International Journal of Enhanced Research in Science Technology & Engineering, ISSN: 2319-7463
Vol. 3 Issue 2, February-2014, pp: (112-118), Impact Factor: 1.252, Available online at: www.erpublications.com

Synthesis and Characterization of Pd (II) Complexes with Thio-1,3,4-Oxadiazole Derivatives

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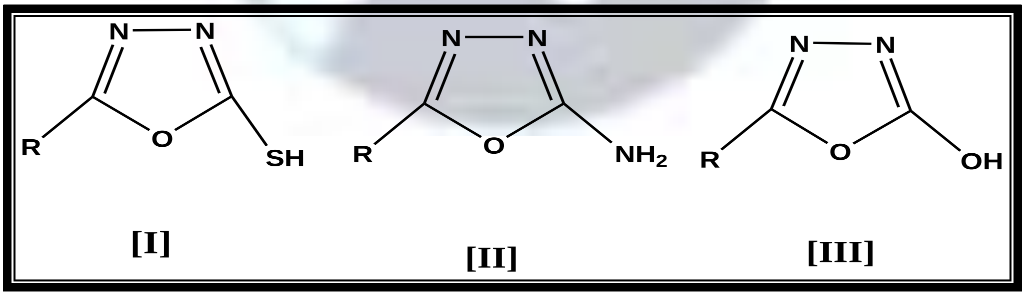
Abstract: Transition Pd(II) complexes with the ligands [L_1= 2-(5-phenyl-1,3,4-oxadiazole-2-ylthio) benzenamine, L_2=(E)-3-(2-(5-phenyl-1,3,4-oxadiazole-2-ylthio)phenylimino)indolin-2-one,L_3=2,2'-(5,5'-1,4-phenylene)bis(1,3,4-oxadiazole-5,2-diyl)bis (sulfanediyl) dibenzenamine], derived from the condensation of 5-phenyl-1,3,4-oxadiazole-2-thiol, 5,5'-(1,4-phenylene) bis (1,3,4-oxadiazole-2-thiol) and 2-aminothiophenol or isatin were synthesized. Characterization has been done on the basis of analytical molar conductivity data, infrared, electronic and ^{1}HNMR specrta for the ligands . The complexes were characterized using IR, UV-visible, molar conductivity measurements, and magnetic susceptibility measurements . IR spectra data suggest that the ligands chelated with ionic metal through S and N atoms. On the basis of physicochemical data as well as magnetic moment measurements, square planner geometries were assigned for the complexes.

Keywords: Pd complexes, 1,3,4-oxadiazole-2-thiol derivatives, spectral data.

Introduction

Oxadiazoles are five-membered, aromatic heterocycles that contain three heteroatoms in the same ring[1]. Heretocycles bearing nitrogen, sulpher, or oxygen constitutes the core structure of a number of biologically interesting compounds, such as tetrazoles, thiazoles, thiadiazoles, oxadiazoles, and triazoles, which are structural subunits of several biologically active compounds[2]. Compounds contain oxadiazole moiety, and it play a pivotal role in various pharmaceutical applications[3]. 1,3,4-oxadiazole is considered to be derived from furan by replacement of two methane (-CH=)groups, by two pyridine type nitrogen (-N=). 1,3,4-oxadiazole is a cyclic compound containing one oxygen and two nitrogen atoms in five membered ring[4]. 1,3,4-oxadiazoles are of significant interest in synthetic and medicinal chemistry due to its wide range of biological activities such as anti fungal, antimicrobial, anti-inflammatory, analgesic, anti tubercular, and anti-convulsant. 1,3,4-oxadiazoles showed antibacterial properties similar to those of well known sulfonamide drugs. The oxadiazole nucleus with N=C-S linkage exhibits a large number of pharmacological activities[5]. Three main derivatives of 1,3,4-oxadiazole were prepared **I, II, III**, and from these three derivatives a large number of compounds were prepared depending upon the nature and type of the substitutions on the position 2 and 5.



The attention has been concentrated on **[I]** due to the presence of biological activity of the thiol group, and the ligand ability to form complexes with many transition metal ions. The 1,3,4-oxadiazole-2-thiones represent an important type of compounds in the field of coordination chemistry because of their potential multifunctional donor sites, viz either exocyclic sulphur or endocyclic nitrogen[6].Since 1,3,4-oxadiazole-2-thiones are biologically active compounds, information about their 3-dimension structures may be of great interest for rational drug design. 1,3,4-oxadiazole-2-thione consist of an equilibrium mixture of its thione and thiol forms, therefore it will be of interest to investigate the mode of coordination oxadiazole in their complexes[7]. We were presenting here the preparation of new ligands [L_1 = 2-(5-phenyl-1,3,4-oxadiazole-2-ylthio) benzenamine, L_2 = (E)-3-(2-(5-phenyl-1,3,4-oxadiazole-2-ylthio)phenylimino)indolin-2-one, L_3=2,2'-(5,5'-1,4-phenylene)bis(1,3,4-oxadiazole-5,2-diyl)bis (sulfanediyl) dibenzenamine], and their Pd(II) complexes.

