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SPECTROSCOPIC AND BIOLOGICAL STUDIES OF Pd(II) COMPLEXES OF 5-(*p*-TOLYL)-1,3,4-OXADIAZOLE-2-THIOL

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ABSTRACT. Reactions of Na_2PdCl_4 with two equivalents of 5-(*p*-tolyl)-1,3,4-oxadiazole-2-thiol (MoxSH), afford complex of the type $[Pd(MoxS)_2]$ (**1**). Further reaction with equivalent mole of diphosphine ligand $\{Ph_2P(CH_2)_nPPh_2\}$ (where n = 1 dppm, 2 dppe, 3 dppp, 4 dppb, $(CH_2)_n$ = dppf) or two equivalents of triphenyl phosphine or triphenyl phosphine sulfide affords mixed-ligand complexes of the type $[Pd(MoxS)_2(Ph_2P(CH_2)_nPPh_2)]$ (**2-6**), $[Pd(MoxS)_2(PPh_3)_2]$ (**7**) and $[Pd(MoxS)_2(SPPh_3)_2]$(**8**). The prepared complexes were characterized using different physical and spectroscopic methods. The results indicated that the MoxS ligand behave as coordinate in a anion monodentate fashion sulfur atom to give a square planer around the metal ion. Preliminary anti-bacterial activity has been assessed against *Escherichia coli*, *Staphylococcus aureus*, and *Bacillus subtilis* bacteria. The prepared complexes show good activity in compared with standard drug. $[Pd(MoxS)_2(dppf)]$ (**6**) displays good activity (18, 22 and 20 mm) against certain tested microbes *Escherichia coli*, *Staphylococcus aureus* and *Bacillus subtilis*, respectively.

KEY WORDS: Complexes, Palladium, Thione, Anti-bacteria, Phosphine

INTRODUCTION

Heterocyclic thiones, consisting of a heterocyclic ring with or without the presence of nitrogen, oxygen or sulfur and an exo-cyclic thione {C(S)NH}, represent an important class of N,S-donor organic thio-ligands, which have shown interesting coordination novelty and thus formed a diverse network of coordination compounds, as revealed by several reviews in this area [1-10]. In addition, the heterocyclic thione complexes are a significant area of study in coordination chemistry due to their unique properties and potential applications. These complexes typically involve heterocyclic thione ligands, which contain sulfur as a part of a heterocyclic, coordinated to various metal centers. Heterocyclic thiones can bind to metals through sulfur (S), nitrogen (N), or both (chelation), or as polydentate ligands, depending on the ligand's structure and the metal's preference. The conditions such as pH, temperature, and the presence of auxiliary ligands can be varied to control the complexation process [1, 2, 6].

The biological activity of 1,3,4-oxadiazoles and their complexes has garnered significant interest. For instance, various 1,3,4-oxadiazole derivatives have been found to possess analgesic, muscle relaxant, tranquillizing, antiproteolytic, anticonvulsive, and anti-inflammatory properties,

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as well as fungicidal activity. According to a report [11], 5-phenyl-l,3,4-oxadiazolethiol has been found to have anti-tubercular properties, while 5-(3-pyridyl)-1,3,4-oxadiazole-2-thiol has been found to be both leprostatic and tuberculostatic. In recent times, 2,5-disubstituted-l,3,4-oxadiazoles have been found to exhibit insecticidal properties. Research on transition metal complexes of 1,3,4-oxadiazoles has been actively pursued [11–14]. Although some of these complexes exhibit biological activity, there have been no previous reports on mixed ligand complexes of oxadiazole and tertiary phosphines. As part of our interests in sulfur containing ligands [15-27], we herein report synthesis mixed ligand complexes of palladium(II) with 5-(*p*-tolyl)-1,3,4-oxadiazole-2-thiol (MoxSH) phosphine, and characterization by different spectroscopic techniques. Furthermore, evaluate the anti-bacterial activity of the prepared complexes against *Escherichia coli*, *Staphylococcus aureus* and *Bacillus subtilis* bacteria species.

