Complexometric Investigation to Differentiate Pd(II) and Pd(IV) ions in Solution

M. A. Zaitoun [a*], A. K. El-Qisairi[a], J. Zoubi[a], K. A. Momani[b], Q. M. Jaradat[c], M. O. Allimoun[d], A. Lataifeh[e], G. M. Al-Mazaideh[e], H. A. Qaseer[a]

[a]*Department of Chemistry, Mutah University-Jordan*
[b]*Chemistry Department, Faculty of Science and Arts at Ar Rass, Qassim University Saudi Arabia*
[c]*Department of Chemistry, Yarmouk University, Jordan*
[d]*Department of Biology, Mutah University, Jordan*
[e]*Department of Chemistry and Chemical Technology, Faculty of Science, Tafila Technical University*

Received on Jul. 4, 2017 **Accepted on** Aug. 3, 2017

Abstract

In an attempt to find a simple, fast, and inexpensive method to differntiate Pd(II) from Pd(IV) ions in aqueous solutions, the organic complexing agent N',N''-bis[(1E)-1-(2-Pyridyl)-ethylidene]ethanedihydrazide (H_2L) was synthesized and used to study complexation with Pd(II) and Pd(IV) in two ways:

(i) Formation of soluble colored complexes employing low concentration levels of both ligand and metal cations. The reaction of a solution of the ligand with Pd(II) or Pd(IV) ions at pH = 5-5.5 in a 1:1 molar ratio proceeded with the formation of two different soluble palladium complexes, Pd(IV)-H_2L and Pd(II)-H_2L. Each of the complexes was accompanied by a characteristic emission and absorption spectra. The ligand imposes a distinct emission and absorption peaks for each ion that could be used to characterize and identify it. The Pd(IV)-H_2L is characterized by an emission peak at 500 nm and an absorption peak at 440 nm while the Pd(II)-H_2L has two absorption shoulders at 460 and 480 nm and two emission shoulders at 440 and 470 nm.

(ii) Continuous stirring for 45 min employing high concentrations of a 1:1 mixture of the ligand H_2L with either of the metal cations Pd(II) or Pd(IV) in 2-propanol/water (5:1) produced solid powders corresponding to the formation of the complexes Pd(II)-H_2L (yellow) and Pd(IV)-H_2L (pale yellow).

Differences between the uncomplexed ligand and the two solid complexes gave an indication that the Pd(II) or Pd(IV) metal ions are really coordinated to the N-atoms of the pyridine ring and hydrazide group. Complexation to Pd(II) or Pd(IV) was proved by (i) FTIR peak shifts in the stretching frequency values of the main peaks for the H_2L ligand. (ii) The H^1-NMR signals due to the enolic form (-OH) were shifted to down field upon complexation and appeared at 9.28- 9.33 ppm. Moreover, the ^{1}H- NMR spectra of the complexes showed a higher number of peaks corresponding to the pyridine protons. Finally, elemental analysis was performed to prove further the complexation process.

Keywords: *Palladium ions; complexation; emission; ligand; spectroscopy.*

* **Corresponding author:** M. A. Zaitoun **E-mail:** zaitoun444@yahoo.com

Introduction

Heavy metals exist as ores in different chemical forms including sulfides and oxides.[1] These metals are released into the environment by natural and anthropogenic exhausts.[2] Environmental pollution by heavy metals is very prominent in areas of mining and old mines sites; these metals are leached out and are carried out in sloppy areas through rivers and streams. The metals are transported as either dissolved species in water or as an integral part of suspended sediments. Heavy metal mobilization in the biosphere by human activities has become an important process in the geochemical cycling of these metals that result from releasing large quantities of heavy metals into the atmosphere.[3-4]

Accumulation of toxic industrial effluents in the soil, air and water is continuously increasing due to rapid urbanization and extensive pollution of the environment. Among these toxic substances, the presence of heavy metals which are ubiquitous in nature causes serious harmful effects on living organisms especially humans. Most heavy metals have adverse effects on human health as they accumulate in the body causing metal poisoning which is a co-factor in any other disease.[5]

Toxicity of heavy metals comes from the fact that heavy metals are not biodegradable and tend to accumulate in living organisms, many of them are known to be toxic or carcinogenic. Zinc, copper, nickel, mercury, cadmium, lead and chromium are known as toxic metals that lead to carcinogenic states. So these toxic heavy metals should be detected and eventually removed to protect people and the environment.[6-8] The excessive amount of these metals in food is associated a number of diseases, especially in kidneys, nervous system as well as bone diseases. Long contact to heavy metals like cadmium, copper, lead, nickel, and zinc results in lethal problems in humans.[9-11] The growing industrial use of palladium as a catalyst, especially in automobile exhaust detoxification, is causing occupational and environmental pollution. Over half of the supply of palladium and its congener platinum goes into catalytic converters which convert up to 90% of harmful gases from auto exhaust (hydrocarbons, carbon monoxide, and nitrogen dioxide) into less-harmful substances (nitrogen, carbon dioxide and water vapor).[12,13]

The significance of palladium as a transition metal lies in its wide spectrum of applications, especially in electrical and electronic industries, catalysis, dentistry, medical devices, jewellery, surgical instruments, hydrogen purification, chemical applications, groundwater treatment and recently as nano-particles for the development of new active catalysts. Moreover, Palladium plays a key role in the technology used for fuel cells, which combines hydrogen and oxygen to produce electricity, heat, and water.[14-18] Chemistry of palladium in its (0), (+2), and (+4) oxidation states is well-established.[19] Many Pd(II) and Pd(IV) complexes were reported by researchers.[20-27] However, as far as the detection of the palladium ions in solution, there is a few data on palladium concentrations in the environment. This is

partly because of the difficulties in palladium analysis in particular due to interferences by other elements like Cd and Zn or Br.[28]

In the present work, we describe the synthesis and spectroscopic aspects of Pd(II) and Pd(IV) complexes with N', N''-bis[(1E)-1-(2- pyridyl)ethylidene]ethane-dihydrazide. Various spectroscopic methods were used to elucidate their structures. This ligand was shown to be a suitable tool to differentiate Pd(II) from Pd(IV) ions in solution.

Experimental

Chemicals and reagents

Ammonium hexachloropalladate(IV), $(NH_4)_2PdCl_6$, and bis(benzonitrile)dibromo-palladium(II), $PdBr_2(phCN)_2$, were of analytical grade and purchased from Sigma-Aldrich. They were employed without any further purification; deionized water produced by a Milli-Q Plus system (Millipore) was used for all preparations.

