

Preparation of some metallic complexes from selected organic ligands and characterization it spectrophotometry as a model of a ligand scavenger to metals in health applications

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ABSTRACT:

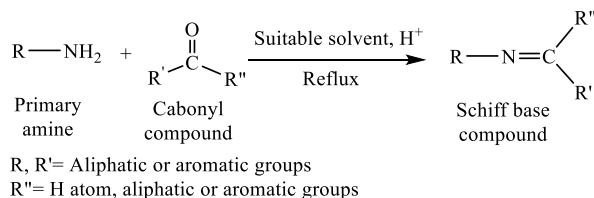
The research included prepare imines from the primary aromatic amine 4.4-dithioaniline with aromatic aldehydes. The imine compounds (R₁-R₆) were characterized spectroscopically by UV / Vis, FT-IR, ¹H-NMR and the melting point was taken for these compounds, when the reaction of the imine compounds with the metal ions Pd(II) leads to the formation of palladium complexes (R₇-R₁₂). The complexes were characterized spectroscopically by UV / Vis, FT-IR, mass spectrometry, C.H.N.S. and molar conductivity, which proved that non-electrolyte palladium complexes. Magnetic measurements have been taken that have an important role in knowing the geometry shape of the complexes, Palladium complexes are square planar.

KEYWORDS: ¹H-NMR, imines, palladium (II) complexes

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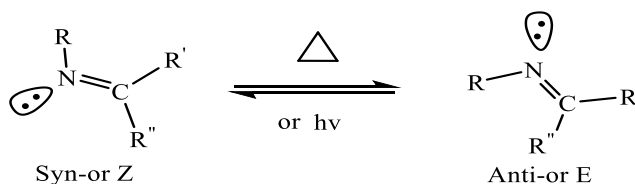
INTRODUCTION:

Imines compounds are containing the group (C=N) and they are preparing by the reaction between primary aromatic amines with aromatic aldehydes [1]. See scheme 1.



Scheme 1. Structure of imines compounds

Other classes of imine compounds depend on the nature and type of the groups associated with the carbon and nitrogen atoms on the ends of the sphincter (C=N) specified for their properties. Aryl is called ketimines when it is derived from ketones and primary amines. R, R', R'', alkyl or aryl groups are called anils, when they are derived from aniline and aliphatic aldehydes or ketones called benzaniles [2]. When it is derived from aniline and benzaldehyde The two geometrical shape of imine compound are based on the spatial distribution of the groups associated with the nitrogen and carbon atoms around the double bond (C=N). The two geometrical called Anti- or E if the high molecular weight of groups are on the opposite side and it called Syn-or Z if they are on the same side, the stability of the two type is dependent on the nature of the compensated groups [3]. See scheme 2.



Scheme 2. Syn- (Z) and Anti- (E) of the two geometrical shape of imine compound

Organic complexes are important compounds in synthesis science. Example of one organic complexes is the prepared complex by imine compound and palladium (II) chloride to prepare two square-planar palladium (II) complexes with P,O-bidentate hybrid ligands [4].

MATERIALS AND METHODS:**General procedure for prepare of imine compounds [5-8]:**

Imine compounds are preparation by mixing 0.01moleof amine and 0.02 mole ofaldehydepresence trace of glacial acetic acid in 25 mL abs. ethanol, the reaction completed for 4hours, the purity of the Imine compounds were monitored with Thin Lear Chromatography. Table1 showedthe physical properties of the prepared imines (R₁-R₆)are recorded in.

General procedure for prepare of palladium complexes [9]:

A mixture of preparedimine compound 0.001 mole with 0.002 mole of Pd(II)chloridedissolved in 25 mL of absolute ethanol, the mixture was refluxed for 3 hours.Table 2 showed the physical properties of the prepared compounds(R₇-R₁₂).

RESULTS AND DISCUSSION:

The best yield of the prepared imineswas for compound R₆86%, the best yield of the preparedPalladium complexeswas for R₉62%. The higher m.p. forimines was for compound R₄ (221-223^oC), the m.p.of all the preparedPalladium complexes wereover (300^oC). See table 1 and table 2 for some physical properties of prepared iminesand Palladium complexes.