EXPERIMENTAL

Materials and instruments

All reactions were carried out in the air using standard bench reagents. All chemical materials were purchased from commercial sources and used as received. CHN Organic Elemental Analyzer 2400 was utilized for carbon, hydrogen, and nitrogen elemental analyses. Molar conductance value of the prepared complexes was measured (digital conductivity meter offered by Coronation) using DMSO (10^{-3} M) as a solvent at room temperature. On a JEOL resonance model JNM-ECZ400S/L1 spectrometer operating at 400 MHz, NMR experiments were carried out using DMSO-d^6 as a solvent and TMS as an internal reference. The FT-IR spectra were recorded as KBr pellets on a Shimadzu FT-IR 8400 spectrophotometer in the range 400–4000 cm^{-1}. The melting point of the compounds was measured by using the Gallankhamp melting point apparatus, which was uncorrected.

*Synthesis of [Pd(Bzoxe)$_2$] (**1**)*

A solution of the 5-(*p*-tolyl)-1,3,4-oxadiazole-2-thiol (0.653 g, 3.400 mmol) in ethanol (10 mL) containing some drops of Et_3N was added to an aqueous solution of Na_2PdCl_4 (0.500 g, 1.700 mmol) (10 mL), directly, a yellow to brown ppt. was formed. The mixture was stirred at room temperature, then filtered off, washed with distilled water, and under vacuum. The product was recrystallized with DMSO to give a brown powder (yield: 92%, m.p. = 221 - 223 °C).

*Synthesis of the complexes (**2-6**)*

The complexes (**2-6**) were produced by the general method, which included the reaction of complexes (**1**) (0.050 g, 0.100 mmol) in CH_2Cl_2 (10 mL) with the diphosphine ligand (0.050 mmol) in CH_2Cl_2 (10 mL). The reaction mixture was stirred for 3 h. The formed solution was left a side for slow evaporate at room temperature, the solid product was collected and recrystallized form DMSO. The physical properties of the prepared complexes are listed in Table 1.

*Synthesis of the complexes (**7** and **8**)*

The complexes (**7** and **8**) were produced by the general method, which included the reaction of complexes (**1**) (0.050 g, 0.100 mmol) in CH_2Cl_2 (10 mL) with the two moles of mono-phosphine {PPh_3 or $SPPh_3$} ligand (0.100 mmol) in CH_2Cl_2 (10 mL). The reaction mixture was stirred for 3 h. The formed solution was left a side for slow evaporate at room temperature, the solid product was collected and recrystallized form DMSO. The physical properties of the prepared complexes are listed in Table 1.