Synthesis of H_2L ligand

The synthesis of the ligand was reported in the literature.[29-32]

Preparation of stock solutions

A $1.0x10^{-4}$ M stock solution of the ligand H_2L was prepared in 2-propanol-water (5:1). For the metal cations, $1.0x10^{-4}$ M stock solutions of ammonium hexachloro-palladate(IV), $(NH_4)_2PdCl_6$, and bis(benzonitrile)dibromopalladium(II), $PdBr_2(phCN)_2$, were prepared in water and dichloromethane, respectively.

Preparation of the soluble colored complexes [Pd(IV)-H_2L and Pd(II)-H_2L]

Employing low concentrations of the ligand and the metal cation results in the formation of soluble complexes Pd(IV)-H_2L and Pd(II)-H_2L. The formed soluble complexes were diagnosed by absorption and fluorecence spectroscopy.

Pd(IV)-H_2L soluble complex

When 2.0 mL of the $1.0x10^{-4}$ M $(NH_4)_2PdCl_6$ stock solution were mixed with 2.0 mL of the $1.0x10^{-4}$ M H_2L stock solution in a test tube, a yellow color starts to develop by shaking. Complexation takes an hour for completion; this was evident by following the absorption of the developed complex at maximum absorption wavelength of the complex.

Pd(II)-H_2L soluble complex

2.0 mL of $1.0x10^{-4}$ M of $PdBr_2(phCN)_2$ stock solution were mixed with 2.0 mL of the $1.0x10^{-4}$ M ligand stock solution in a test tube. Two layers appear immediately upon mixing. After shaking for 5 min, the two layers become miscible and a yellow color shows up. Absorbance of the developed complex at the maximum wavelength reaches a constant value after one hour of mixing.

When $PdCl_2$ was used, mixing of 2.0 mL of $1.0x0^{-4}$ M $PdCl_2$ solution with 2.0 mL of the $1.0x10^{-4}$ M ligand stock solution is followed by the addition of an excess chloride ion for the color to develop.

Synthesis of the solid complexes

Refluxing higher concentrations of the ligand and the metal ions resulted in the formation of solid powders corresponding to Pd(IV)-H_2L and Pd(II)-H_2L complexes. The produced solid powders were characterized by FTIR, H-NMR, and elemental analysis.

Pd(IV)- H_2L solid complex

(0.5 mmol, 0.162 g) of H_2L dissolved in 2-propanol/water (5:1) was placed in a 250-mL round bottom flask. A solution of (0.5 mmol, 0.178 g) of $NH_4)_2PdCl_6$ dissolved in H_2O was added dropwise and the mixture was stirred at 50 ^oC for one hour. A light yellow solid of Pd(IV)-H_2L complex was filtered off, washed with water and dried. (melting point = 330 ^oC).

Pd(II)- H_2L solid complex

In a 500-mL beaker, (0.5 mmol, 0.236 g) of $PdBr_2(phCN)_2$ (FW = 472.47 g/mol) dissolved in CH_2Cl_2 was added dropwise to (0.5 mmol, 0.162 g) of H_2L dissolved in 2-propanol/water (5:1). A yellow powder of Pd(II)-H_2L complex was formed after one hour of stirring at 50 ^oC. The produced solid was filtered and dried (melting point = 220 ^oC).

Instrumentation

All glassware used were initially cleaned with soap, washed thoroughly with tap water, distilled water, and 1%HNO3 (v/v) and dried overnight to remove any contamination by heavy metals. Then they were washed thoroughly with distilled and deionized water.

Photoluminescence data were obtained under continuous Xe lamp (150 W) excitation in a Jobin Yvon Fluoromax P spectrofluorometer at room temperature. The emission was collected at 90° from the excitation beam. The entrance and exit slits were placed at 5.0 nm.

The optical absorption measurements were determined using a PerkinElmer (Lambda 25) double beam. The spectra were recorded in the visible region using 1.00 cm quartz cuvettes. Fourier Transform infrared (FTIR) absorption spectra of the synthesized ligand and complexes were recorded on a Bruker Alpha FTIR spectrometer using KBr discs. ^1H- Nuclear Magnetic resonance (^1H-NMR) spectra were recorded on a Bruker 500 MHz-Avance III in DMSO-d_6 using TMS as an internal standard. Carbon, nitrogen, and hydrogen contents of the synthesized compounds were determined by elemental analysis carried out on a Euro Vector 3000 elemental analyzer.

Results and Discussion

Absorption and emission

The ligand H_2L was found to produce characteristic emission and absorption spectrum for each of the studied ions in the synthesized soluble complexes. Emission spectra of the soluble complexes Pd(IV)-H_2L and Pd(II)-H_2L were measured for the excitation at 300 nm (π to π^* transition of the ligand *H_2L*) and are displayed in Figures 1 and 2, respectively.

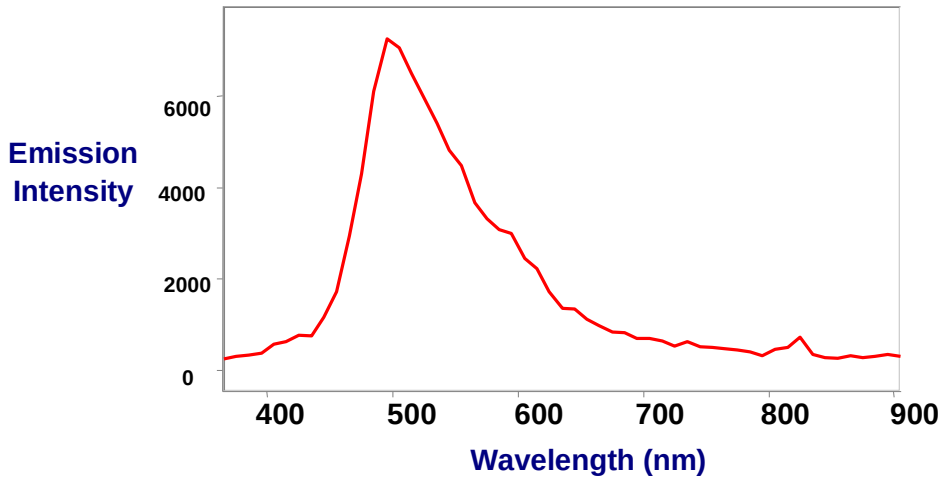


Figure 1: Emission spectrum of the soluble complex Pd(IV)-H_2L (2.0 mL of $1x10^{-4}$ M of $(NH_4)_2PdCl_6$ and 2.0 mL of $1x10^{-4}$ M H_2L).