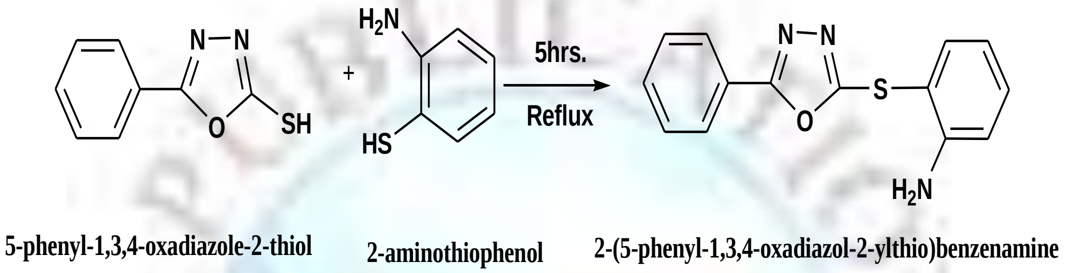
Experimental

All chemicals were of reagent grade, were used as supplied (Fluka), (Merk),(Alpha), or (B.D.H). Conductivity measurements for 10^{-3}M solution of the complexes in (DMSO) were carried out with on Jenway conductivity meter 4200 (093 cell constant) (UK.). Infrared spectra were recorded on Shimadzu FT-IR. 8400 spectrometer in the (200-4000)cm^{-1} range. The UV/Vis spectra were recorded on a UV-Vis spectrophotometer, AE-UV1609 (UK) CO., LTD in DMSO solvent. Melting point were measured using Melting Point-MPD-100 Pixel Technology CO. , Limited. Magnetic susceptibility was measured on Bruker Magnet BM6 measurement at 25^0C. ^{1}H-NMR spectra of ligands were carried on Bruker ultra shield 300 MHz with TMS as internal reference, in (Al-ALBayt) University Central Labs (Jordon), in DMSO as a solvent.

General procedure for the synthesis of the ligands:

Synthesis of L_1 = 2-(5-phenyl-1,3,4-oxadiazole-2-ylthio) benzenamine

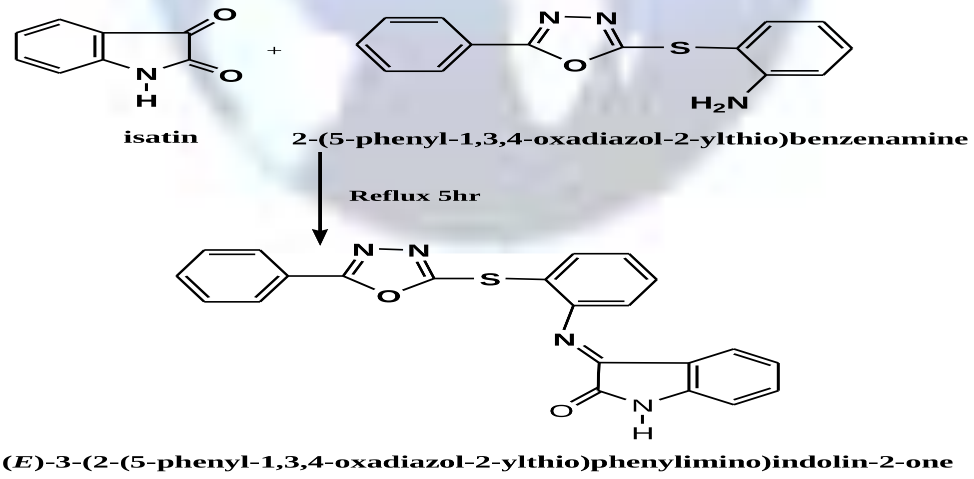
A solution of 2-aminothiophenol (0.375g, 0.3ml, 3mmole) was added to a solution of (5-Phenyl-1,3,4-oxadiazole-2-thiol) (0.534g, 3mmole) in 50ml of ethanol. The mixture was refluxed for 5 hrs. The reaction of mixture was poured into an ice-water. The light green precipitate was filtered off dried and re-crystallized from methanol.