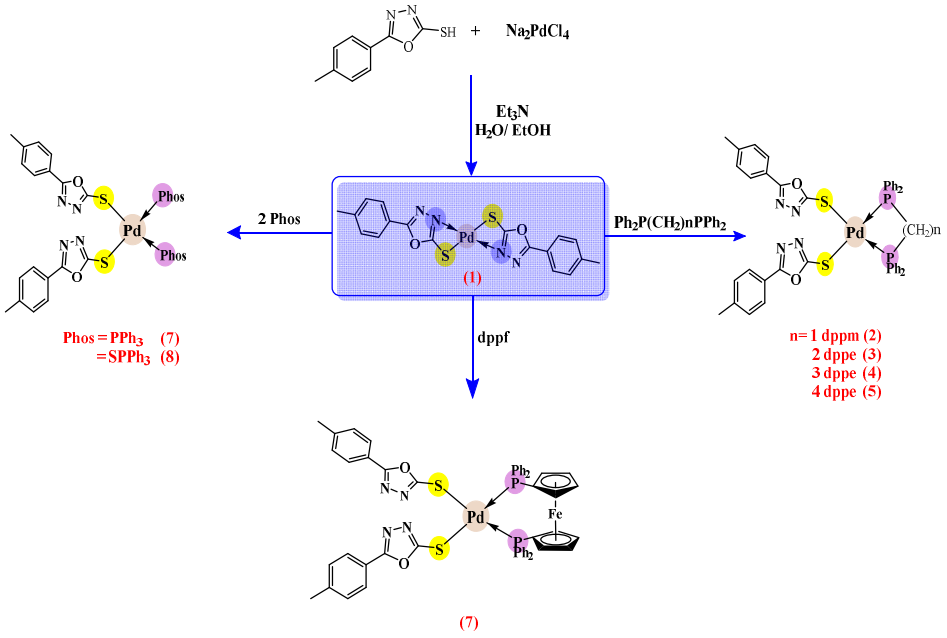
Antibacterial activities

The antimicrobial effect of the free ligand and their prepared palladium complexes was screened in vitro for restraining the growth of some pathogens using the agar well diffusion method employing Mueller Hinton agar [28]. The antibacterial potential was screened against *Escherichia coli*, *Staphylococcus aureus* and *Bacillus subtilis*. Bacterial culture was inserted into nutrient broth agar and then incubated for 24 hours at 37 °C. The melting of a soft agar tube was carried out, and then, after cooling it to 47 °C, bacterial culture (10 µL) was added, and a tube was gently shaken. The culture was then transferred to the nutrient agar plate and solidified. Holes were made in the agar plate with the help of a borer. The test samples were injected into the holes. The free ligand and its complexes were incubated for 24 hours at 37 °C. Zones of inhibition were measured in millimeters in each case and compared with streptomycin as a standard agent.

RESULTS AND DISCUSSION

Chemistry

The mixed ligand complexes of the palladium(II) complexes were prepared from the reaction of equivalent molar of $Ph_2P(CH_2)_nPPh_2$ {n = 1 dppm; n = 2 dppe ; n = 3 dppp ; n = 4 dppb ; $(CH_2)_n$ = $(Cp)_2Fe$ dppf} or two equivalent molar of triphenyl phosphine (PPh_3) or triphenyl phosphine sulfide ($SPPh_3$) with the starting complex $[Pd(MoxS)_2]$ (**1**) to give complexes of the type $[Pd(MoxS)_2(Ph_2P(CH_2)_nPPh_2)]$ (**2-6**), $[Pd(MoxS)_2(PPh_3)_2]$ (**7**) and $[Pd(MoxS)_2(SPPh_3)_2]$ (**8**) (Scheme 1).



Scheme 1. Synthesis of the complexes (**1-8**).

The palladium(II) complexes were characterized by CHN analysis, molar conductivity measurements, infrared and nuclear magnetic resonance (^{1}H and ^{31}P NMR) spectroscopy. These Pd(II) complexes were isolated in good yields as orange solids and were soluble in CH_2Cl_2, $CHCl_3$, DMSO and DMF. The elemental analysis data were found to be in good agreement with the proposed molecular formula. The molar conductivity measurements in DMSO at 10^{-3} M shown that the prepared complexes are non-electrolytes [29] and the results are recorded in Table 1-3.

Table 1. CHN analysis, color, m.p. (°C), yield (%) and molar conductivity.

Seq.	Compounds	Color	m.p. (c°)	Yield %	Λ*	CHN analysis % calc. (found)		
						C	H	N
1	[Pd(Moxs)$_2$]	Dark yellow	221-223	92	19.5	44.22 (44.32)	2.89 (2.72)	11.46 (11.59)
2	[Pd(Moxs)$_2$(dppm)]	Brown	148-150	85	24.6	59.14 (59.33)	4.16 (4.30)	6.42 (6.55)
3	[Pd(Moxs)$_2$(dppe)]	Brown	150-152	81	32.0	59.56 (59.78)	4.32 (4.47)	6.31 (6.40)
4	[Pd(Moxs)$_2$(dppp)]	Light yellow	146-148	94	22.0	59.97 (60.11)	4.47 (4.56)	6.22 (6.31)
5	[Pd(Moxs)$_2$(dppb)]	Light yellow	233-235	84	19.67	60.36 (60.20)	4.63 (4.79)	6.12 (6.20)
6	[Pd(Moxs)$_2$(dppf)]	Dark red	196-198	91	7.62	59.87 (59.93)	4.06 (4.13)	5.37 (5.48)
7	[Pd(Moxs)$_2$(PPh$_3$)$_2$]	Yellow	272-274	92	2.78	64.00 (64.12)	4.38 (4.52)	5.53 (5.66)
8	[Pd(Moxs)$_2$(SPPh$_3$)$_2$]	Brown	196-198	89	13.51	60.19 (60.27)	4.12 (4.09)	5.20 (5.29)
*The molar conductivity recorded by (ohm^{-1}.cm^2.mol^{-1}) unit in 10^{-3} M of DMSO solution								