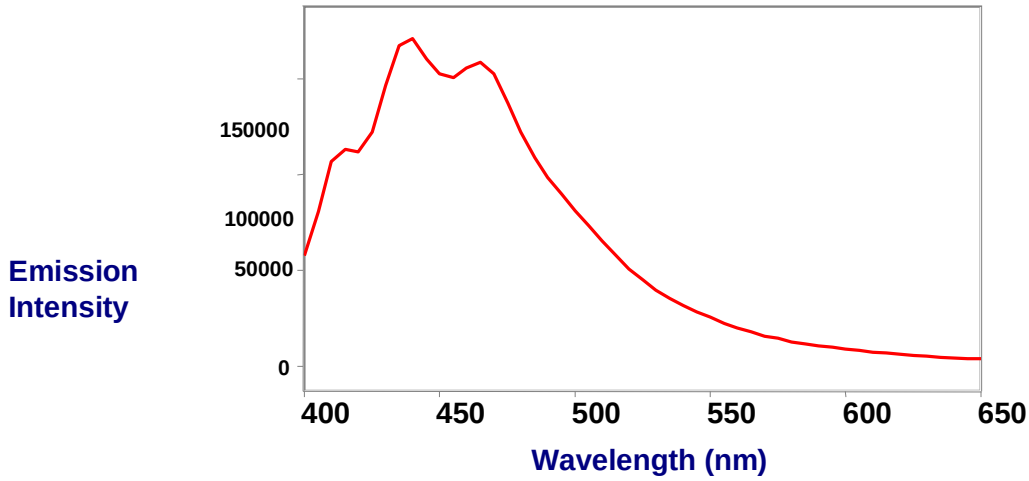


Figure 2: Emission spectrum of the soluble complex Pd(II)-H_2L (2.0 mL of $1x10^{-4}$ M of $PdBr_2(phCN)_2$ and 2.0 mL of $1x10^{-4}$ M H_2L).

Pd(IV)-H_2L is identified by the 500 nm emission peak in Figure 1 while Pd(II)-H_2L is characterized by two emission peaks at 440 and 470 nm in addition to a small shoulder at 420 nm (Figure 2).

The absorption spectra of the soluble complexes are clarified in Figures 3-7. The absorption spectrum of the free ligand, uncomplexed free ions Pd(IV) and Pd(II) are displayed in Figures 3, 4 and 5, rerspectively. The soluble complexes exhibit the absorption specra shown in Figures 6 (Pd(IV)-H_2L) and 7 (Pd(II)-H_2L).

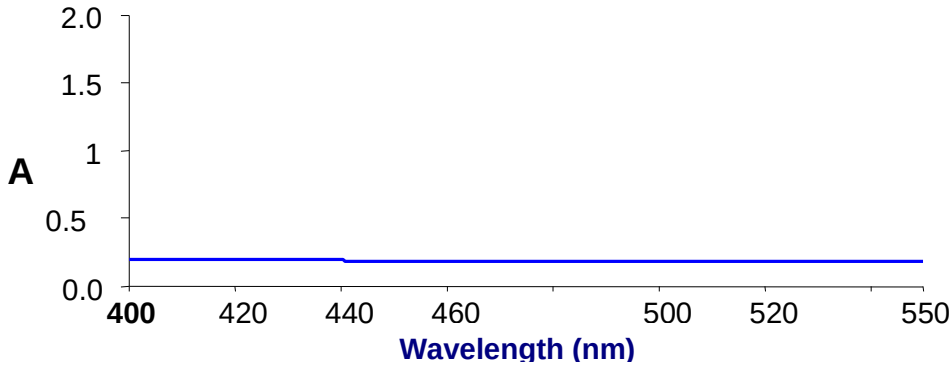


Figure3: Absorption spectrum of a $1x10^{-4}$ M H_2L dissolved in 2-propanol/water (5:1).

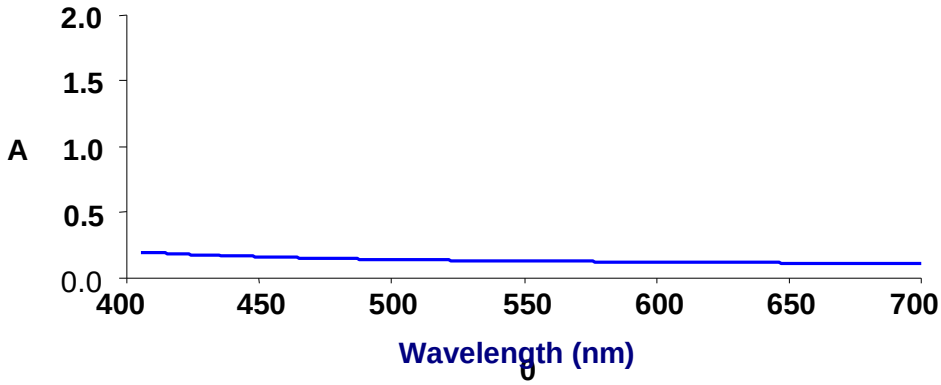


Figure 4: Absorption spectrum of a $1x10^{-4}$ M Pd(IV) ion solution.

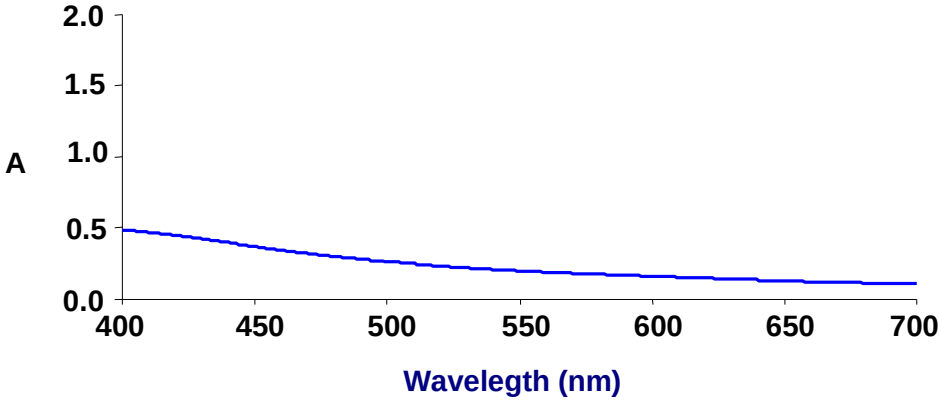


Figure 5: Absorption spectrum of a $1x10^{-4}$ M Pd(II) ion solution.