Scheme(1): L_1 = 2-(5-phenyl-1,3,4-oxadiazole-2-ylthio)benzenamine

Synthesis of L_2 = (E)-3-(2-(5-phenyl-1,3,4-oxadiazole-2-ylthio)phenyl imino) indolin-2-one: Scheme(2)

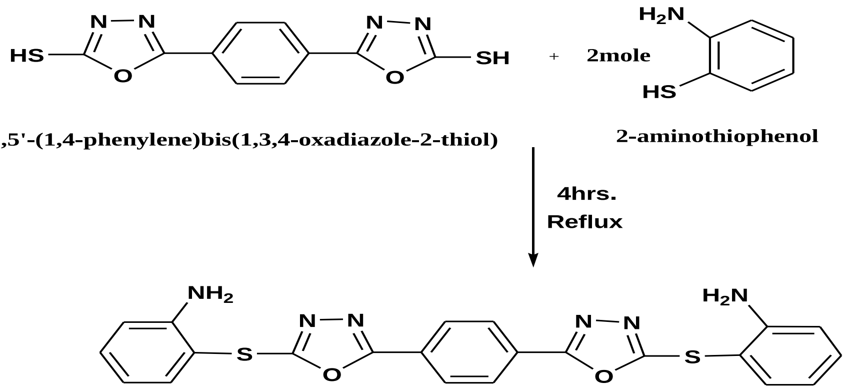
A solution of (L_1) (0.807g, 4mmol) in 20ml of ethanol was added to isatin solution (0.58g, 4mmol) which dissolved in 10ml of ethanol, 2-drops of glacial acidic acid were added, then refluxed for 5 hrs. The reaction of the mixture was poured into an ice-water to give an orange precipitate. The precipitate was filtered off, washed with diethyl ether, dried and re-crystallized from ethanol.



Scheme(2): L_2 = (E)-3-(2-(5-phenyl-1,3,4-oxadiazole-2-ylthio)phenyl imino) indolin-2-one

Synthesis of L_3 = 2,2'-(5,5'-1,4-phenylene)bis(1,3,4-oxadiazole-5,2-diyl)bis (sulfanediyl) dibenzenamine]: Scheme(3)

A solution of 2-aminothiophenol (0.5g, 0.4ml, 4mmol) was added to a solution of (5,5'-(1,4-phenylene)bis (1,3,4-oxadiazole-2-thiol)) (0.55g, 2mmol) in a 30ml of ethanol. The mixture was refluxed for 4hrs, then poured into an ice-water to give a light green precipitate. The precipitate was filtered off dried and re-crystallized from ethanol.



2,2'-(5,5'-(1,4-phenylene)bis(1,3,4-oxadiazole-5,2-diyl))bis(sulfanediyl)dibenzenamine

Scheme(3): L_3 = 2,2'-(5,5'-1,4-phenylene)bis(1,3,4-oxadiazole-5,2-diyl)bis (sulfanediyl)dibenzenamine

General procedure for the synthesis for synthesis metal complexes Synthesis of dichloro(2-[5-phenyl--1,3,4-oxadiazol-2-ylthiol] aniline)-palladium(II): [Pd(L_1)Cl_2]

A solution of $PdCl_2$ (0.5mmole, 0.088g) dissolved in hot methanol (20ml) and stirred for 20mins . To this solution (0.5mmole, 0.134g) of (L_1) dissolved in 10ml methanol was added. The mixture was refluxed for 2hrs, to give a brown precipitate which was filtered off and washed with diethylether (d.p.=255-258 °C).

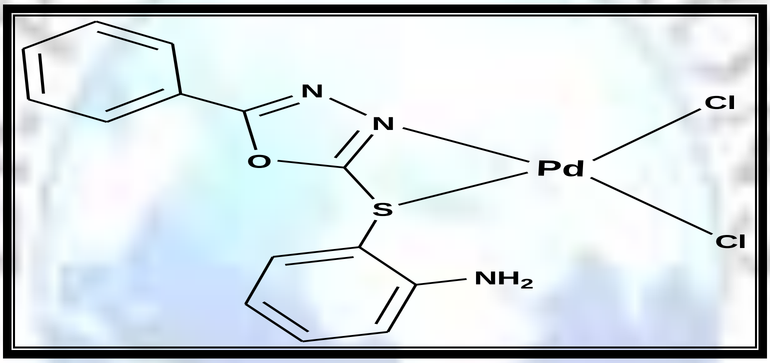


Fig. (1): The proposed geometrical structure of [Pd(L_1)$_2$$Cl_2$] complex

Synthesis of dichloro(3-(2-(5-phenyl-1,3,4-oxadaizole-2-yl-thio) phen ylimino)indolin-2-one)-palladium(II): [Pd(L_2)Cl_2]

To a solution of $PdCl_2$ (0.3mmole, 0.053g) in hot methanol (20ml) and stirred for 20min, a solution (0.3mmole, 0.119g) of (L_2) dissolved in 10ml methanol was added . The mixture was refluxed for 2hrs, to give brown precipitate which was filtered off and washed with diethyl ether (d.p.= 220-223°C).