Spectroscopic data

Selected IR spectroscopic bands of the free ligand and their palladium(II) complexes are listed in Table 2. The IR spectrum of complex **1** clearly showed the disappearance of the thiol group (which showed at 2566 cm^{-1} in free ligand), which proves that the S-H proton has been deprotonated and the frequency of the C=N group was shifted to a lower frequency (which appeared at 1603 cm^{-1}) compared with free ligand (which showed at 1627 cm^{-1} in free ligand) indicating that the MoxS ligand attaches to the central metal ion in a bidentate chelate, but we do not rule out the binuclear bridging mode through both of its SN donor atoms [18-20].

The spectra of the complexes (**2-8**) showed two strong and distinguished bands that were not present in the [Pd(MoxS)$_2$] complex within the range (530-509) cm^{-1} and (1437–1435) cm^{-1}, which were attributed to the stretching frequency of the phosphine group υ(P-C) and υ(P-Ph) respectively. Further, the IR spectra of the complexes (**2-8**) showed a strong band within the (1628-1618) cm^{-1} range, which was attributed to the stretching frequency of the ν(C=N) group, and it appeared at the same position or slightly shifted position compared with the free ligand, which suggests the (C=N) are not participating in coordination with the palladium ion [18-20]. Further the IR spectra showed the ν(C-H) stretching of the aliphatic and aromatic groups within the range (2920-2947) cm^{-1} and (3084-3034) cm^{-1}, respectively. Additionally, two new bands close to (520-439) cm^{-1} and (413-487) cm^{-1} can be assigned to ν(Pd–P) and ν(Pd−S), respectively [30, 31]. Other IR bands are listed in Table 2.

Table 2. Selected IR bands of the free ligand and their palladium(II) complexes.

Assigned band	Compounds								
	MoxSH	**1**	**2**	**3**	**4**	**5**	**6**	**7**	**8**
υ(=C-H)	3084	3034	3049	3053	3051	3051	3053	3076	3053
υ(C-H)	2947	2922	2920	2924	2921	2920	2920	2940	2930
υ(C=N)	1627	1603	1618	1626	1628	1626	1626	1620	1624
δ(P-C)	--	--	1437	1435	1435	1435	1435	1435	1435
υ(N-N)	1352	1323	1346	1336	1333	1357	1333	1359	1338
υ(P-C)	---	--	1101	1103	1101	1099	1097	1095	1101
υ(C-O-C)	1070	1072	1070	1070	1070	1070	1070	1066	1070
υ(C-S)	--	694	692	690	696	696	696	696	690
ρ(P-C)	--	--	503	530	511	513	515	515	514
υ(Pd- P)	--	482	439	520	505	498	493	478	502
υ(Pd- S)	435	456	471	462	481	470	439	413	438

The ^{31}P NMR chemical shifts of the prepared complexes (**2-8**) are listed in Table 3. In the ^{31}P NMR spectra of the complexes (Figure 1), a singlet was observed for phosphine ligands. There is a downfield shift in the ^{31}P resonance of the complexes because an electron pair is donated from the phosphorus to the metal. This makes the phosphorus nucleus less shielded. The singlet peak indicates a single isomer was formed for each complex.

The ^{1}H NMR spectrum of complex **1** (Figure 1) presented three separated peaks, which demonstrate three different proton groups in the MoxS ligand structure, a singlet peak at δ 2.37 ppm due to the protons of the CH_3 group, whereas the protons of the phenyl rings displayed as two doublet peaks at δ 7.34 ppm and δ 7.79 ppm.