Table 1.Structure, melting points, colors and percentages of yield of prepared imines [R₁-R₆]

Compound Code	Structure	Yield %	Melting point °C	Color
R ₁		54	162-165	White
R ₂		57	213-215	Yellow
R ₃		66	120-123	Yellow
R ₄		78	221-223	Orange
R ₅		75	180-182	White
R ₆		86	198-200	White

Table 2. Structure, melting points, colors and percentages of yield of Palladium complexes(R₇-R₁₂)

Compound code	Structure	Yield %	Melting point °C	Color
R ₇		51%	>300	Yellow
R ₈		45%	>300	Yellow
R ₉		62%	>300	Orange
R ₁₀		48%	>300	Yellow
R ₁₁		55%	>300	Yellow
R ₁₂		56%	>300	Yellow

Preparedimine compounds:

Uv-Visible showed peaks indicative of aromatic C=C at (218-270nm), peaks at (312- 425nm) indicative of imine group C=N [10], see table 3 of all prepared imines.

Table 3.The Uv-Visible spectrum of prepared imines(R₁-R₆)

Compound Code	Max/nmλ	(cm ⁻¹)υ	Transition
R ₁	270nm	37037cm ⁻¹	π→π*
	335nm	29850cm ⁻¹	n→π*
R ₂	238-246nm	42016-40650cm ⁻¹	π→π*
	326-380nm	30674-26315cm ⁻¹	n→π*
R ₃	218nm	45871cm ⁻¹	π→π*
	390nm	25641cm ⁻¹	n→π*
R ₄	258-270nm	38759-37037cm ⁻¹	π→π*
	312-425nm	32051-23529cm ⁻¹	n→π*
R ₅	220-250nm	45454-40000cm ⁻¹	π→π*
	315-385nm	31746-25974cm ⁻¹	n→π*
R ₆	227-290nm	44052-34482cm ⁻¹	π→π*
	315-366nm	31746-27322cm ⁻¹	n→π*

The absorption of -C=N- at (1558-1627)cm⁻¹ indicative of the formation of the imine compounds,the absorption C-S at (555-764) cm⁻¹see other bands of the groups in all prepared imines[11],see scheme3,table 4, figure 1 and figure 2.

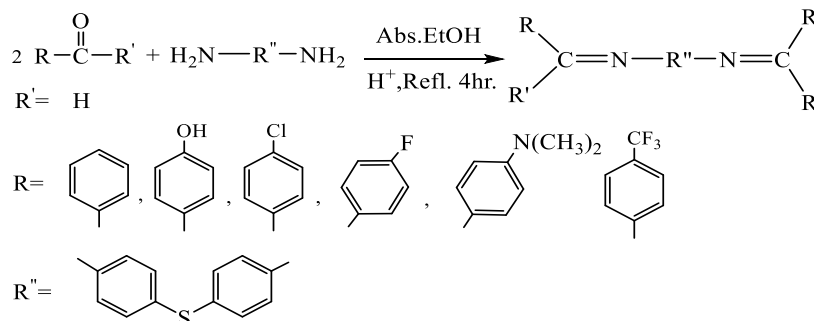

Scheme 3. Structure of the prepared dimines

Table 4.The FT-IR spectra of prepared dimines

Comp. Code	νC=N	νC=C Arom.	ν=C-H Arom.	ν=C-H Alk.	νC-S	Other Groups
R ₁	1627	1572	3061	2878	689	-
R ₂	1609	1581	3052	2987	683	C-O: 1250 O-H: 3332
R ₃	1558	1484	3080	2991	687	C-Cl: 825
R ₄	1600	1574	3030	2879	555	C-N: 1228 C-H: 2799
R ₅	1620	1599	3068	2876	720	C-F:1241
R ₆	1623	1570	3040	2876	764	C-F:1323