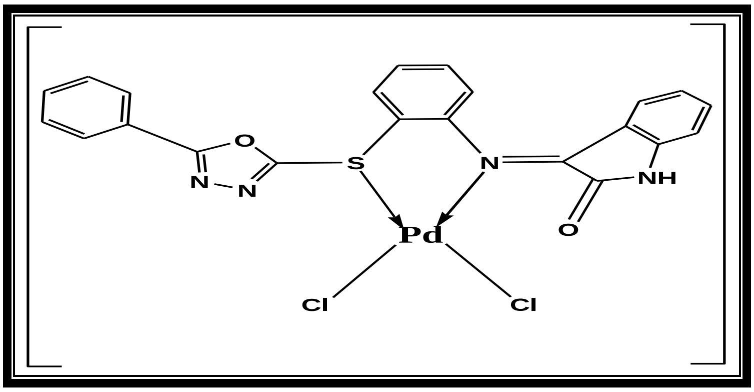


Fig. (2): The proposed geometrical structure of [Pd(L_3)Cl_2] complex

Synthesis of tetrachloro(2,2'-(5,5'-1,4-phenylene)bis(1,3,4-oxa dia zole-5,2-diyl)bis(sulfanediyl) dianiline)-dipalladium(II): $[Pd_2(L_3)Cl_4]$

To a solution of $PdCl_2$ (1mmole, 0.177g) in hot methanol (20ml) and stirred for 20min a solution (0.5mmole, 0.230g) of (L_3) dissolved in 10ml methanol was added. The mixture was refluxed for 2hrs, to give a brown precipitate which was filtered off, washed with ethanol, and diethylether (d.p.= 210-213°C).

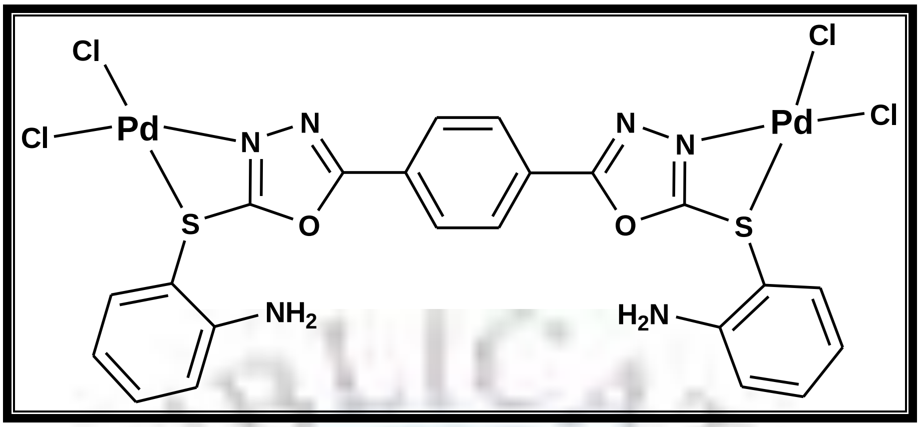


Fig. (3): The proposed geometrical structure of $[Pd_2(L_3)Cl_4]$complex

Table (1) : Physical properties of ligands

Ligand No.	Chemical Formula	Yield %	M.P (°C)	Color	Band absorption cm^{-1} (nm)	Molar conductivity ($Ohm^{-1}.cm^2.mol^{-1}$)	Selected IR				^{1}H-NMR (ppm)		
							ν(NH_2)	ν(C=N)	ν(C-S)	ν(C-O-C)	δarom.(5H)	δ arom. (4H)	δ(N-H)
L_1	$C_{14}H_{11}N_3OS$	94	172-173	Light green	37878 (264) 32467 (308)	0.5	3379(m) 3299(m)	1616 (s)	690(s)	1062(m)	(7.1-7.3)	(6.4-7.0)	(5.4-5.9)
L_2	$C_{22}H_{14}N_4O_2S$	79	154-156	Orange	38759(258) 33334 (300)	5.5	3305(m) 3230(m)	1650 (m) 1614 (s)	684(m)	1058(m)	(7.4-8.0)	(6.3-6.9) (7.0-7.6)	(10.8-11.0)
L_3	$C_{22}H_{16}N_6O_2S_2$	87	200-202	Light green	38461 (260) 292411(340)	7.8	-	1620 (s)	698(m)	1072(s)	–	(6.4-7.0) 7.11	5.4

