

Synthesis and Characterization of a New Azo Ligand Derivative from 4,5-BIS(4-Methoxyphenyl) Imidazol and its Metal Complexes and Biological Activity Study of its PD(II) Complex

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ABSTRACT

In the current work, the azo ligand and its Pd (II), Cd (II), Zn (II) and Hg (II) complexes were synthesized, characterized and their spectroscopic characteristics were studied. The new ligand was synthesized from the coupling reaction between 4,5-bis(4-methoxy phenyl)imidazole and the diazonium salt of 4-Amino benzoic acid in an alkaline medium at 0-5 °C. the new azo metal complexes were prepared by the reaction between the ligand and metals chlorides. All the synthesized compounds were characterized by FT-IR, ¹H-NMR, Mass spectral analysis, UV-Vis spectrophotometric, molar conductivity, and magnetic sensitivity. The biological activity of the azo ligand and its Pd (II) complex was also studied.

keywords: Azo compound, 4,5-di (4-methoxy phenyl) imidazole, azo metal complexes

INTRODUCTION

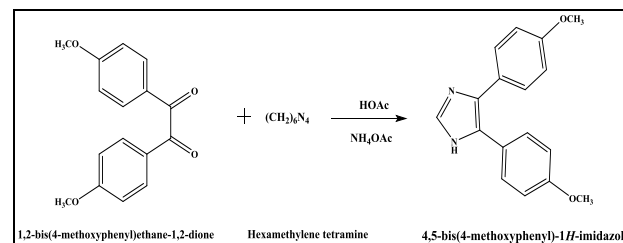
Azo compounds are a substantial group of organic chemical compounds that include one or more azo chromophore which is responsible for the color of these dyes [1]. These compounds are important in both academic and applied research [2]. Azo compounds have a wide range of applications in the pharmaceutical, food, textile industry, cosmetic and analytical chemistry filed, due to their particular physical and chemical characteristics and biological activities. The antifungal, antibacterial, and anti-HIV properties of azo compounds are widely recognized in medicine [3, 4]. Azo dyes are important analytical reagents for the estimation of trace concentrations of metal ions [5]. Aromatic azo compounds, in particular, are employed as acid-base indicators, as commercial colorants for polymers and textiles and in biological strains [6]. Recently, they have also been used as corrosion inhibitors [7,8].

Azo-transition metal complexes are attracting increasing attention in both fundamental and applied researches, due to their distinctive geometric and electronic characteristics [9, 10]. Azo-transition metal complexes are distinguished by the ability to obtain novel compounds with a wide range of biological activity, in addition to their low cost [11]. This type of complexes is critical for the development of metal-based anticancer drugs [12, 13]. These different fields of interest have prompted inorganic chemists to develop new methods for the preparation of anticancer drugs not covalently linked [14, 15]. In the presented paper, a new azo compound with its four complexes with Pd (II), Cd (II), Zn (II) and Hg (II) has been synthesized and characterized, in addition to studying the biological activity of the new azo and its complex with palladium (II) ion.

Chemicals and Instrumentation: All chemicals used were purchased from Merck, Fluka, BDH and Sigma - Aldrich and all were of analytical grade except for 4,5-bis(4-methoxy phenyl)imidazole, which was prepared as mentioned earlier [16]. The uncorrected melting points were measured using Stuart-SMP10 melting point apparatus. FT-IR spectra were studied by employing Shimadzu FT-IR 8400 spectrophotometer as KBr pellets. ¹H-NMR spectra were recorded by using Bruker Biospin Gmph (500 MHz) spectrophotometer in DMSO-d₆ as a solvent, employing TMS as internal standard. Mass spectrum was performed using Shimadzu Agilent HP (5973). UV- Vis spectra were obtained by using Shimadzu (UV-1700) spectrophotometer. Magnetic susceptibility was measured by Sherwood Scientific balance magnetic susceptibility, molar conductivity measurements were done by using digital conductivity series ion. lab. 720 in DMSO solvent.