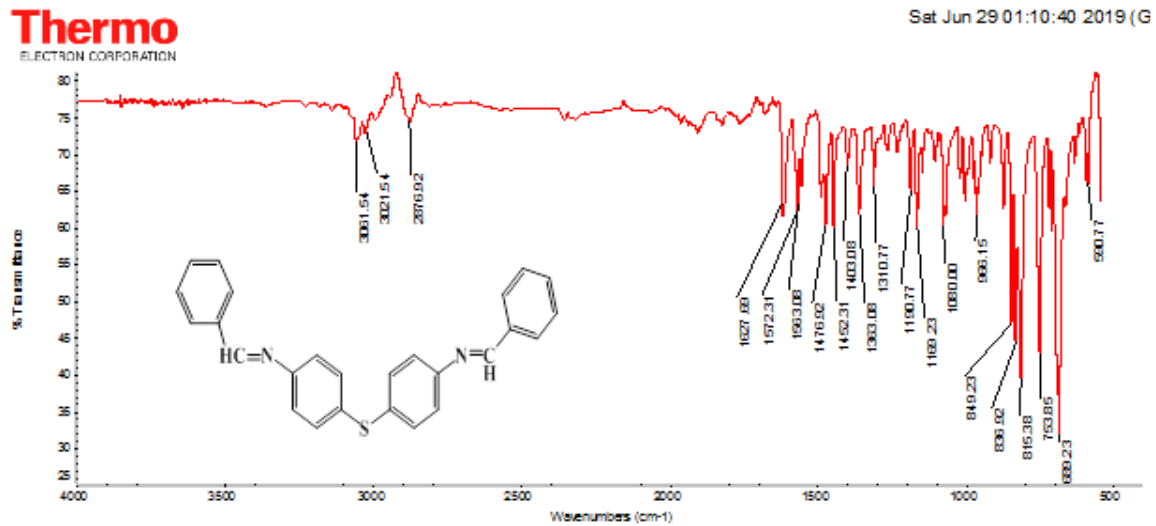


Figure 1. The FT-IR spectrum of R₁

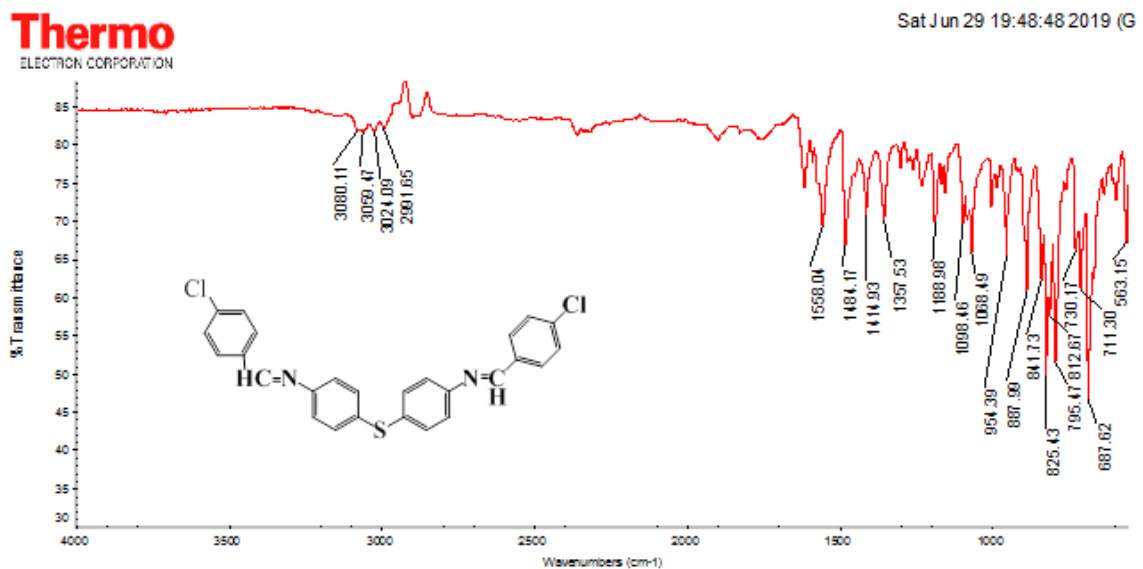
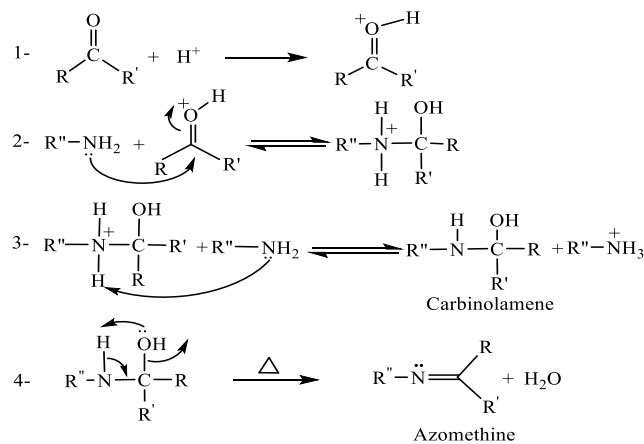


Figure 2. The FT-IR spectrum of R₃

The mechanism of imine compound formation given by scheme 4, double-electronic of the nitrogen atom in NH₂ group on the carbon atom of the C=O group to form a hemiaminal N-substituted [12, 13], see scheme 4.