s= strong, m= medium

Table (2) : Physical properties of complexes

No	Complex	Color	Decomposition (°C)	Yield%	Molar conductivity ($cm^2.ohm^{-1}.mol^{-1}$)	Magnetic susceptibility (B.M)	Band absorption (nm)	Selected IR					
								ν(O-H)	ν(C=N)	ν(C-S)	ν(M-N)	ν(M-S)	ν(M-Cl)
1	$[Pd(L_1)_2Cl_2]$	Brown	255-258	76	11.0	0.0	368 460 495	-	1612(s)	688(s)	547(w)	443(m)	383(s)
2	$[Pd(L_2)Cl_2]$	Brown	220-223	78	14.5	0.0	350 420 466	-	1652(m) 1618(s))	676(m)	526(s)	453(m)	391(m)
3	$[Pd_2(L_3)Cl_4]$	Brown	210-213	68	13.7	0.0	345 395 460	-	1612(s)	678(m)	522(w)	445(m)	379(s)

Results and Discussion

The new ligands (L_1), (L_2) and (L_3) were prepared by the reaction of [5-phenyl-1,3,4-oxadiazole-2-thiol], [5,5'-(1,4-phenylene) bis (1,3,4-oxadiazole-2-thiol)] with 2-aminothiophenol and[2-(5-phenyl-1,3,4-oxadiazole-2-ylthio) benzenamine] with isatin in a high yield table(1). The complexes were prepared through direct reaction of Palladium chloride, $PdCl_2$(II) with the above ligands. All the metal complexes are colored, and all of them are soluble in DMF and DMSO. Conductance measurements were carried out to ascertain the electrolytic/ non electrolytic nature of metal complexes in (10^{-3}M) DMSO solution at room temperature suggest the non electrolytic nature for all complexes.

^{1}HNMR data: The ^{1}HNMR spectrum of the ligands (L_1), (L_2) and (L_3) were recorded in DMSO solution. The results showed that the signals at (δ =5.4)ppm for(L_1), (L_3) ligands due to the N-H proton. Aromatic ring protons appeared at (δ =6.41, 6.79, 6.50, 7.0) ppm for (L_1) ligand and at (δ =6.40, 6.74, 6.45, 7.0)ppm for (L_3) ligand. Signals at (δ =7.39, 7.20, 7.11)ppm for (L_1) ligand and at (δ =7.11)ppm for(L_3) ligand due to the chemical shift of aromatic ring protons that linkage with oxadiazole ring. The ^{1}H-NMR spectrum of (L_2) ligand showed a signal at (δ =11.0)ppm due to the N-H proton of isatin. Aromatic ring protons of isatin which appeared in (δ =7.61, 7.58, 7.33, 7.09) ppm for (L_2) ligand. In addition of these peaks there are onother signals at (δ =6.99, 6.72, 6.55, 6.35)ppm for (L_2) ligand, which also refer to the presence of aromatic protons. Signals were appeared at (δ =8.05, 7.89, 7.48)ppm due to the chemical shift of aromatic ring protons that linkage with oxadiazole ring.

Infrared spectral studies: The infrared spectrum of (L_1),(L_3) ligands showed new bands in the range (3379,3299)cm^{-1}for (L_1) ligand, (3305,3232)cm^{-1}for (L_3) ligand and (3247)cm^{-1} for (L_2)respectively, which are corresponding to ν(N-H) of (NH_2) amine[8,9].Strong and broad bands in the range (3419-3560) cm^{-1} can be assigned to ν(O-H) coordinated water molecules [10,11]. A strong absorption at 1616 cm^{-1}, 1614 cm^{-1}and 1650cm^{-1} appeared in a spectrum of (L_1), (L_2) and (L_3) respectively which indicated to the ν(C=N) indocyclic of oxadiazole ring. A negative and positive shift in ν(C=N) of the chelates suggest the involvement of nitrogen in coordination[7,12,13,14]. The ν(C-S) band of the free ligands in the range (698-684)cm^{-1} , shifted to (688-676) cm^{-1} for complexes, these shifting to a lower frequency from ligand indicated coordination of (C-S) to the metal ions[64]. Further support for this argument came from the IR of the complexes which showed new bands at 522-547cm^{-1} attributed to ν(M-N) [7,13]. They also showed a band in the region 379-391cm^{-1} which may be due to ν(M-Cl)[15,16]. Further support for this coordination has been provided by the appearance of new bands in the 443-453cm^{-1} ranges which are relatively attributed to ν(M-S) [17].