Experimental preparation of 4,5-bis (4-methoxyphenyl) imidazole: This compound was prepared as mentioned earlier [16]. In 100 mL

round-bottom flask, (2.70 g, 0.01 mol) of benzyl derivative (4,4-dimethoxy benzyl), (0.28g, 0.002 mol) of hexamethylene tetramine and (6.0g, 0.077 mol) of ammonium acetate were mixed. After mixing with (150 mL) of acetic acid, the solution was escalated for (90) minutes. After cooling, the product is poured into an ice bath. Ammonium hydroxide solution was added to neutralize the acidic function. The precipitate was then filtered and washed with distilled water several times to get rid of undesirable impurities. The organic compound is recrystallized from ethanol to obtain a semi-white crystalline precipitate. The measured melting temperature was (75-74) °C and the product ratio stood at 80%. Scheme. 1 shows the preparation of the imidazol derivative.

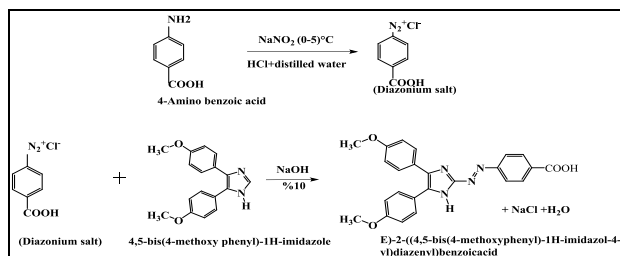


Scheme. 1: Preparation of the imidazol derivative

Preparation of (E)-2-(4,5-bis(4-methoxyphenyl)-1H-imidazol-4-yl) diazenyl benzoic acid : The new azo-imidazole compound was prepared by dissolving (0.428g, 0.001mol) of the aromatic amine 4-Amino benzoic acid in a mixture of 3 mL of concentrated hydrochloric acid and 20 mL of distilled water. Cool the mixture to (0 – 5) °C and add (0.70 g, 0.01 mol) of dissolved sodium nitrite in 10 mL of distilled water drop by drop with constant stirring and note that the temperature does not rise above (0-5) °C. Leave the solution to settle for 30 minutes to complete the nitrogenous process. This diazonium salt solution was then mixed with 5,4-di (4-methoxyphenyl) imidazole solution (2.80 g, 0.01 mol) dissolved in a mixture of 150 mL methyl alcohol and 5 mL of sodium hydroxide solution (10%). The coloration of the solution is observed in dark orange color, the solution left until the next day to complete the coupling reaction. Add drops of 0.1N HCl to the solution to make the acidic function reach (7) to precipitate the crystals. Leave to settle, filter and wash many times with distilled water to get rid of inorganic salts. Dried in the air and recrystallized from the ethanol, dried, and its melting point was then measured. The preparation of the azo ligand is shown in Scheme. 2.

Biological Activity Study: The antimicrobial activity of azo ligand and its Pd (II) complex was examined against (Staphylococcus aureus and Enterococcus faecalis) as gram-positive bacteria and (Escherchia coli and Klebsiela pneumonia) as gram-negative

bacteria using agar well diffusion method.



Scheme. 2: Preparation of the azo ligand

solid complexes were prepared by mixing (10 mmol) of the ligand in 25 mL of hot absolute ethanol and (10 mmol) of metal chloride in 25 mL of distilled water. The mixtures then were left over night until the precipitation was formed then filtered, dried in air and recrystallized from absolute ethanol. Table 1 illustrates some of analytical and physical properties of the ligand and its complexes

The test bacteria were swabbed on the solidified agar medium then 6 mm diameter wells were made in the agar plates and each well was filled with 0.1 mL of the ligand and its complex at five different concentrations of (25, 50, 100, 200 and 400 $\mu\text{g mL}^{-1}$), then incubated at (37 °C) for one day. The biological activity was recorded by measuring the diameter of the inhibition zone in the mm unit.

Preparation of the Metal Complexes (general method): The

Table 1: Analytical and Physical properties of the ligand and its metal complexes

Compound	Color	m. p °C	Yield %	M. f (M. wt)	Found (Calc.)%			
					C	H	N	M
Ligand L (C ₂₄ N ₄ O ₄ H ₂₀)	Red	105-107	92%	428	67.289 67.275	4.678 4.677	13.084 13.080	-----
[Zn(C ₂₄ N ₄ O ₄ H ₂₀) ₂ Cl ₂].H ₂ O	Violet	115-117	89%	1010.409	57.006 57.004	3.958 3.955	11.084 11.081	6.473 6.470
[Cd(C ₂₄ N ₄ O ₄ H ₂₀) ₂ Cl ₂].H ₂ O	Violet	170-173	80%	1057.4	54.473 54.472	3.782 3.781	10.592 10.591	10.629 10.627
[Hg(C ₂₄ N ₄ O ₄ H ₂₀) ₂ Cl ₂].H ₂ O	Violet	182-185	90%	1145.59	50.279 50.275	3.491 3.490	9.776 9.774	-----
[Pd(C ₂₄ N ₄ O ₄ H ₂₀)Cl ₂].H ₂ O	Violet	-----	77	623.45	46.194 46.193	3.207 3.205	8.982 8.980	17.074 17.073