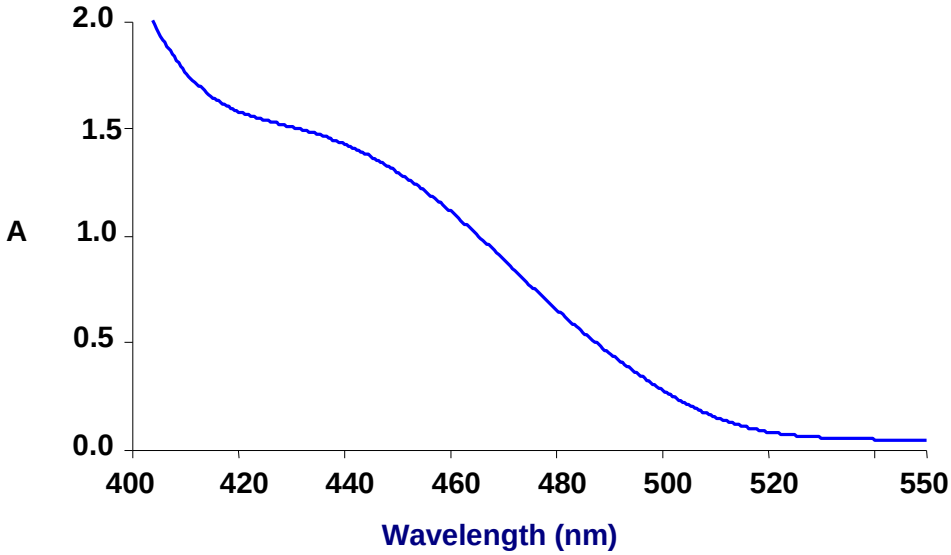


Figure 6: Absorption spectrum of the soluble complex *Pd(IV)-H_2L (*2.0 mL of $1x10^{-4}$ M of $(NH_4)_2PdCl_6$ and 2.0 mL of $1x10^{-4}$ M H_2L).

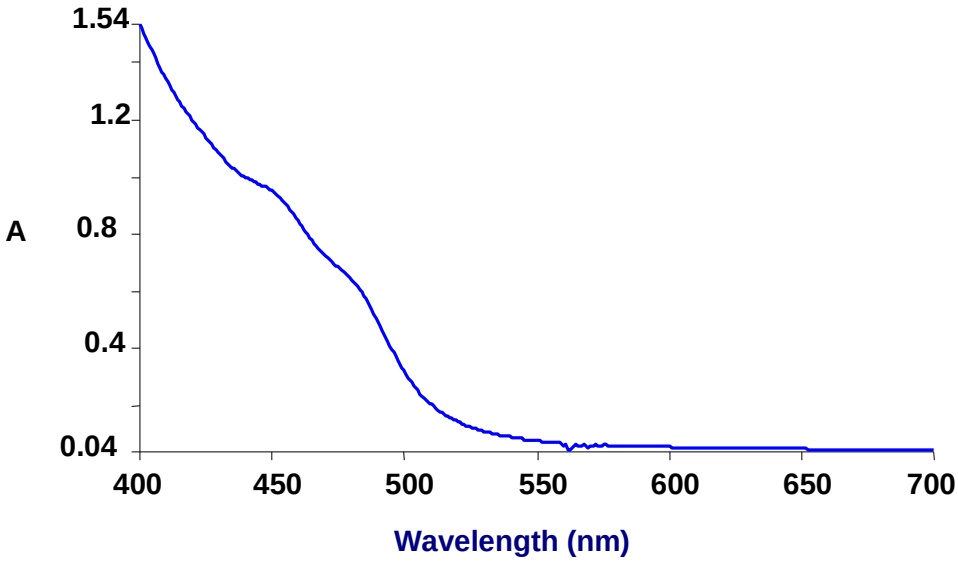


Figure 7: Absorption spectrum of the soluble complex *Pd(II)-H_2L (*2.0 mL of $1x10^{-4}$ M of $PdBr_2(phCN)_2$ and 2.0 mL of $1x10^{-4}$ M H_2L).

FTIR

Infrared specta of the ligand and the synthesized powdered complexes *Pd(IV)-H_2L* and *Pd(II)-H_2L* are presented in Figures 8, 9, and 10, respectively. Figure 8, shows the FTIR spectrum of the free ligand. As shown in the figure, the sharp feature of the peaks at 3343 cm^{-1} indicated ν(N-H) stretching vibrations. The bands observed at 3005 and 3061cm^{-1} indicated ν(C-H) stretch while the peaks at 854, 782, and 738 cm^{-1} refer to the ν(α C-H) stretching vibrations. The strong and sharp peaks at 1698 cm^{-1} indicated the ν(C=O). The presence of the peaks around 1577 and 1562 cm^{-1} indicated ν(C=N) stretching vibrations. Further, the sharp peaks between 1365 and 1503 cm^{-1} were assigned to ν(C=C) stretching vibrations. The stretching vibration peak around

1140 cm^{-1} indicated ν(N-N). Finally, the stretching vibrations of the pyridine ring showed up at 977 cm^{-1}.

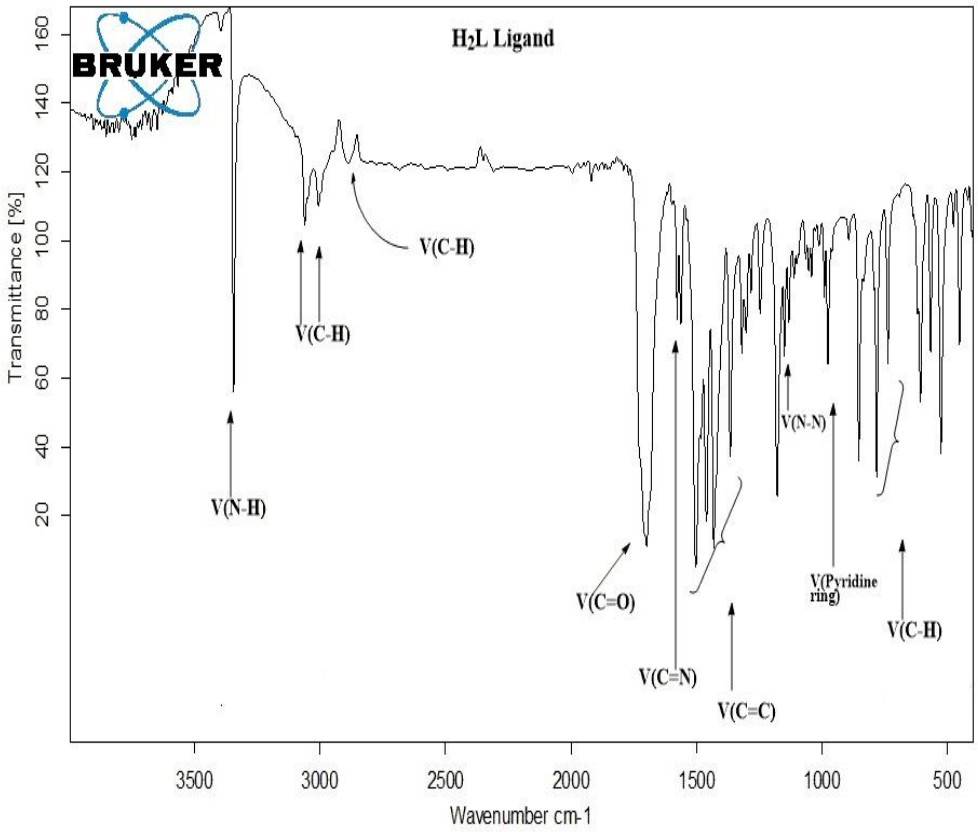


Figure 8: FTIR of the solid H_2L ligand.