Magnetic susceptibility measurements: The magnetic moments were measured at 25^{0}C. The results indicated square planner form for Pd(II) (μ_{eff}. = 0.0) complexes.

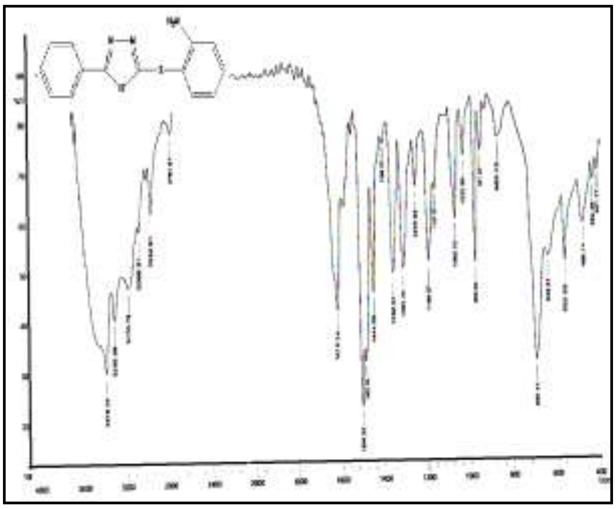
Electronic spectral studies: The electronic spectra of the ligands and their complexes in 10^{-3} M solution DMSO was recorded, the results were listed in Table(1,2), the bands at 254-340 nm were due to π- π* and n-π* transition within the ligands. The UV-visible spectrum of Pd(II) complex(1), gave three spins allowed transitions at 20203 cm^{-1} (v_1) , 24630cm^{-1} (v_2) , and 27173cm^{-1} (v_3) were assigned to transitions $^1A_1g\rightarrow {}^1A_2g$, $^1A_1g\rightarrow {}^1B_1g$ and $^1A_1g\rightarrow {}^1Eg$ respectively, Fig. (4.18) and Table (4.2), it's reasonable to assigned square plannar geometry [18,19]. The UV-visible spectrum of Pd(II) complex(2), gave three spins allowed transitions at 21459 cm^{-1} (v_1) , 23809 cm^{-1} (v_2) , and 28571 cm^{-1} (v_3) were assigned to transitions $^1A_1g\rightarrow {}^1A_2g$, $^1A_1g\rightarrow {}^1B_1g$ and$^1A_1g\rightarrow {}^1Eg$ respectively. The UV-visible spectrum of Pd(II) complex(3), gave three spin allowed transitions at 21739 cm^{-1} (v_1) , 25316cm^{-1} (v_2) , and 28985 cm^{-1} (v_3) were assigned to transitions $^1A_1g\rightarrow {}^1A_2g$, $^1A_1g\rightarrow {}^1B_1g$ and$^1A_1g\rightarrow{}^1Eg$ respectively, These transitions value are indicated to square plannar geometry[18].

Conclusion

The present work includes synthesis of new ligands of 1,3,4-oxadaizole derivatives, and palladium complexes with these ligands. On the basis of IR, UV-Visible spectra, and magnetic susceptibility values, we concluded that the complexes of Pd(II) metal ions most probably to have square planner geometries. According to the Molar conductivity data, it has been suggested that all synthesized complexes are non-electrolyte type.

Acknowledgement

The authors are thankful to the chemistry Department. College of Education for their accomplishing our present work, University of AL-AI bayt central Labs (Jordon) for ^{1}HNMR study and University of Tikrit for IR-measurements.



