe, J. H. and Jones, A. L. **1994**. Colorimetric Determination of Iron with Disodium-I, 1-Dihydroxybenzene-3, 5-Disulfonate. *Ind. End, Chem.Anal.*, **16**(2): 111-115.
18. Miller, J.N. and Miller. J. C. **2006**. *Statistics and Chemometrics for Analytical chemistry*. 6th ed, Prentice Hall, England.
19. Gouda, A. A., El-sheikh, R., El Shafey, Z., et al. **2008**. Spectrophotometric Determination of Pipazethate HCl and Dextromethorphan HBr Using Potassium Permanganate. *Int. J. Biomde.Sc* **4**(4): 294-302.
20. Zanje, S. B., Kokare, A. N., Suryavanshi, V. J., et al. **2016**. Extractive Spectrophotometric Determination of Platinum in Cisplatin Injection, Alloys and Catalysts Assisted by 2-nitrobenzaldehydethiocarbohydrazone. *J. T. Anal. F. D.* **2**(1): 1-24.
21. Bagal, M. R., DHOKTE, A. O., Vaidya, S.R. **2016**. Spectrophotometric Determination of Pt(IV) With N- Decyl Pyridine -4-Amine from Succinate Media. *I J CT*, **23**(1): 71-76.
22. Sawant, S.S. **2010**. Spectrophotometric Determination of Traces of Platinum With 5-Chloro-2-Hydroxythiobenzhydrazone After Extraction into Molten Naphthalene. *Anal Sci.* **26**(1): 95-100.