Characterization of Azo Ligand and Its Metal Complexes: New ten compounds were synthesized from several starting materials like (4-Amino benzoic acid, azo compound) via several various procedures to produce compounds like (imidazole derivatives). The synthesized compounds have been characterized by their melting points and spectroscopic techniques (FT-IR, ¹H-NMR, C.H.N analysis) and other physical properties [17, 18].

Infrared Spectra of Azo Ligand and its Metal Complexes: The FT- IR spectrum showed clear absorption bands at the IR spectrum. The free azo dye exhibited bands at 1460 and 1463 cm^{-1} due to the azo group of the imidazole. The bands at 1604-1697 cm^{-1} appeared almost at the same position in the spectra of all complexes suggesting that the N-atom of these groups is not

participated [19]. The infrared spectra of the complexes showed a weak band to medium intensity and at frequencies (3417-3400 cm^{-1}), which are due to the asymmetric and asymmetric vibrations of the N-H [20]. In the metal complexes, the aromatic C-H stretching bands were observed at 2837 cm^{-1} , however, there were not seen in the spectrum of the ligand, its appearing in the spectra of the complexes indicated that the ligand was coordinated with the metals ions through the azo groupe. The weak band was (M-N) vibrations were seen at (418 – 538) cm^{-1} [21]. The spectral data of the ligand and its complexes are shown in Table 2. The FT-IR spectrum of the ligand was showed in Figure 1 and its complexes were showed in Figure 2.

Table 2: Selected IR absorption bands (4000-400) cm^{-1} for azo ligand and its metal complexes (KBr disc)

Compound	ν (N-H) _{im} . + ν (H ₂ O)	ν (C-H) _{ar} .	ν (C-H) _{al} .	ν (C=N) _{im} .	ν (N=N)	ν (M-N)
(C ₂₄ N ₄ O ₄ H ₂₀)	3417 b	3417 w.	2837 w.	1697 m.	1460 w.	-----
[Zn(C ₂₄ N ₄ O ₄ H ₂₀) ₂ Cl ₂].H ₂ O	3452 b	3452 w.	2837 w.	1695 m.	1462 w.	462 w.
[Cd(C ₂₄ N ₄ O ₄ H ₂₀) ₂ Cl ₂].H ₂ O	3479 b	3005 w.	2837 w.	1689 m.	1463 w.	538 w.
[Hg(C ₂₄ N ₄ O ₄ H ₂₀) ₂ Cl ₂].H ₂ O	3479 b	2966 w.	2837 w.	1693 m.	1462 w.	505 w.
[Pd(C ₂₄ N ₄ O ₄ H ₂₀)Cl ₂].H ₂ O	3400 b	3134 w.	2837 w.	1604 m.	1461 w.	418 w.