The result above, was supported by ^{13}C-NMR spectrum of the complex is in good agreement with the suggested structure, since [Pd(MoxS)$_2$] has six different carbon atoms (Figure 3). The significant peaks in the ^{13}C NMR spectrum are the carbon of the C=S group at δ165.13 ppm and the methyl group at δ 21.57 ppm. Other chemical shifts are listed in Table 3.

In complexes (**2**–**8**), the ^{1}H NMR spectra displayed the protons of the methyl groups at δ 2.36-2.38 ppm. Also the spectra displayed the chemical shifts of the aliphatic protons of the backbone of the diphosphine ligands at δ 4.86 (*t*, 2H) for the complex (**2**), and δ 2.41 (*s*, 4H) for the complex (**3**), and δ 1.85 (*bs*, 2H); 2.89 (*bs*, 4H) for the complex (**4**) and δ 1.77 (*m*, 4H); 2.82 (*bs*, 4H) for the complex (**5**). The spectrum of the [Pd(MoxS)$_2$(dppf)] (**6**) displayed the protons of the cyclopentadiene rings as two singlet peaks at δ 4.37 (*s*, 4H); 5.57 (*s*, 4H) and the integration value indicates that signal corresponds to four protons for each peaks. In addition, the aromatic protons of MoxS$^-$ and phosphine ligands displayed in the up-field shifted region, within (7.18-7.93) ppm range. Other chemical shifts are listed in Table 3.

