

Synthesis, Characterization and Antimicrobial Activity of Complexes Metal Ions Ni(II), Zn(II), Pd(II) and Pt(IV) with Polydentate 1,2,4-Triazole Ligand

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Abstract: A new ligand of 1,2,4-triazole derivative was produced by cyclization of sodium dithiocarbamate derivative of ethyl 4-ethoxy-3-nitrobenzoate with carbon disulfide in an alkaline medium. The new ligand, entitled name: L: 4-amino-5-(3-ethoxy-5-nitrophenyl)-2,4-dihydro-3H-1,2,4-triazole-3-thione, was fully characterized depending on HPLC-MS, FTIR, ¹H-NMR and ¹³C-NMR spectroscopies. In addition, the elemental microanalysis was carried out to confirm the skeletal structure of the ligand L. A library of complexes with Ni(II), Zn(II), Pd(II), and Pt(IV) metal ions was prepared by coordination with the ligand. These complexes were characterized by using FTIR, UV-Vis, ¹H-NMR, ¹³C-NMR, spectrophotometric techniques, elemental analysis C.H.N.S, and FAAS. The physicochemical properties of these complexes were determined at 25 °C, such as melting point, magnetic susceptibility and molar conductivity. The microbial study confirmed that the novel ligand and its complexes have the potential to be applied as antimicrobial agents.

Keywords: 1,2,4-triazole ligands; platinum(IV); palladium(II) complexes of triazole; microbial activity

■ INTRODUCTION

1,2,4-Triazole moiety and their derivatives have attracted great attention in the last decade due to their unique properties [1]. The triazole ring is easily formed and many of these functionalized compounds are readily accessible; thus they are talented rich and flexible coordination chemistry. Triazole rings contain π -conjugated systems with easy coordination abilities to metal ions, and they have the ability to exhibit phosphorescence properties. They own nitrogen atoms as hydrogen bond acceptors and aromatic systems, which correspond to π - π stacking [2]. The 1,2,4-triazole moiety contains three atoms of nitrogen in a five-membered aromatic ring, each two atoms are adjacent for stability, increasing the solubility in water. It is able to get two isomers of tautomerism, 1H-isomer 1 and 4H-isomer 2 (Fig. 1). The preferred and more stable structure is the 1H-tautomer was confirmed by both DFT and empirical study. The carbon atom is connected to both nitrogen

atoms in 1,2,4-triazole and thus, the ring of triazole has a deficit in electrons. It was illustrated that the electrophilic reaction with the triazole ring is deactivated. In the parent, the compound is not responsive to the nitration or other common carbon reactions of aromatic chemistry. Though electrophilic attacks on the nitrogen atom are widely mentioned in literature [3-5].

The literature study demonstrated that 1,2,4-triazole derivatives exhibited a wide variety of bioactivities, including antimicrobial, anticancer, anti-inflammatory, analgesic, antiviral, antidepressant, insecticide and plant growth regulator bacteria [6-9]. 1,2,4-Triazole derivatives,

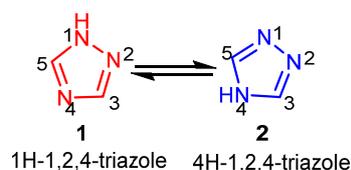


Fig 1. Tautomerism of (1H- and 4H-) 1,2,4-triazoles

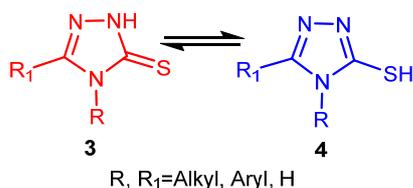


Fig 2. Thione-thiol tautomeric forms

including the -SH group, are one of the subclasses of 1,2,4-triazoles and are considered one of the most interesting compounds due to their biological activity [9-10]. It was found that the main component of mercapto-1,2,4-triazole is in most natural products and pharmaceuticals (Fig. 2).