m.= medium, w.= weak, b.= broad, im.= imidazole, ar.= aromatic, al.= aliphatic

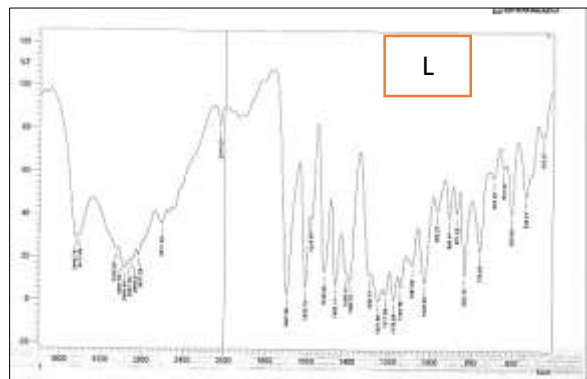


Figure 1: The FT- IR spectrum of the ligand

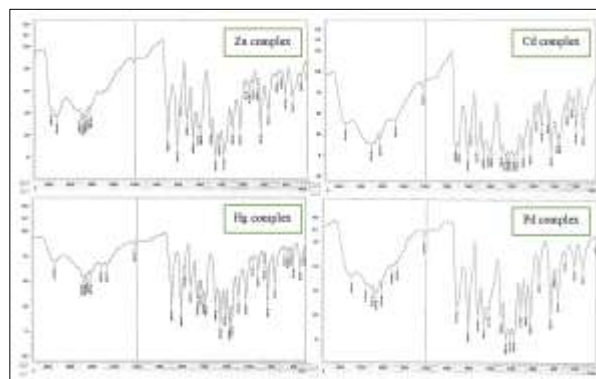


Figure 2: FT-IR Spectrum of the metal – ligand complexes

Electronic Spectra of Azo Ligand and its Metal Complexes:

The electronic spectra of the azo dye ligand and its metal complexes were studied at room temperature using absolute ethanol (10^{-3} M) as a solvent. This data is given in Table 3. The free ligand shows two bands in UV-Visible region. The first band at 309 nm (22172cm^{-1}) due to $\pi \rightarrow \pi^*$ transition of the azo group ($-\text{N}=\text{N}-$), this band observed a red shift because of coordinated between the metal ion and the nitrogen atom of azo group. The second band located at 426 nm (23154cm^{-1}) corresponds to the $n \rightarrow \pi^*$ transition [22]. For the Pd (II) azo dye complex, the electronic spectral data exhibit one band at 543 nm (18382cm^{-1}) due to ($^1\text{A}_{1g} \rightarrow ^1\text{B}_{1g}$) transition. The intensity of the band suggest a

square planer geometry with dsp^2 hybridization [23]. The electronic spectra of Zn (II), Cd (II) and Hg (II) complexes were studied in absolute ethanol (10^{-3}M) did not show any (d→d) transitions because of this complexes is diamagnetic (having a d^{10} system), the absorption bands at 309 nm (32362cm^{-1}), 284 nm (35211cm^{-1}) and 515 nm (19417cm^{-1}) could be attributed to the presence of a charge transfer (MLCT [$d\pi(\text{M}^{2+} \rightarrow \pi^*(\text{L}))$]) transition complexes respectively [24]. Figure 3 shows the UV-Vis spectra of the ligand and Figure 4 shows the UV-Vis spectra the Zn(II), Pd (II) complex. Figure 5 illustrate the suggested structures for the Zn (II), Cd (II), Hg (II)-ligand complexes and Pd (II)-complex.

Table 3: the data of Electronic spectra, electronic transition, magnetic moments (μ_{eff}), proposed hybridization and geometry of the ligand and its metal complexes

Compound	Absorption band (nm)	Absorption band (cm^{-1})	Transition	μ_{eff} (B.M)	Hybridization	Geometry
($\text{C}_{24}\text{N}_4\text{O}_4\text{H}_{20}$)	451 310	22172 32154	$n \rightarrow \pi^*$ $\pi \rightarrow \pi^*$	-----	-----	-----
[Zn($\text{C}_{24}\text{N}_4\text{O}_4\text{H}_{20}$) $_2$ Cl $_2$].H $_2$ O	309 261	32362 38314	MLCT	Dia.	SP^3d^2	Octahedral
[Cd($\text{C}_{24}\text{N}_4\text{O}_4\text{H}_{20}$) $_2$ Cl $_2$].H $_2$ O	284	35211	MLCT	Dia.	SP^3d^2	Octahedral
[Hg($\text{C}_{24}\text{N}_4\text{O}_4\text{H}_{20}$) $_2$ Cl $_2$].H $_2$ O	515	19417	MLCT	Dia.	SP^3d^2	Octahedral
[Pd($\text{C}_{24}\text{N}_4\text{O}_4\text{H}_{20}$) Cl $_2$].H $_2$ O	543	18382	$^1\text{A}_{1g} \rightarrow ^1\text{B}_{1g}$	Dia.	dsp^2	Square planer