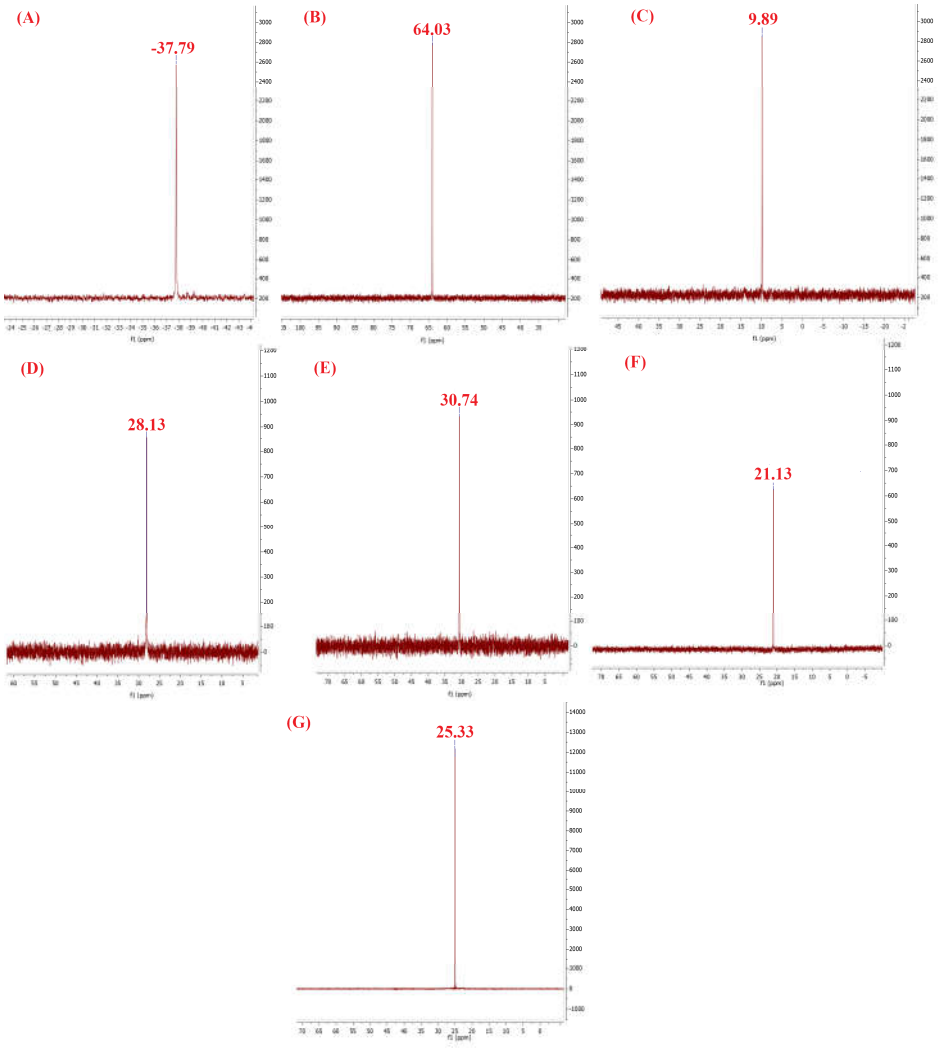


Figure 1. ^{31}P NMR spectra of the prepared complexes (A) [Pd(MoxS)$_2$(dppm)]; (B) [Pd(MoxS)$_2$(dppe)]; (C) [Pd(MoxS)$_2$(dppp)]; (D) [Pd(MoxS)$_2$(dppb)]; (E) [Pd(MoxS)$_2$(dppf)]; (F) [Pd(MoxS)$_2$(PPh$_3$)$_2$] and (G) [Pd(MoxS)$_2$(SPPh$_3$)$_2$].

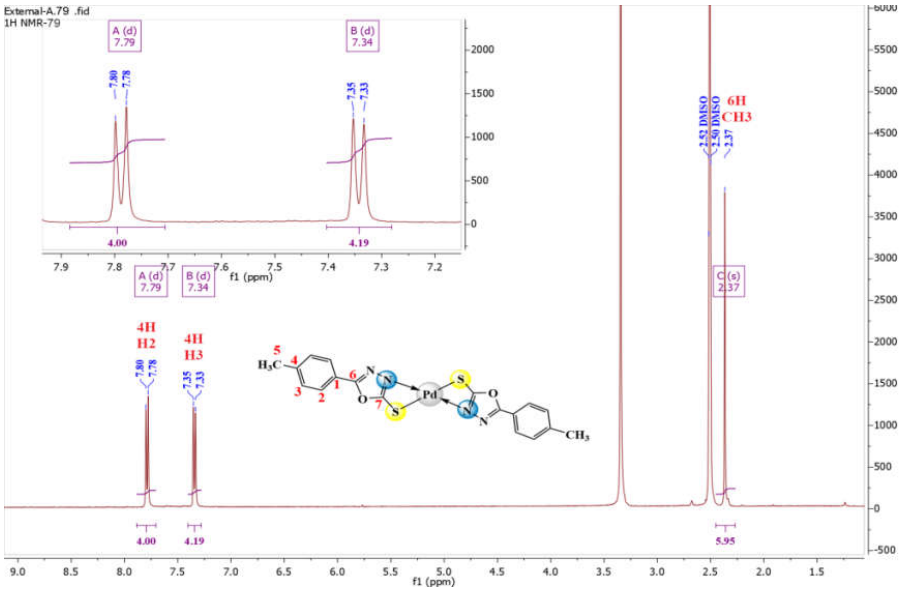


Figure 2. ^{1}H NMR spectrum of the complex [Pd(MoxS)$_2$] (**1**).