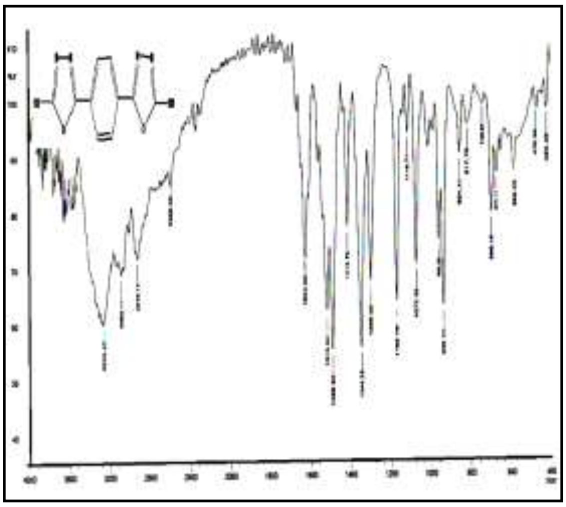
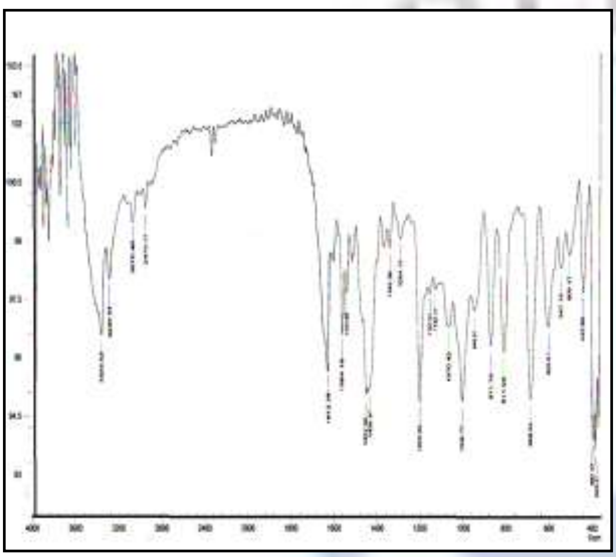


Fig.(4): The Infrared spectrum of (L_1) ligand Fig. (5): The Infrared spectrum of (PBOT) ligand



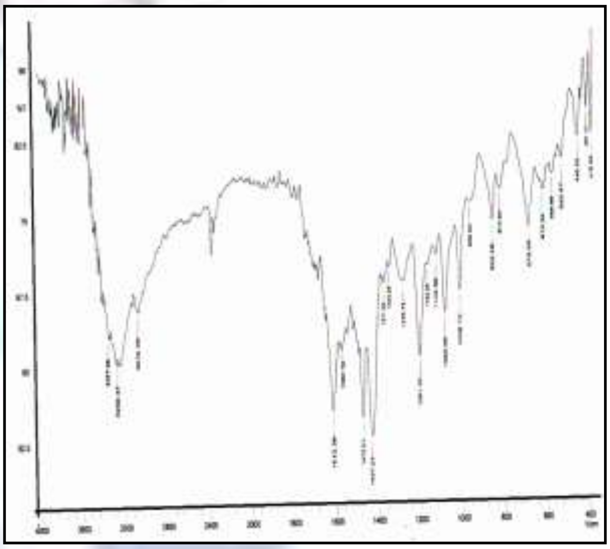
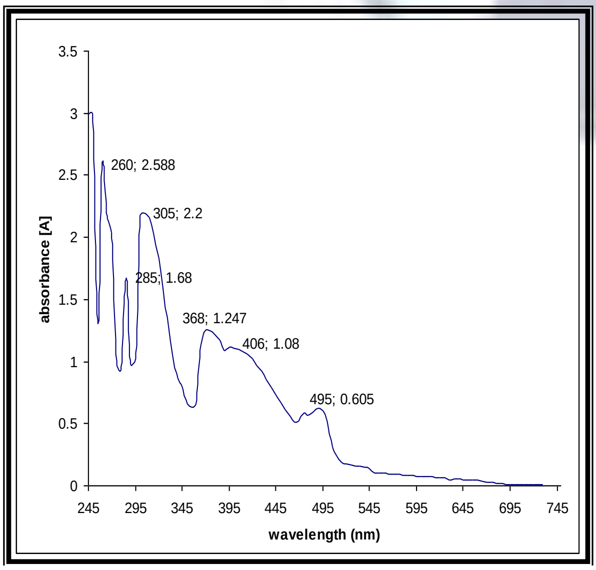


Fig.(6): The Infrared spectrum of [Pd(L_1)Cl_2] complexFig. (7): The Infrared spectrum of [Pd_2(L_3)Cl_4] complex