Scheme 4. Mechanism of imine compound formation

The proton nuclear magnetic resonance $^1\text{H-NMR}$ of R_1 in DMSO (figure 3) showed the chemical shifts, $\delta(\text{ppm})$, Singlet in 8.7 indicative of 2H for two groups of N=CH , multiplet in 7.5-8 indicative of 18H for aryl protons. Spectrum of compound R_2 (figure 4) showed singlet in 8.9 indicative of 2H for two groups of N=CH , singlet in 12.8 indicative of 2H for two groups of $-\text{OH}$, multiplet in 7-7.8 indicative of 16H for aryl protons [11]. Chemical shifts of R_3 - R_6 , $\delta(\text{ppm})$ are presented in table 5.

Table 5. The $^1\text{H-NMR}$ Spectra of imine compounds DMSO

Compound Code	Chemical Shift δ ppm
R_1	Singlet in 8.7 indicative of 2H for 2N=CH , multiplet in 7.5-8 indicative of 18H for aryl protons.
R_2	Singlet in 8.9 indicative of 2H of 2N=CH , singlet in 12.8 indicative of 2H for two groups of $-\text{OH}$, multiplet in 7-7.8 indicative of 16H for aryl protons.
R_3	Singlet in 8.8 indicative of 2H for 2N=CH , multiplet in 7.3-7.8 indicative of 16H for aryl protons.
R_4	Singlet in 8.3 indicative of $2\text{H } 2\text{N=CH}$, singlet in 2.9 indicative of 12H for two groups of $\text{N}(\text{CH}_3)_2$, multiplet in 6.8-7.8 indicative of 16H for aryl protons.
R_5	singlet in 8.7 indicative of 2H for 2N=CH , multiplet in 7.3-8 indicative of 16H for aryl protons.
R_6	singlet in 8.8 indicative of 2H 2N=CH , multiplet in 7.3-8.3 indicative of 16H for aryl protons.