The presence of active sites in triazole derivatives has intensively enhanced the researchers to synthesize metal complexes with such types of ligands [11-13]. Kanagarajan et al. [13-14] have studied two biologically active Schiff base ligands derived from 1,2,4-triazole in equimolar reaction of 4-amino-5-(pyridin-4-yl)4*H*-1,2,4-triazole-3-thiol with thiophene-2-carbaldehyde and furan-2-carbaldehyde. Furthermore, Co(II), Ni(II) and Cu(II) metal complexes were isolated in their solid state and spectroscopically identified. The anti-proliferative reactivity against many cancer cells have described for Pt(II), Pd(II), Ni(II), Co(II), and Sn(IV) chelates derived from 4,5-diphenyl-1,2,4-triazole-3-thione as a primary ligand and 1,2-bis(diphenylphosphanyl) ethane as a secondary ligand. The results explained that Pt(II) complex had an important antitumor activity with IC₅₀ values 0.4–0.8 μM. The 1,2,4-triazoles have been explored for linking ligands among transition metal ions.

In recent years, there is much attention to preparing coordination ligands using 1,2,4-triazole moiety particular, those consisting of S and N in their construction due to their biological activities compared with native ligands [15-16]. A few complexes, including 1,2,4-triazole moiety with two sites for coordination with metal ions, including S and N atoms have been reported. In the current work, we designed and synthesized new derivatives for the triazole ligand as a bi dentate ligand as well as its complexes with transition metals ions such as Ni(II), Zn(II), Pd(II) and Pt(IV). The novel prepared complexes were characterized by diverse spectroscopic

methods to find out the potential of these new metal complexes as antimicrobials.

■ EXPERIMENTAL SECTION

Materials

All starting materials and solvents were obtained from commercial companies and used without further purification. Metal chlorides, NiCl₂·6H₂O, ZnCl₂, K₂PtCl₆ and PdCl₂, were supplied from Sigma Aldrich. Hydrazine hydrate, carbon disulfide, absolute ethanol and dimethyl sulfoxide (DMSO) were supplied from Fluka Company with 99% purity.

Instrumentation

A Stuart melting point (digital) SMP30 apparatus was used to record the Melting point. FTIR spectra were measured by a Shimadzu (FTIR) model 4800 s Spectrophotometer between the ranges (4000–400) cm⁻¹ as KBr discs. UV-Vis 16 ultraviolet Spectrophotometer model Shimadzu is used to measure the UV-visible spectra at R.T.°C using 1 cm quartz cell and examined between 200–1100 nm at 10⁻³ M in DMSO. The atomic absorption (A.A.) technique has been measured using a Shimadzu AA680G atomic absorption spectrophotometer at the laboratories of Ibn-Sinaa Company. Elemental analysis is used to determine (C, H, N) for the new ligand [L] and its complexes by Linear Regression Euro EA elemental analysis. Mass spectra were performed for a ligand on GC-MS (DIRECT PROBE) via the ES technique. The ¹H- and ¹³C-NMR spectrum of ligand was recorded at a Bruker DMX-500 spectrophotometers (400 MHz) by using DMSO-*d*₆. Measurement of Conductivity was carried out at room temperature in DMSO using an Inolab multi 740, WTW 82362-Germany. Magnetic susceptibility of novel synthesized complexes was recorded at room temperature by Auto magnetic susceptibility Balance in Al-Mustansiriyah University, College of Science, Chemistry Department.

Procedure

Synthesis of benzamide derivative, A1

Hydrazine hydrate (5 mL, 1 mmol) was added to

the solution of ethyl 4-ethoxy-3-nitrobenzoate (135 mg, 5 mmol) in 15 mL of absolute ethanol. The mixture was refluxed for 10 h, and the TLC was used to monitor the reaction. After that, the mixture reaction was allowed to cool down to room temperature. A final product was isolated by filtered and then washed the ice cold water three times, dried and recrystallized using hot ethanol to obtain compound A1 (Fig. 3); m.p. 124–126 °C; Color white crystal; Yield 95%; FTIR ν (cm⁻¹): 3320 (NH₂, asym.), 3185 (NH₂, sym.), 1670 (C=O, amide); R_f = 0.37 (chloroform:ethyl acetate; 3:2), ¹H-NMR (400 MHz, DMSO-*d*₆), 8.05 (d, 1H, 10-NH), 7.96 (s, 1H, 1-CH), 7.78 (d, 1H, 6-CH), 7.22 (d, 1H, 7-CH), 4.45 (d, 2H, 10-NH), 4.25 (m, 2H, 4-CH), 2.09 (t, 3H, 5-CH₃), ¹³C-NMR (100 MHz, DMSO), 188.4 (9-C=O), 140.09 (3-C), 137.7 (2-C), 133.6 (7-C), 132.3 (8-C), 130.9 (1-C), 127 (6-C), 58.8 (4-C), 30.8 (5-C).