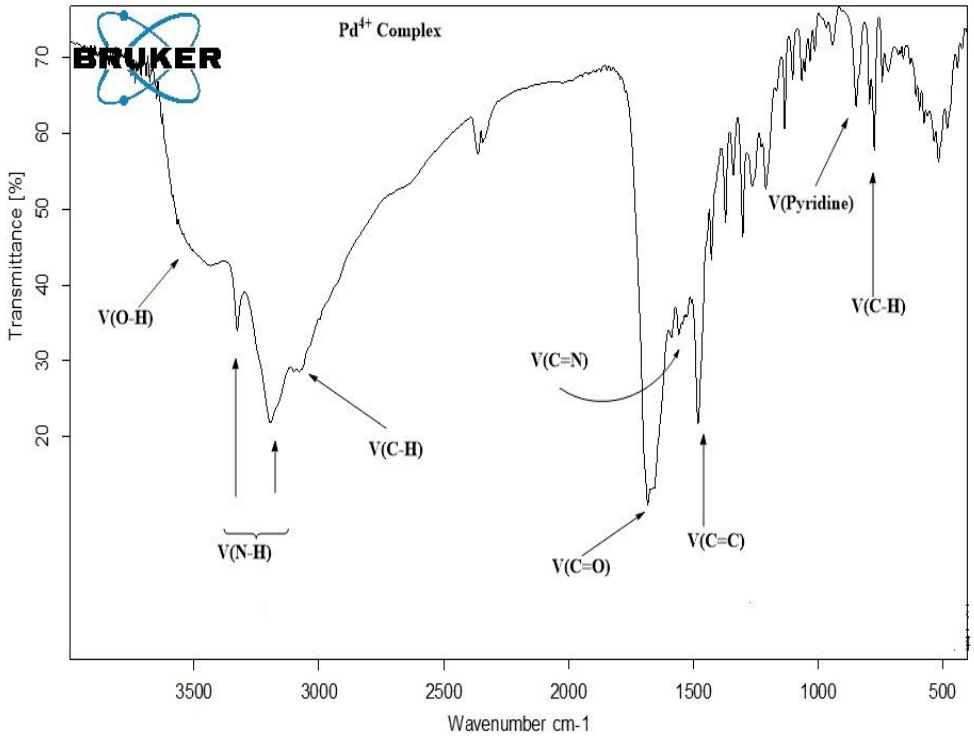


Figure 9:. FTIR spectrum of the solid Pd(IV)-H_2L powdered complex.

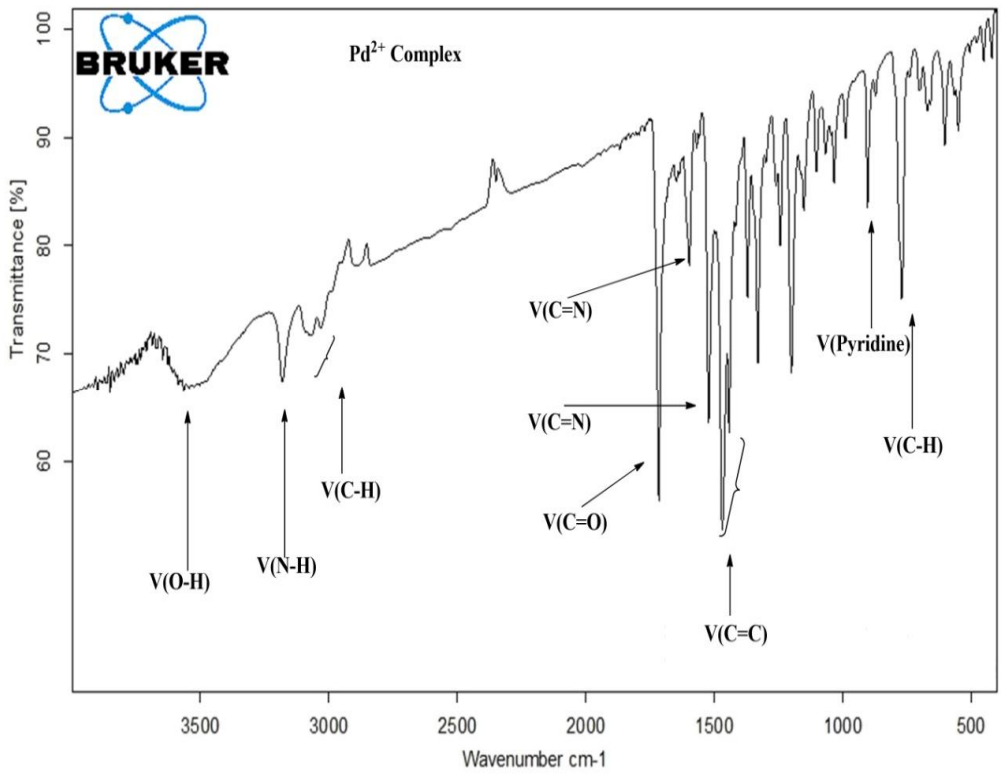


Figure 10: FTIR of the solid Pd(II)- H_2L powdered complex.

As shown in Figures 9 and 10, the presence of Pd(II) and Pd(IV) metal ions coordinated to the H_2L ligand was reflected in shifts of the stretching frequency values of the main peaks of the free ligand (Figure 8). Comparison of the IR frequency values of the free H_2L ligand to those in the synthesized powder complexes are presented in Table 1.