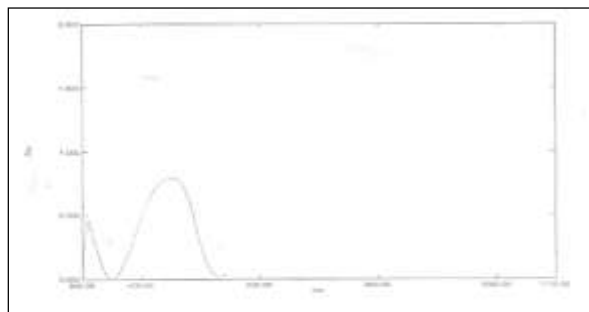


Figure 3: UV-Vis spectra of the ligand L

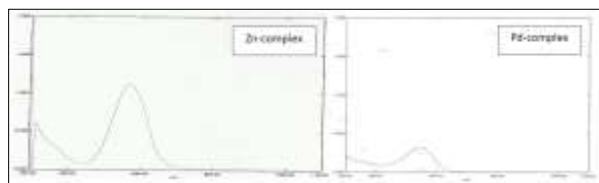


Figure 4: UV-Vis spectra of Zn(II), Pd (II) complexes with the ligand

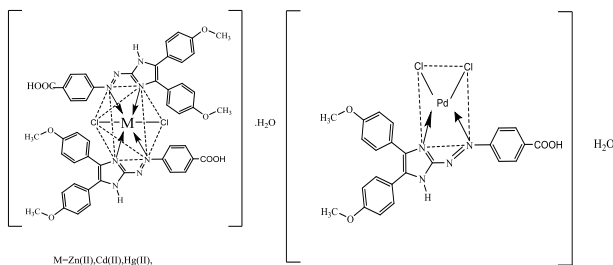


Figure 5: The suggested structures for ligand complexes

$^1\text{H-NMR}$ Spectra of Azo Ligand: The $^1\text{H-NMR}$ spectrum of the azo ligand has cleared all the signals within their expected and indicated ranges as shown in Figure 6. The multiple signals at the chemical shift $\delta=8.0736\text{-}6.9168$ ppm were attributed to the group of the aromatic ring protons [22], whereas, a bilateral signal that appeared at the chemical shift $\delta=3.770$ ppm was attributed to the protons of the methoxy group belonging to the imidazole derivative [18]. The spectrum also showed a mono signal at the chemical shift $\delta=2.530$ ppm due to the solvent protons DMSO- d_6 .

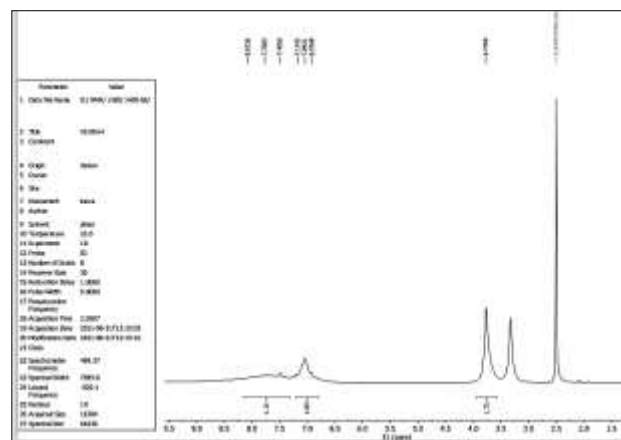


Figure 6: $^1\text{H-NMR}$ spectrum of imidazolylazo dye ligand

Mass Spectra of Azo Ligand: To confirm the validity of the preparation process for imidazole derivative and the azo dye derived from it, the mass spectrometry of this ligand was recorded. As shown in Figure 7, there is a group of mass fractionation peaks that differed in their molecular weights and their relative abundance, the most important of which is the peak fractionation at ($m/z^+ = 428.4$) which is returned to the azo ligand molecule. The peak fractionation at (304.73) return to the molecular ion ($\text{C}_{17}\text{H}_{13}\text{N}_4\text{O}_2$) $^+$. This molecule was accompanied by the appearance of other peaks at ($m/z^+ = 278.35$) due to the molecular ion [$\text{C}_{18}\text{H}_{18}\text{N}_2\text{O}$] $^+$ and other peaks at ($m/z^+ = 281.25$) for the molecular ion [$\text{C}_{17}\text{H}_{17}\text{N}_2\text{O}_2$] $^+$, while the other peaks appear at ($m/z^+ = 159.3$, $m/z^+ = 172.7$ and $m/z^+ = 123.67$). It was attributed to the other partial ions [$\text{C}_9\text{H}_7\text{N}_2\text{O}$] $^+$, [$\text{C}_9\text{H}_8\text{N}_4$] $^+$, [$\text{C}_7\text{H}_7\text{O}_2$] $^+$. Scheme. 3 illustrate the mass spectrum fragmentation of the azo ligand.