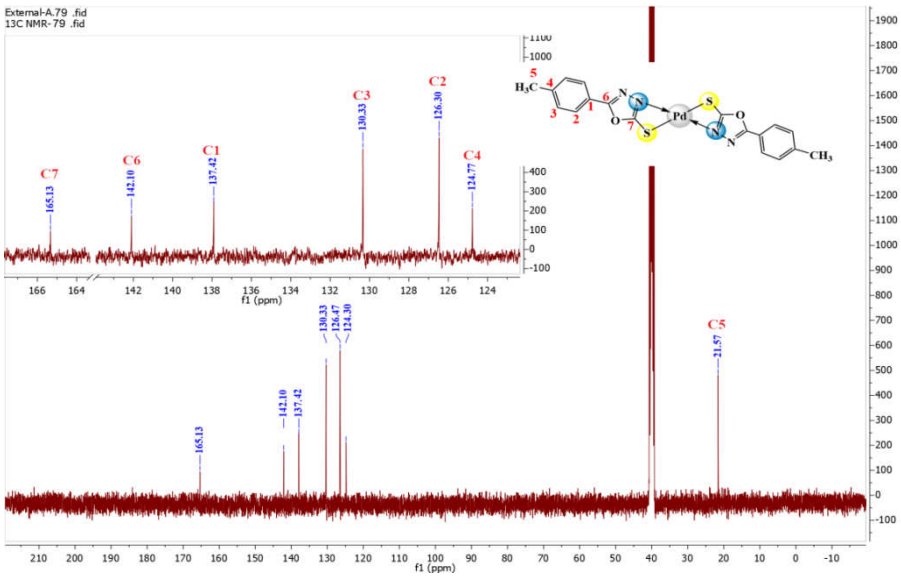


Figure 3. ^{13}C NMR spectrum of the complex [Pd(MoxS)$_2$] (**1**).

Table 3. NMR data of the free ligand and their palladium(II) complexes.

Seq.	Chemical shift (δ ppm)
1	^{1}H NMR: δ 2.37(*s*, 6H, CH_3); 7.34 (*d*, *J* = 8.00 Hz, 4H, H-phenyl); 7.79 (*d*, *J* = 8.00 Hz, 2H, H-phenyl). ^{13}C NMR: δ 165.13 (**C**7); 142.10 (**C**6); 137.42 (**C**1); 130.33(**C**3); 126.30 (**C**2); 124.77 (**C**4); 21.57 (**C**H_3).
2	^{31}P NMR: δ 37.79 (s) ^{1}H NMR: δ 2.37 (*s*, 6H, CH_3); 4.86 (*t*, J_{P-H} = 24.00 Hz, 2H, CH_2-dppm); 7.87-7.24 (*m*, 28H, H-phenyl rings).
3	^{31}P NMR: δ 64.03 (s). ^{1}H NMR: δ 2.38 (*s*, 6H, CH_3); 2.41 (*s*, 4H, CH_2-dppe); 7.23 (*d*, *J* = 8.00 Hz, 4H, H-phenyl); 7.93-7.35 (*m*, 28H, H-phenyl rings).
4	^{31}P NMR: δ9.86(s). ^{1}H NMR: δ 1.85 (*bs*, 2H, CH_2-dppp); 2.38(*s*, 6H, CH_3); 2.89 (*bs*, 4H, P-CH_2-dppp); 7.87-7.29 (*m*, 28H, H-phenyl rings).
5	^{31}P NMR: δ 28.13 (s). ^{1}H NMR: δ 1.77 (*m*, 4H, CH_2-dppb); 2.38(*s*, 6H, CH_3); 2.82 (*bs*, 4H, P-CH_2-dppb); 7.86-7.29(*m*, 28H, H-phenyl rings).
6	^{31}P NMR: δ 30.74 (s). ^{1}H NMR: δ 2.37 (*s*, 6H, CH_3); 4.37(*s*, 4H, Cp); 5.57(*s*, 4H, Cp); 7.90-7.18 (*m*, 28H, H-phenyl rings).
7	^{31}P NMR: δ 21.13 (s). ^{1}H NMR: δ 2.36 (*s*, 6H, CH_3); 7.83-7.20 (*m*, 38H, H-phenyl rings).
8	^{31}P NMR: δ 25.33 (s). ^{1}H NMR: δ 2.39 (*s*, 6H, CH_3); 7.73-7.37 (*m*, 38H, H-phenyl rings).

Anti-bacterial activity study

The focus on developing novel antimicrobial agents has intensified due to the remarkable rise in multidrug-resistant pathogens and the growing incidence of emerging infections. Therefore, it is imperative to differentiate novel compounds that exhibit activity against these drug-resistant pathogens. We wanted to know what the compounds we made meant biologically, so we tested the unbound ligand and its synthesized complexes against three harmful bacteria (*Escherichia coli*, *Staphylococcus aureus* and *Bacillus subtilis*) in a lab setting using the diffusion method at a concentration of 10^{-3} M.