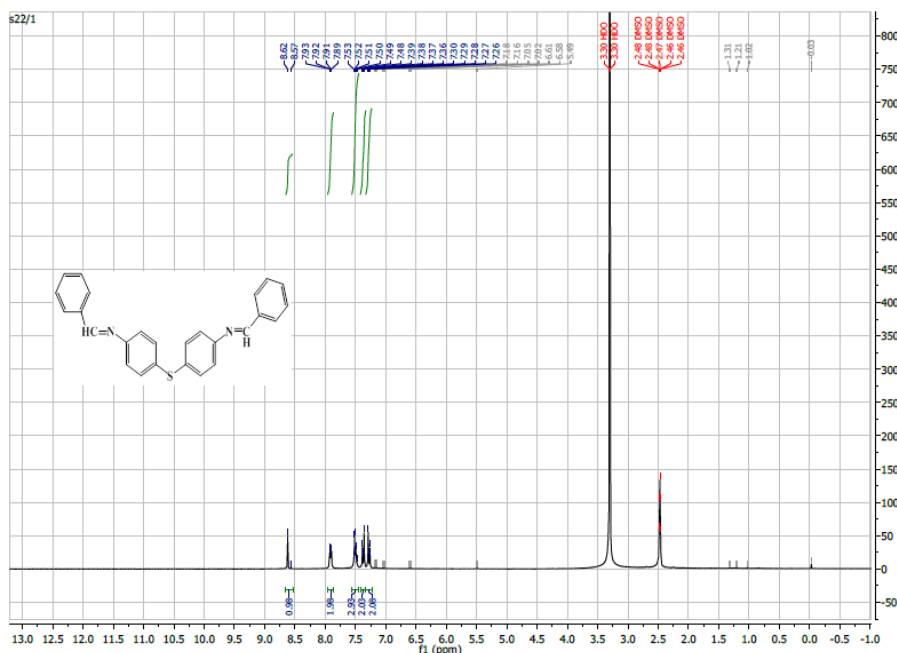


Figure 3. The $^1\text{H-NMR}$ Spectrum of R_1

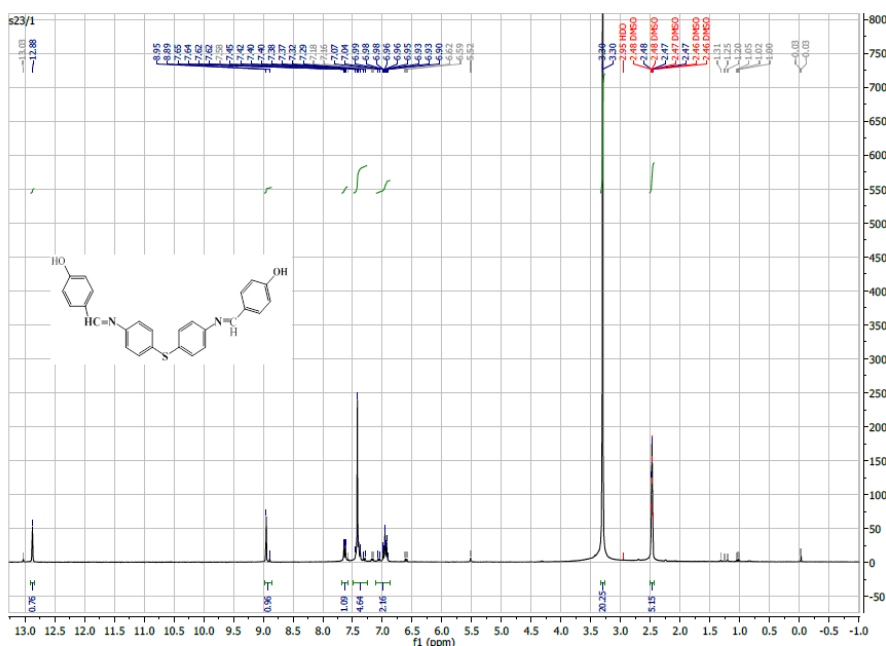


Figure 4. The ¹H-NMR Spectrum of R₂

Prepared Palladium complexes:

Uv-Visible showed peaks indicative of aromatic C=C at (204-289 nm), peaks at (307-368 nm) indicative of C=N [10], see table 3 of all synthesized Palladium complexes.

Table 6. Uv-Visible spectrum of Palladium complexes(R₇-R₁₂)

Compound Code	Max/nmλ	ν(cm ⁻¹)	Transition	Suggested Structure
R ₇	239	41841	π→π*	Square planar
	307	32573	n→π*	
	409	24449	C.T	
	762	13123	¹ A _{1g} → ¹ A _{2g}	
R ₈	216	46296	π→π*	Square planar
	311	32154	n→π*	
	431	23201	C.T	
R ₉	765	13071	¹ A _{1g} → ¹ A _{2g}	Square planar
	289	34602	π→π*	
	386	25906	n→π*	
	457	21881	C.T	
R ₁₀	758	13192	¹ A _{1g} → ¹ A _{2g}	Square planar
	225	44444	π→π*	
	307	32573	n→π*	
	424	23584	C.T	
R ₁₁	729	13717	¹ A _{1g} → ¹ A _{2g}	Square planar
	209	47846	π→π*	
	352	28409	n→π*	
	422	23696	C.T	
R ₁₂	761	13140	¹ A _{1g} → ¹ A _{2g}	Square planar
	204	49019	π→π*	
	323	30959	n→π*	
	425	23529	C.T	
	762	13123	¹ A _{1g} → ¹ A _{2g}	
R ₁₂	368	27173	C.T	Square planar
	709	14104	⁴ A _{2g} → ⁴ T _{1g}	

Prepared Palladium complexes showed the absorption at (1590-1643) cm^{-1} of the lactam $\text{C}=\text{N}$, bands at (610-750) cm^{-1} of $-\text{C}-\text{S}-$, bands at (1483-1584) cm^{-1} of aryl $\text{C}=\text{C}$, bands at (566-593) cm^{-1} of $\text{M}-\text{N}$, see the bands of Palladium complexes[11], see the table 7, figure 3 and figure 4.

Table 7.The FT-IR of Prepared Palladium complexes

Compound Code	$\nu\text{C}=\text{N}$	$\nu\text{C}=\text{C}$ Arom.	$\nu\text{C}-\text{H}$ Arom.	$\nu\text{C}-\text{S}$	$\nu\text{N}=\text{C}-\text{H}$	$\nu\text{M}-\text{N}$	νOH Water	Other Group
R ₇	1593	1584	3193	750	3120	593	3283	---
R ₈	1590	1484	3193	610	3110	566	3489	O-H 3489 C-O 1218
R ₉	1643	1579	3052	732	2956	583	3476	C-Cl 665
R ₁₀	1590	1483	3190	630	3110	566	3476	C-N1120 N-CH ₃ 2600
R ₁₁	1596	1486	3200	750	3116	567	3480	C-F 1116
R ₁₂	1590	1486	3193	630	3113	569	3483	C-F 1120