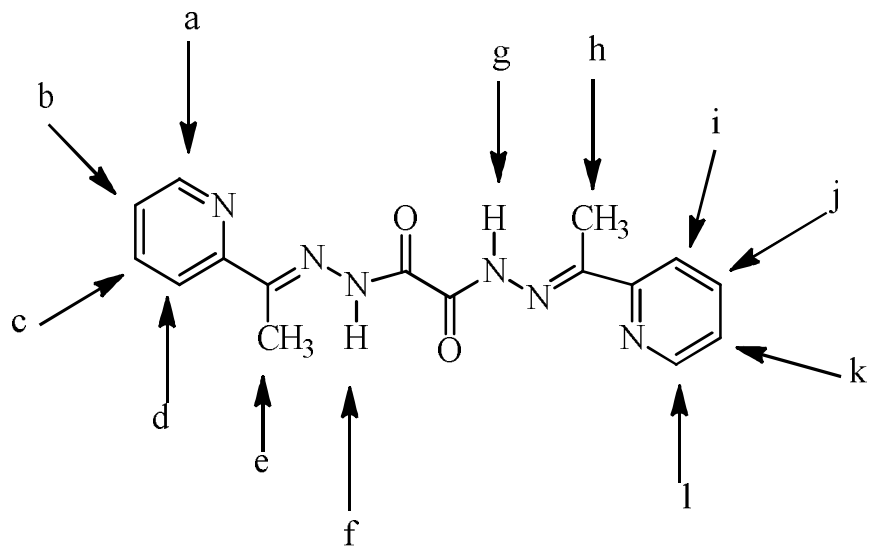
Table 1: Comparison of stretching frequency values of the free H_2L ligand and the powder complexes (H_2L- Pd(II) and H_2L- Pd(IV))

Chemical bond	v in H2L (cm-1)	v in Pd(II) complex (cm-1)	v in Pd(IV) complex (cm-1)
O-H	-	3500	3550
N-H	3343	3181	3327, 3194
C-H	3061, 3005	3067, 3031	3078
α C-H	854, 782, 738	771	774
C=O	1698	1716	1682
C=N	1577, 1562	1597, 1522	1588, 1558
C=C	1503, 1365	1469, 1442	1480
N-N	1140	1065	1045
Pyridine	977	903	847

As shown in Table 1, the coordination of the metal ion Pd(II) or Pd(IV) to the H_2L ligand showed shifts of the stretching frequency values of the main peaks of the H_2L ligand. The blue shifts of the pyridine ring (N-N and C=N) results from the coordination of the Pd(II) or Pd(IV) metal ion to the N- atoms of the pyridine and hydrazide group. Another blue shift appeared for the N-H bond and C=O bonds that could be attributed to the resonance coordination of H-atom to O-atom of the carbonyl group and the N-atom of the hydrazide group. The above shifts in the stretching frequency values of the main peaks of the H_2L ligand give an indication that the Pd(II) or Pd(IV) metal ion are really coordinated to the N-atoms of the pyridine ring and hydrazide group.

H-NMR

To further characterize the synthesized complexes, proton NMR spectra of the ligand and powdered complexes Pd(IV)-H_2L and Pd(II)-H_2L are shown in Figures 11, 12 and 13, respectively. Scheme 1 and Table 2 give a summary of the assignments of the major peaks for each atom of the ligand. In general, the DMSO-d_6 solvent has two characteristic peaks at 2.46 and 3.30 ppm while the methyl (-CH_3) protons appear at δ = 2.34 and 2.31 ppm. Interference of the solvent and the methyl protons at 2.4 ppm always occurs.



Scheme 1: The letters (a-l) are assigned to each type of the 16 protons of H_2Lligand

Table 2: Chemical shifts (ppm) for each type of hydrogen atom of H_2L ligand.

Hydrogen number	δ (ppm)
a, l	(d, 8.50)
b, k	(t, 7.30)
c, d, j, i	(m, 7.74)
e, h	(s, 2.31)
f, g	(s, 11.53)

*s: singlet; d: doublet; t: triplet; m: multiplet.

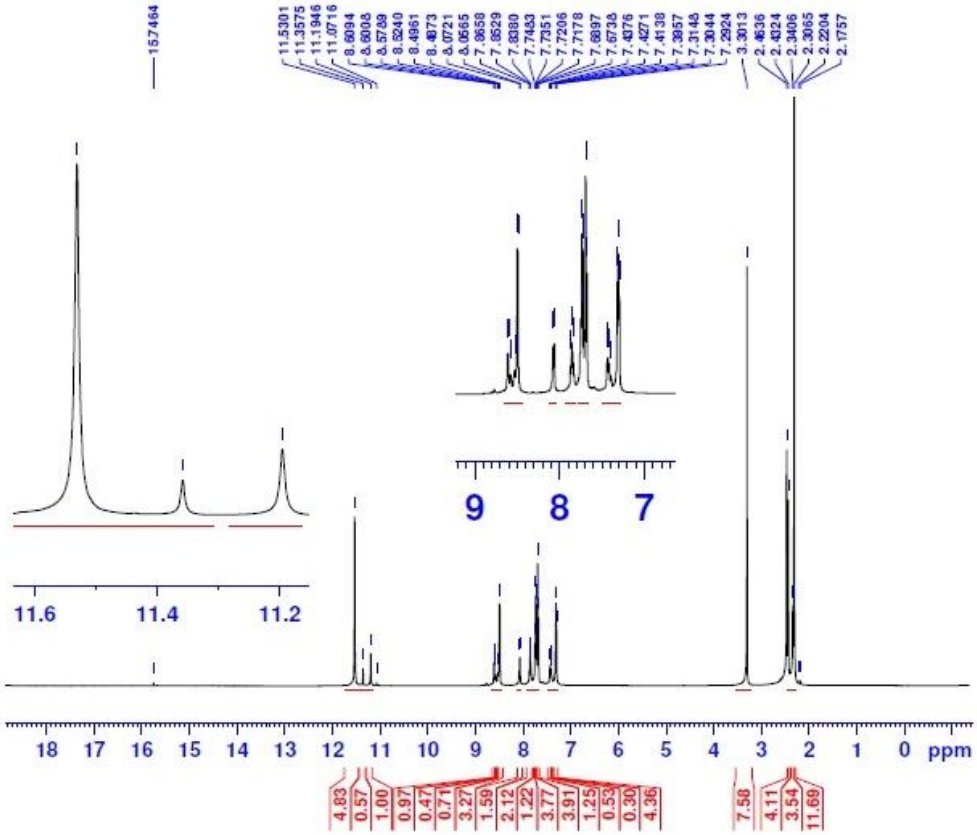


Figure 11: ^{1}H-NMR of the solid H_2L ligand.