The obtained results were compared to streptomycin, a positive antibiotic drug, and DMSO, a negative control [17]. The diameter of the inhibition zone for the compounds that prevented visible growth is given in Table 4. It was determined that the solvent did not exhibit any antibacterial activity against any of the pathogenic bacteria. Streptomycin was employed as the standard reference medication, and it was subjected to identical conditions in order to facilitate comparison. As predictable, all of the test mixed ligand of the Pd(II) complexes with oxadizole-thione and phosphine ligands had good level of activity against the pathogenic bacteria.

The inhibition zone diameter (DIZ) was between 13 and 26 mm. This level of activity is similar to that of previously documented palladium(II) complexes [18, 19, 25].

Notably, [Pd(MoxS)$_2$(dppf)] (**6**) displays good activity (18, 22 and 20 mm) against certain tested microbes *Escherichia coli, Staphylococcus aureus* and *Bacillus subtilis,* respectively (Table 4) which is found to be superior to other analogues compounds. The complex (**6**) showed the highest activity against all pathogenic bacteria species can be discuses to the presence of contains ferrocene unit in structure and this part is significant interest in different biological area such as anticancer, antibacterial, antifungal and antiparasitic drug candidates

The data in Table 4 can be abbreviated as following:

The order of the activity against the *Escherichia coli* bacteria is:

Streptomycin > **6** > **8** > **3** > **2** > **5** > **4** > **7** > **1** > **MoxSH**

Whereas the activity order against the *Staphylococcus aureus* is:

Streptomycin > **6** > **8** > **5** > **4** > **2** > **3** > **1** > **7** > **MoxSH**

And the activity order against *Bacillus subtilis* is:

Streptomycin > **6** > **8** > **4** > **3** > **2** > **7** > **5** > **1** > **MoxSH**

Table 4. Diameter inhibition zone of the prepared compounds against the pathogenic bacteria at 10^{-3} M.

Seq.	Diameter inhibition zone (mm)		
	Escherichia coli	*Staphylococcus aureus*	*Bacillus subtilis*
MoxSH	9	8	9
1	11	14	14
7	12	14	15
4	13	17	19
2	14	16	16
5	14	18	14
3	15	15	17
6	18	22	20
8	18	20	19
Streptomycin	23	24	23

There are two theories that can explain this increased activity of complexes: (1) the overtone concept [32], which considers that the compound solubility in the cell membrane has an important role in antibacterial activity because it allows for the passage of only soluble materials in lipids, and (2) Tweedy's chelation theory [33], which explains that the polarity of a metal ion is highly reduced because of the ligand orbital overlap and the positive charge division of the central metallic ion with the donor atoms of the ligand.

CONCLUSION

The present work describes the synthesis of a series of mixed ligand palladium(II) complexes including the mono-anion thione ligand and phosphine ligand, which was synthesized by reacting one mole of $[Pd(MoxS)_2]$ complex with one mole of diphosphine ligands (dppm, dppe, dppp, dppb, and dppf) or two mole of mono-phosphine ligands (Ph_3P or Ph_3PS) to afford complexes of the type $[Pd(MoxS)_2(diphosphine)]$ (**2-6**), $[Pd(MoxS)_2(PPh_3)_2]$ (**7**) and $[Pd(MoxS)_2(SPPh_3)_2]$ (**8**). The complexes have been fully characterized by the CHN analysis, and NMR (^1H, ^{13}C and ^{31}P) and IR techniques. The spectroscopic results showed that the thione ligand coordinate in the monodentate fashion through S atom with Pd(II) ion in the complexes (**2-8**). The biological activity study against the *Escherichia coli*, *Staphylococcus aureus*, and *Bacillus subtilis* was carried out and indicated that $[Pd(MoxS)_2(dppf)]$ (**6**) displays good activity (18, 22 and 20 mm) against certain tested microbes *Escherichia coli, Staphylococcus aureus* and *Bacillus subtilis*, respectively.

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