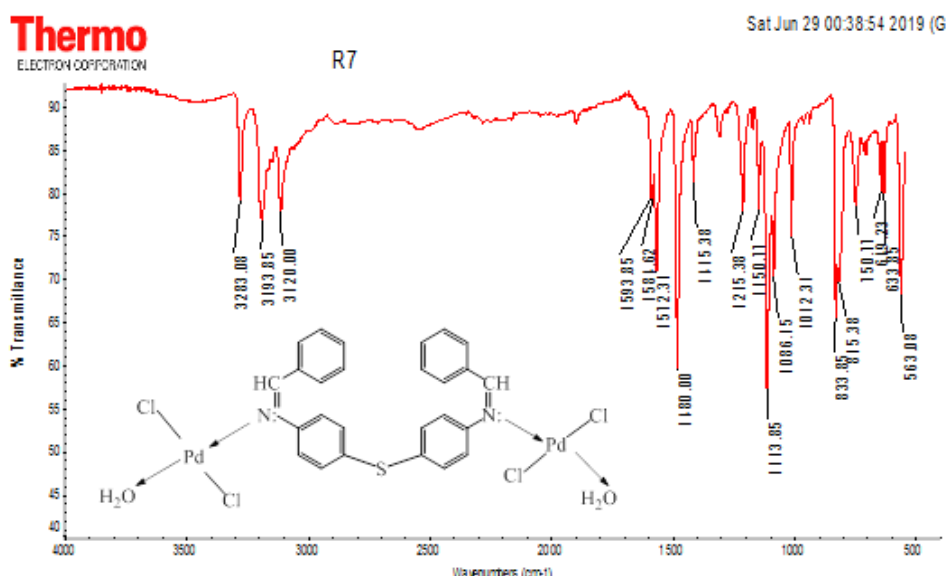


Figure 5.The FT-IR spectrum of R₇

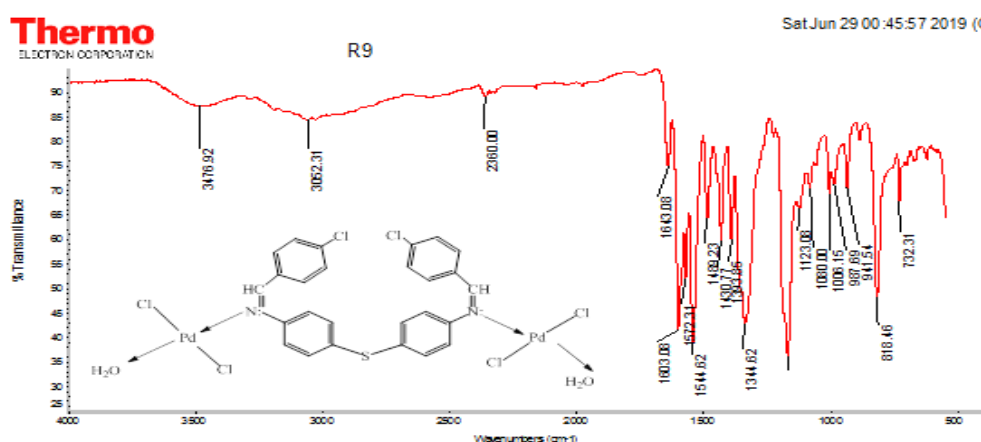


Figure 6. The FT-IR spectrum of R₉

Tables 8-10 and figures 7-9 of Mass spectra showed the molecular weight of the all fragments for the Palladium complexes (R₈, R₉ and R₁₁).

Table 8. Mass spectra of R₈

Fragment	Mass/ Charge (m/z)
M+ = [C ₂₆ H ₂₄ N ₂ O ₄ SCl ₂ Pd ₂] ⁺	812
[C ₁₈ H ₁₉ N ₂ O ₄ SCl ₂ Pd ₂] ₊	711
[C ₁₁ H ₁₂ NO ₄ SPd ₂] ₊	466
[C ₁₃ H ₁₁ Cl ₂ Pd] ⁺	343
[C ₇ H ₇ Cl ₄ N] ⁺	245
[CH ₃ PdO ₂] ⁺	153
[PdH ₂ OH ₂] ⁺	126
[C ₅ H ₅ NO] ⁺	95

Table 9. Mass spectra of R₉

Fragment	Mass/ Charge (m/z)
M+ = [C ₂₆ H ₂₂ N ₂ O ₂ SCl ₆ Pd ₂] ⁺	848
[C ₈ H ₁₂ N ₂ O ₄ SCl ₄ Pd ₂] ⁺	552
[C ₁₁ H ₁₂ N ₂ SCl ₂ Pd ₂] ⁺	472
[C ₁₁ H ₉ O ₂ Cl ₂ Pd ₂] ⁺	349
[C ₁₀ H ₇ O ₂ Cl ₂] ⁺	229
[PdOH] ⁺	123