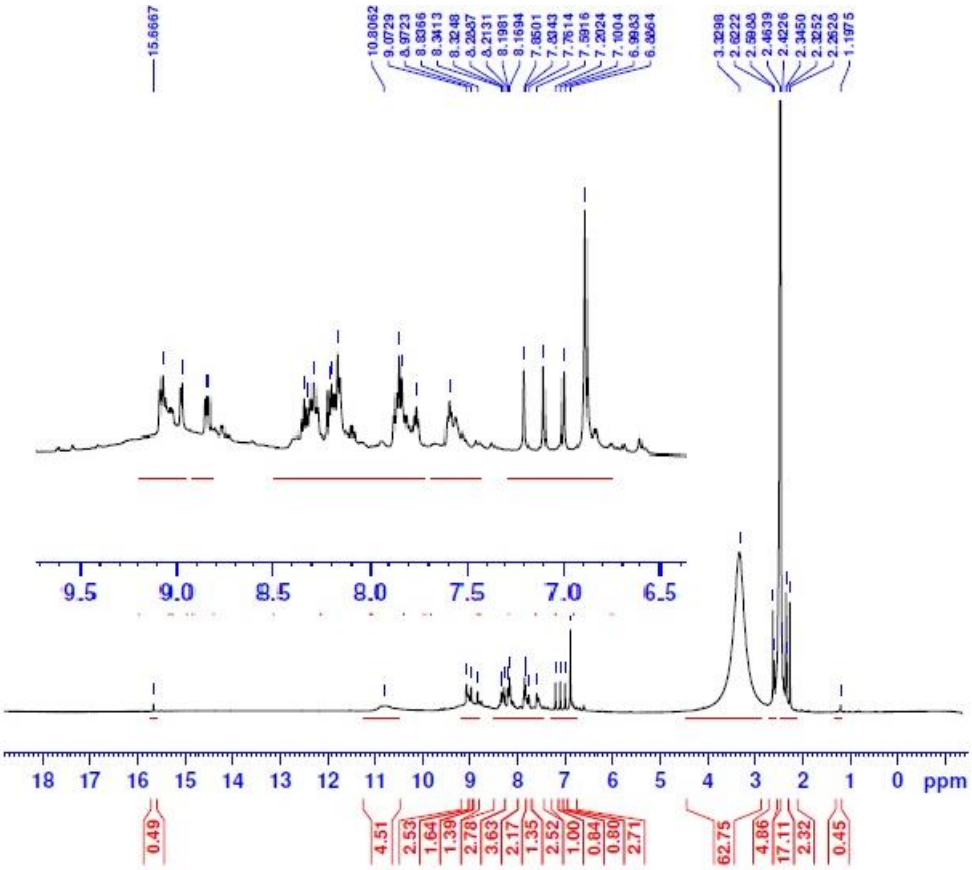


Figure 12: ^{1}H- NMR spectrum of the solid Pd(IV)-H_2L powdered complex.

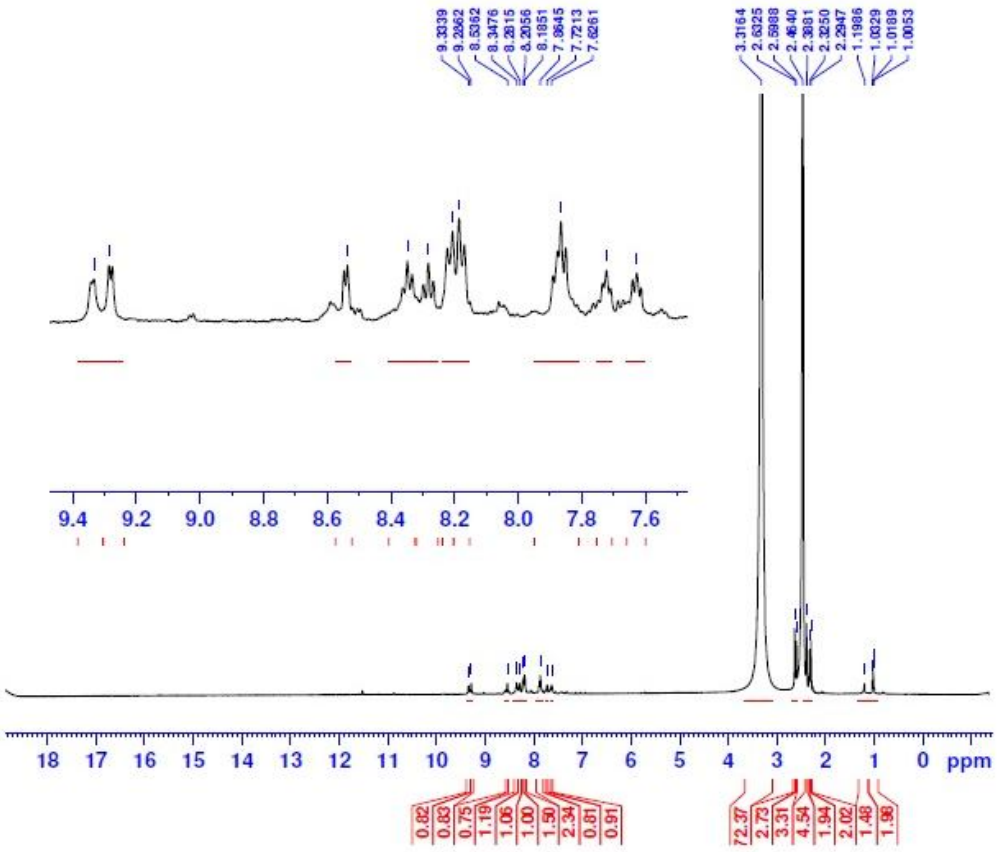


Figure 13: ^{1}H- NMR spectrum of the solid Pd(II)-H_2L powdered complex.

According to Figure 12, three types of peaks appear in pd(IV)-H_2L: a singlet at δ = 2.34 and at 2.26 ppm, a doublet at δ = 8.97 and at 8.84 ppm, a multiplet at δ = 9.07, 8.34-8.29, 8.21-8.17, 7.85-7.76 and at 7.59 ppm. The singlet peaks at 7.20, 7.10, 6.99 and 6.89 ppm are attributed to impurities. The observed and characteristic peaks for the Pd(II)-H_2L complex (Figure 13) are: a singlet at δ = 2.39 and 2.33 ppm, a doublet at δ =9.33, 9.29 and at 8.54 ppm, a triplet at δ = 8.35,8.28, 7.72 and at 7.63 ppm, a quartet at δ = 8.21-8.19 ppm and a multiplet at δ = 7.86 ppm.

The ^{1}H- NMR spectrum of the H_2L ligand (Figure 11) showed the existence of the ligand in the enol form as confirmed by the appearance of the signals at δ = 11.5, 11.4 and 11.2 ppm. These signals were assigned to the protons of the OH group (due to enolization of carbonyl group and –NH). The signals found at δ = 2.31 ppm were assigned to the two methyl protons (6 H). Protons for the two pyridine rings (8 H) were observed as a doublet signal at 8.50 (2 H), a multiplet at 7.74 (4 H) and a triplet at 7.30 (2 H) ppm. These resonances were consistent with reported values.[29]

The signals due to the enolic form (-OH) were shifted down field upon complexation to Pd(II) or Pd(IV) and appeared at 9.28-9.33 ppm. Also, the ^{1}H-NMR spectra for the complexes showed a higher number of peaks corresponding to the pyridine protons which indicates that the pyridyl groups become upon complexation chemically inequivalent.