Synthesis of sodium 2-(4-ethoxy-3-nitrobenzoyl)hydrazine-1-carbodithioate (A2)

Compound A1 (2.50 g, 11 mmol) was added to the solution of sodium hydroxide (1.50 g, 20 mmol) in methanol 20 mL at 0 °C with stirring, then carbon

disulfide (5 mL, 13 mmol) was added as a drop-wise and the reaction mixture was stirred for 18 h at room temperature. The reaction was allowed to cool down, and then adding 100 mL of diethyl ether with stirring for 20 min. The solid precipitate was isolated and then washed with the cold methanol to produce compound A2 (Fig. 4). Color yellow powder; m.p. (170–172) °C; Yield 95%; FTIR ν (cm⁻¹): 3400 (N-H), 3178 (N-H), 1656 (C=O), 1270 (C=S); m/z 300.

Synthesis of 4-amino-5-(3-ethoxy-5-nitrophenyl)-2,4-dihydro-3H-1,2,4-triazole-3-thione (L)

Compound A2 (323 mg, 11 mmol) was mixed with the excess amount of hydrazine hydrate (about 20 mL) and refluxed for 8 h. A color change from black-green to light yellow was observed; due to liberating hydrogen sulfide gas and changing the color of lead acetate paper from black to white, TLC is used to monitor the reaction. The final solution was poured into ice-cold water of about 25 mL and acidified with conc. HCl (pH = 3–5). The solid precipitate was isolated, washed by adding cold water, and then dried by vacuum, purified by recrystallized with ethanol to give compound L (Fig. 5).

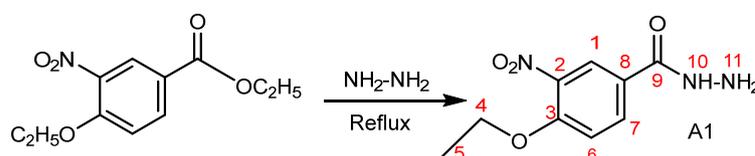


Fig 3. Synthesis of ligand A1

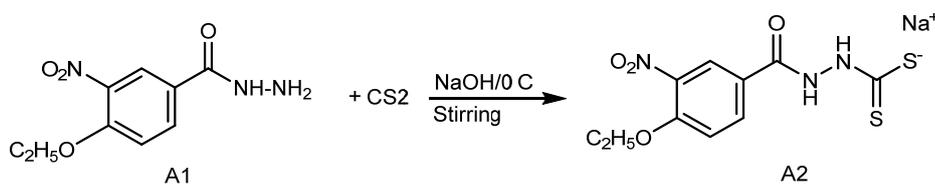


Fig 4. Synthesis of dithiocarbamate salt derivative A2

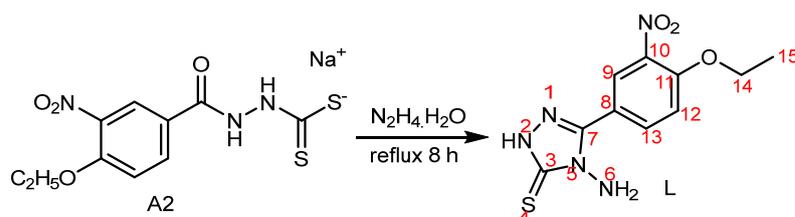


Fig 5. Cyclization reaction to synthesis 4-amino-5-(3-ethoxy-5-nitrophenyl)-2,4-dihydro-3H-1,2,4-triazole-3-thione (L)

Pale yellow solid; Yield 70 %; m.p. 188–190 °C, FTIR ν (cm⁻¹): 3290 (NH₂, asym), 3300 (NH₂, sym.), 3190 (N-H), 1280 (C=S) and 1620 (N-NH₂); R_f = 0.32 (*n*-hexane: methanol; 3:1). ¹H-NMR (400 MHz, DMSO-*d*₆), 8.59 (d, 1H, 2-NH_{triazol}), 7.86 (d, 1H, 13-CH), 7.71 (d, 1H, 12-CH), 7.36 (s, 1H, 9-CH), 5.69 (s, 2H, NH₂-N_{triazol}), 4.25 (m, 2H, 14-CH₂), 2.08 (t, 3H, 15-CH), ¹³C-NMR (100 MHz, DMSO-*d*₆), 176.4 (3-C), 154.1 (11-C), 145.7 (7-C), 132.12 (10-C), 130.6 (13-C), 129.4 (9-C), 127.01 (4-C), 125 (12-C), 79.6 (14-C), 31.8 (15-C); *m/z* 282.