Table 10. Mass spectra of R₁₁

Fragment	Mass/ Charge (m/z)
M= [C ₂₆ H ₂₂ N ₂ O ₂ SCl ₂ Pd ₂ F ₂] ⁺	816
[C ₂₆ H ₂₀ N ₂ O ₂ SCl ₂ Pd ₂] ⁺	706
[C ₁₁ H ₁₀ N ₂ O ₂ SPd ₂ F] ⁺	465
[C ₁₂ H ₇ Cl ₂ PdF] ⁺	346
[C ₇ H ₉ NSPd] ⁺	245
CH ₃ PdO ₂	153

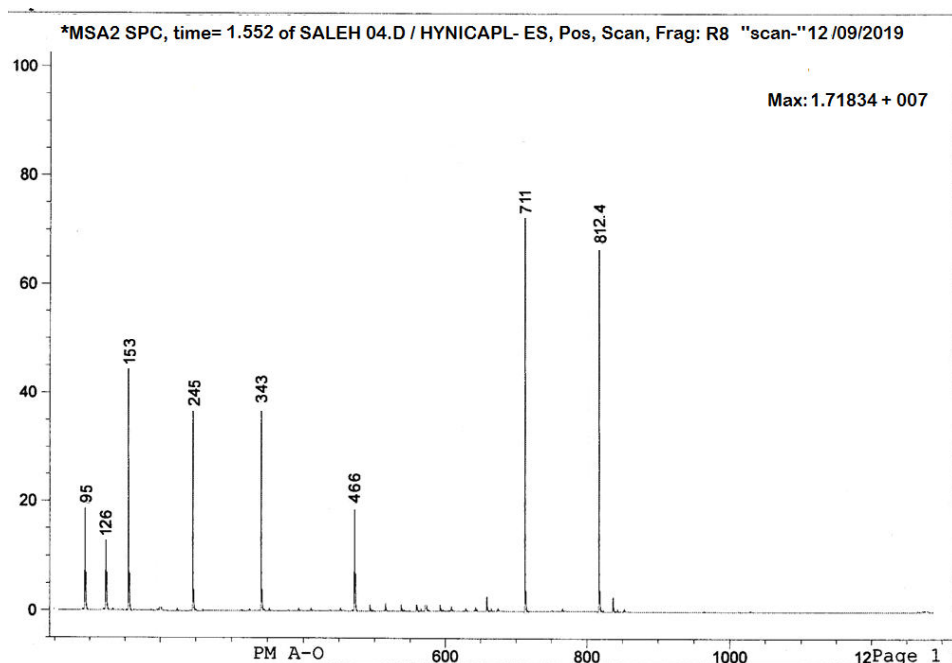


Figure 7. The mass spectra of R₈

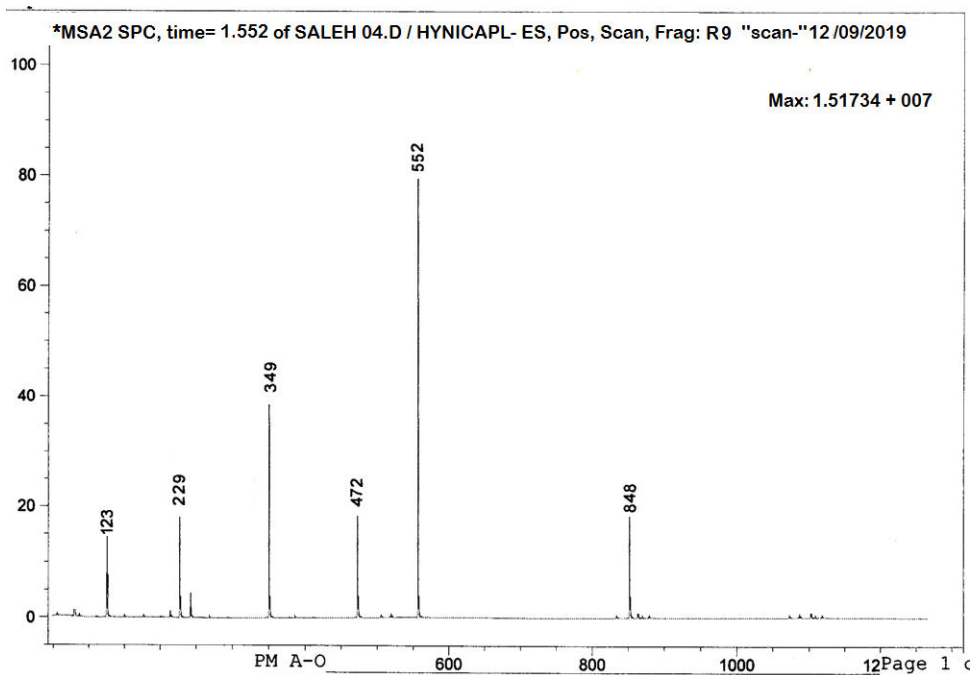


Figure 8. The mass spectra of R₉

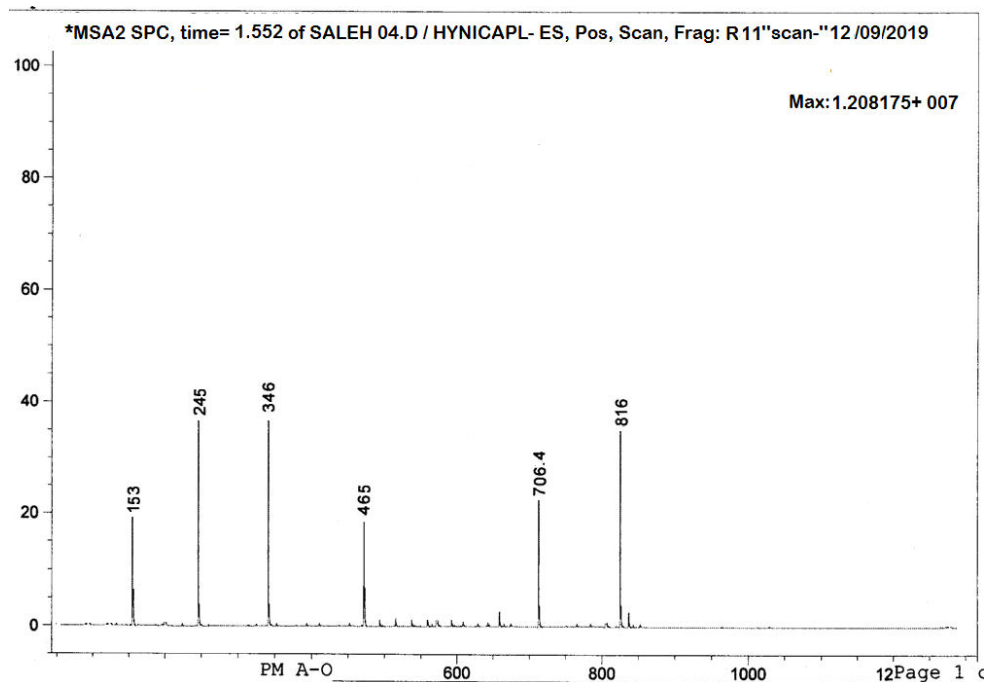


Figure 9. The mass spectra of R₁₁

Table 11 of C.H.N.S. of some Palladium complexes (R₈, R₉, R₁₁) and Molar conductance of palladium complexes is non-electrolyte.

Table 11.The Elemental analysis C.H.N.S

Compound Code	Molecular formula	M.Wt g/mol	Element analysis (Calc.) theoretical				M%	Cl%
			C%	H%	N%	S%		
			R₈	C ₂₆ H ₂₄ Cl ₄ O ₄ N ₂ Pd ₂ S	812	38.31 (39.73)		
R₉	C ₂₆ H ₂₂ Cl ₆ O ₂ N ₂ Pd ₂ S	848	36.65 (35.96)	2.60 (3.60)	3.28 (4.96)	3.76 (4.05)	24.98 (25.01)	24.96 (23.81)
R₁₁	C ₂₆ H ₂₂ Cl ₄ O ₂ F ₂ N ₂ Pd ₂ S	816	38.12 (39.01)	2.70 (1.96)	3.41 (4.07)	3.91 (4.15)	25.98 (26.19)	17.31 (18.18)

Table 12 Magnetic moment measurements of some palladium complexes[14].

Table 12. The Magnetic measurements of (R₇, R₈, R₉ and R₁₁)

Complexes	X _g × 10 ⁻⁶ mass susceptibility	X _M × 10 ⁻⁶ Molar susceptibility	X _A × 10 ⁻⁶ Atomic susceptibility	μ _{eff} B.M Exp.	Suggested Structure
R ₇	Zero	Zero	391.2	0.84	Square planer
R ₈	Zero	Zero	407.5	0.84	Square planer
R ₉	Zero	Zero	426.1	0.84	Square planer
R ₁₁	Zero	Zero	409.5	0.84	Square planer

CONCLUSION:

It was possible to prepare derivatives of Palladium complexes. Molar conductance which proved that non-electrolyte palladium complexes, Magnetic measurements have an important in the geometry shape of the complexes are square planar.

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