Elemental Analysis

The elemental analysis of H_2L along with its powder complexes (H_2L-Pd(II) and H_2L-Pd(IV)) are displayed in Table 3. The calculated values are based on the following chemical formulas (i) $C_{16}H_{16}N_6O_2.H_2O$ (FW=342.364 g/mol) for H_2L, (ii) $C_{16}H_{16}N_6O_2PdBr_2.4H_2O$ (FW=662.632 g/mol) for H_2L-Pd(II) complex, and (iii) $C_{16}H_{16}N_6O_2Pd_2Cl_8.4NH_4Cl$ (FW=1034.756 g/mol) for H_2L-Pd(IV) complex.

Table 3: Elemental analysis of the free ligand and the complexes H_2L-Pd(II), H_2L-Pd(IV**)**

Compound	C%	H%	N%	C%	H%	N%
	Found			Calculated		
H_2L	58.55	7.326	25.739	56.13	5.30	24.55
H_2L-Pd(II)	26.353	3.501	11.346	28.99	3.65	12.68
H_2L-Pd(IV)	16.578	3.427	13.871	18.56	3.12	13.53

Conclusions

A spcetroscopic investigation was carried to show how the two palladium ions (Pd(II) and Pd(IV)) can be distinguished. Our experiments were designed to show the complexation of the two palladium ions to the organic ligand both in solution as well as in solid form. Absorption and emission characteristics were used to diagnose the soluble ions. The solid complexes were studied by FTIR, NMR and elemental analysis

References

[1] Ghorade, I.; Jadhavar, I.; Patil, V. S., *World Journal of Pharmacy and Pharmaceutical Sciences*, 2015, 4, 1853-1860.

[2] Addo, M.; Darko, E.; Gordon, C.; Nyarko, B.; Gbadago, J.; Nyarko, E.; Affum, A.; Botwe, B., *Int'l. J. of Sci. and Technolgy,* 2012, 2, 40-49.

[3] Feka, F.; Dreshaj, A.; Beqiraj, I.; Topi, D., *Int'l J. of Computing, Communications & Instrumentation Engg*., 2016, 3, 27-28.

[4] Jarup, L., *British Medical Bulletin*., 2003, 68, 167–182.

[5] Behera, B.; Bhattacharya, S., *Tang Humanities and Medicine*, 2016, 6, 37- 40.

[6] Fu, F.; Wang, Q., *J. of Environmental Management*., 2011, 92, 407- 418.

[7] Veerakumar, P.; Veeramani, V.; Chen, S.; Madhu, R.; Liu, S., *Appl. Mater. Interfaces*., 2015, 8, 1319–1326.

[8] Machado, R.; Monteggia, L.; Arenzon, A.; Curia, A., *Environmental Monitoring and Assessment*, 2016,188, 373-382

[9] Sardar, K.; Ali, S.; Hameed, S.; Afzal, S.; Fatima, S.; Shakoor, M.; Bharwana, S.; Tauqeer, H., *J. of Environmental Management and Public Safety*, 2013, 2, 172-179.

[10] Mandal, S.; Sarkar, B.; Bolan, N.; Ok, Y.; Naidu, R., *J. of Environmental Management,* 2017, 186, 277-284.

[11] Wiseman, C.; Pour, Z.; Zereini, F., *Chemosphere,* 2016, 145, 61- 67.

[12] Bunger, J.; Stork, J.; Stalder, K., *Int. Arch. Occup. Environ*., 1996, 69, 33-38.

[13] Albers, P.; Pietsch, J.; Parker, S., *J. Molecular Catalysis: Chemical*., 2001, 173, 275-286.

[14] Rayner, H., “Palladium, Jewelry-Making through History: An Encyclopedia”, Greenwood Publishing Group., 2007, 146.

[15] Nancy, T., “The Flute Book: A Complete Guide for Students and Performers”, Oxford University Press, 2006, 20.

[16] Martin, W., Precious Metals, Foreign exchange: A Practical Guide to the FX Markets, 2006, 34.

[17] Al- Harbi, E., *J. of Taibah University for Science*, 2016, 10, 1- 8.

[18] Bahadir, Z.; Bulut, V.; Betktas, H.; Soylak, M., *RSC Advances,* 2016, 6, 6896-6904.

[19] Powers, D.; Ritter, T., *Topics in Organometallic Chemistry,* 2011, 35, 129-156.

[20] Vicente, J.; Arcas, A.; Julia-Hernandez, F.; Bautista, D.: Jones, P., *Organometallics,* 2010, 29, 3066-3076.

[21] Vicente, J.; Arcas, A.; Julia-Hernandez, F.; Bautista, D., *Chem. Commun*., 2010, 46, 7253-7255.

[22] Xu, L.; Li, B.; Yang, Z.; Shi, Z.,*Chem. Soc. Rev*., 2010, 39, 712-73.

[23] Vicente, J.; Arcas, A.; Julia-Hernandez, F.; Bautista, D., *Angew. Chem. Int. Ed*., 2011, 50, 6896 -6899.

[24] Schindler, T.; Lux, M.; Peters, M.; Scharf, L.; Osseili, H.; Maron, L.; Tauchert, M., *Organometallics*, 2015, 34, 1978–1984.

[25] Moosun, S.; Blair, L.; Coles, S.; Bhowon, M.; Jhaumeer-Laulloo, S., *J. Saudi Chemical Society*, 2017, 21, 441-449.

[26] El-Qisairi, A.; Qaseer, H.; Zagha, M.; Magaireh, S.; Saymeh, R.; Yousef, Y., *Jordan Journal of Chemistry*, 2007, 2, 255-264.

[27] El-Qisairi, A.; Qaseer, H., *Jordan Journal of Chemistry*, 2007, 2, 69-78.

[28] Kuchekar, S.; Naval, R.;Han, S-H., *S. Afr. J. Chem*., 2014, 67, 226-232.

[29] El-Gammal, O.; El-Shazly, R.; El-Morsy, F.; El-Asmy, E., *J. Molecular Structure,* 2011, 998, 20-29.

[30] Andelkovic, A.; Sladic, D.; Bacchi, A.; Pelizze, G.; Filipovic, N.; Rajkovic, M., *Transition Metal Chemistry*, 2005, 30, 243-250.

[31] Sen, S.; Choudhury, C.; Talukder, P.; Mitra, S.; Westerhausen, M.; Keifel, A.; Desplanches, C.; Daro, N.; Sutter, J., *Polyhedron*, 2006, 25,1271-1278.

[32] Zaitoun, M.; Momani, K.; Jaradat, Q.; Qurashi, I., *Spectrochemica Acta A*, 2013, 115, 810-814.