Biological Activity Study: The biological activity of the synthesized ligand and its Pd (II) complex was studied against *Staphylococcus aureus* (*S. aureus*) and *Enterococcus faecalis* (*E. faecalis*) as gram-positive bacteria and *Escherichia coli* (*E. coli*) and *Klebsiella pneumoniae* (*K. pneumoniae*) as gram-negative bacteria using agar well diffusion method. The results showed in Table 4 that the azo ligand exhibited a high inhibition zone against *E. faecalis* and a moderate inhibition zone against *E. coli* bacteria. Whereas has no inhibition activity against any type of bacteria at the concentration of $25\text{ }\mu\text{g mL}^{-1}$. While its Pd (II) complex showed higher inhibition activity against *E. coli* bacteria than *E. faecalis* bacteria and moderate inhibition activity against *K. pneumoniae*.

There is no inhibition activity against any type of bacteria at the concentration of 25 $\mu\text{g mL}^{-1}$.

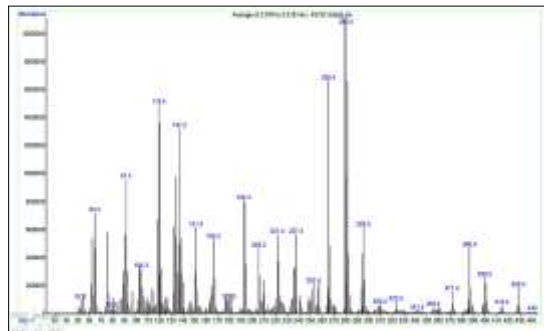
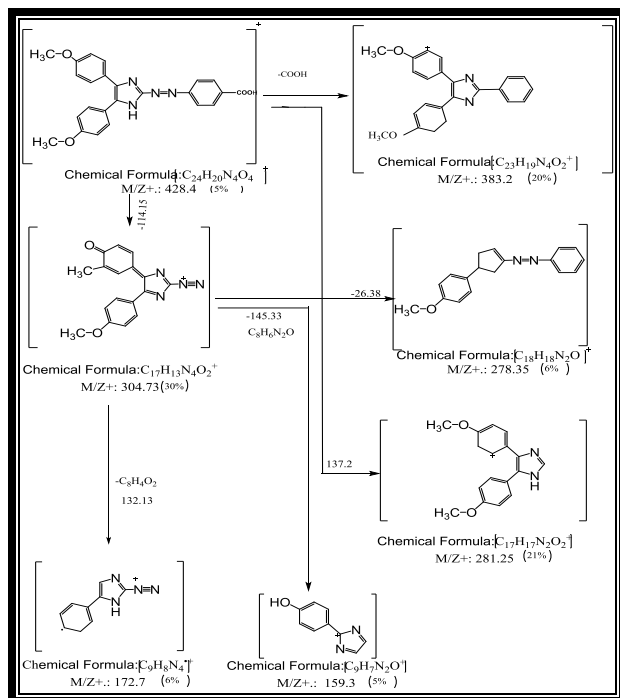


Figure 7: Mass spectrum of azo dye ligand



Scheme. 3: Mass spectrum fragmentation of the azo ligand

Table 4: biological activity of the ligand and its Pd (II) complex against pathogenic microorganism

Compound	Concentration $\mu\text{g mL}^{-1}$	gram positive bacteria		gram negative bacteria	
		S. aureus	E. faecalis	E. coli	K. pneumoniae
L ligand	25	-	-	-	-
	50	11	11	10	-
	100	13	15	13	14
	200	15	17	16	15
	400	16	19	17	16
Pd (II) complex	25	-	-	-	-
	50	-	11	11	11
	100	13	13	14	13
	200	15	15	17	14
	400	16	18	19	17

CONCLUSION

In this paper, a new azo ligand and its metal complexes were prepared and have been characterized by spectral and analytical data. Depending on all the obtained results, the suggested

geometrical shape for all complexes was octahedral shape except for Pd (II) complex which has a square planar shape. The biological activity study reveals that the ligand and its Pd (II) complex exhibit antimicrobial properties.

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