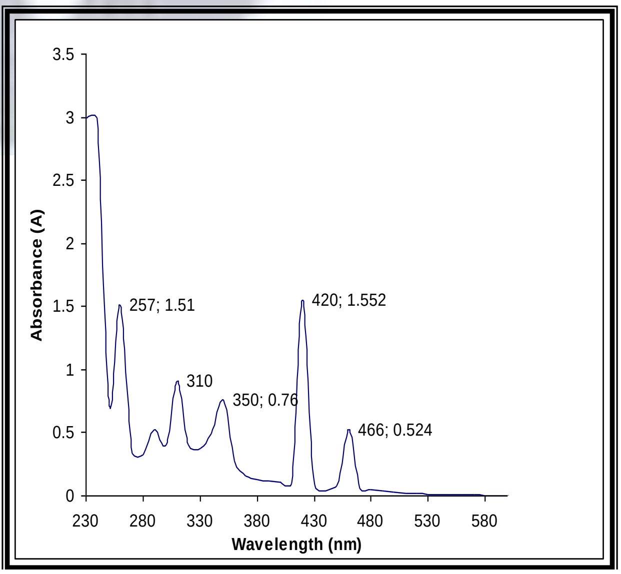


Fig. (8): Electronic spectrum of [Pd(L_1)$_2$$Cl_2$] complex

Fig. (9): Electronic spectrum of [Pd(L_2)Cl_2] complex

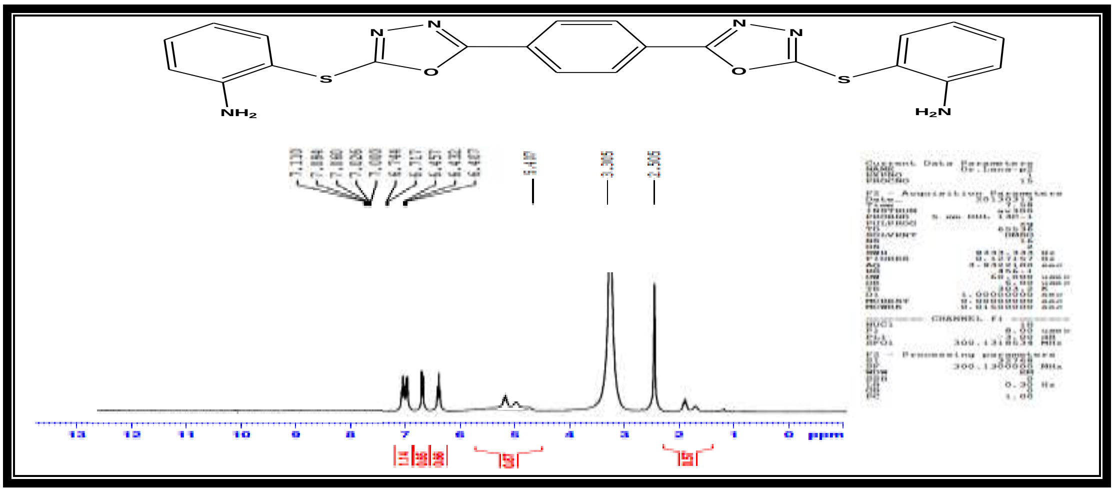


Fig. (10): ^{1}H-NMR of (L_3)ligand

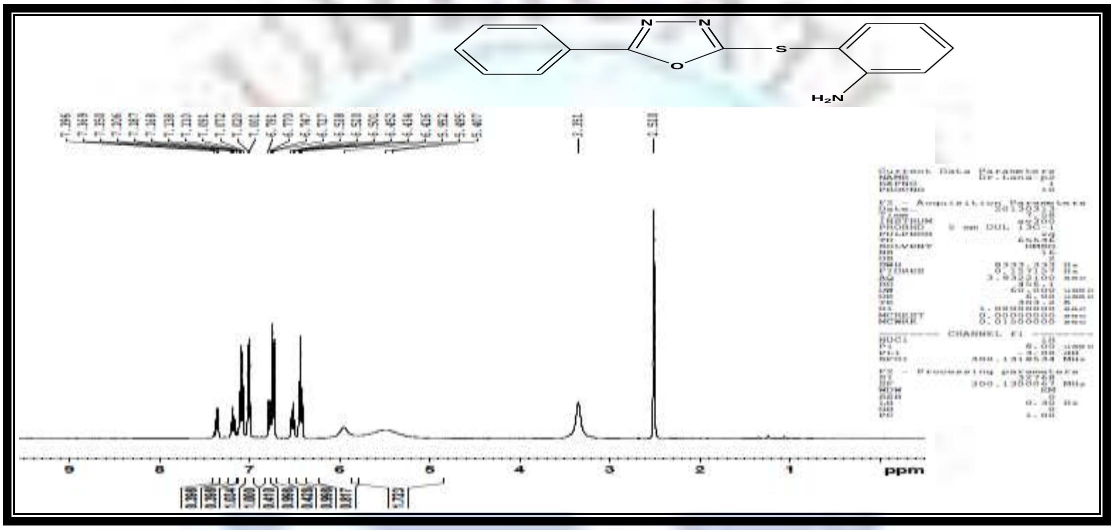


Fig. (11): ^{1}H-NMR of (L_2)ligand

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