Metals complexes synthesis

To a solution of the metal salts in ethanol, where the salts of (NiCl₂·2H₂O, ZnCl₂, PdCl₂ and PtCl₄) were added to (562 mg, 2.00 mmol) of the ligand L. Mixed solution was reflux using a water bath as long as 3 h. The product was isolated and washed with ethanol, then dried at room temperature. The color, melting point, yield, metal analysis and solubility of the ligand and its complexes are given in Table 1.

RESULTS AND DISCUSSION

¹H-NMR Characterization

The identification of the intermediates, the free 1,2,4-triazole ligand and some selected metal complexes

were carried out with ¹H- and ¹³C-NMR spectra, and the results are summarized in Table 2.

¹H-NMR spectrum for ligand A1

The NMR spectrum of A1 exhibited three signals in the aromatic region between (8.05–7.2) ppm corresponding to the aromatic ring. The new signal was observed at 9.01 ppm corresponding to NH adjacent to the C=O group, which confirmed the formation of a compound with title A1. Also, the NMR spectrum shows a doublet signal with two integrals at 4.45 ppm corresponding to the NH₂ group.

¹H-NMR spectra for ligand L

Compound L was characterized by NMR and mass spectroscopy in addition to IR and UV-Vis spectrometry. The ¹H-NMR spectrum shows the characteristic of a singlet at 8.59 ppm due to the -NH of triazole ring; but no signal was shown in the NMR spectrum for A1 or A2 compound. Thus, giving further evidence to the formation of ligand L. Another signal around 3.5 ppm attributed to the NH₂ group closer to the N-triazole ring confirmed the formation of this ligand. Also, multiples signal at (1.19 ppm) attributed to the ethyl group (Fig. S1 and S2). The spectrum of ¹³C-NMR showed peaks at 174, 154 and 145 ppm corresponding –C=S thione moiety

Table 1. Physical properties and elemental analyses of the prepared compounds

Compound	Color	m.p (°C)	M.wt (g/mol)	Elemental analysis %			M% Obs. (cal.)	M:L	Chemical formula
				Found (cal.)					
				C	H	N			
A1	White	124–126	225	47.70 (48.0)	3.85 (4.88)	17.94 (18.7)			C ₉ H ₁₁ N ₃ O ₄
A2	Yellow	170–172	300	36.11 (40.0)	3.00 (3.33)	12.26 (14.0)			C ₁₀ H ₁₀ N ₃ O ₄ S ₂ Na
L	Pale yellow	188–190	281	41.90 (42.7)	3.08 (3.91)	24.60 (24.9)			C ₁₀ H ₁₁ N ₅ O ₃ S
Ni-L	Dark brown	280–282	692	33.88 (34.7)	3.07 (3.18)	18.64 (20.24)	7.66 (8.48)	1:2	[Ni(C ₁₀ H ₁₁ N ₅ O ₃ S) ₂]Cl ₂
Zn-L	Yellow	278d*	769	30.40 (28.7)	3.04 (2.60)	17.20 (16.7)	16.70 (15.5)	1:1	[Zn(C ₁₀ H ₁₁ N ₅ O ₃ S)Cl ₂]
Pd-L	Pale orange	290d*	739	35.10 (32.4)	3.10 (2.97)	19.72 (18.93)	13.74 (14.4)	1:2	[Pd(C ₁₀ H ₁₁ N ₅ O ₃ S) ₂]Cl ₂
Pt-L	Dark yellow	315d*	900	27.76 (26.7)	2.19 (2.44)	15.30 (15.55)	4.55 (5.17)	1:2	[Pt(C ₁₀ H ₁₁ N ₅ O ₃ S) ₂]Cl ₂

d*: dissociation, obs.: observed

Table 2. ^1H -NMR data of compounds and ^{13}C -NMR of ligand L in $\text{DMSO-}d_6$

Compound	^1H -NMR	^{13}C
A1	8.05-7.2 ppm aromatic ring; 9.01 ppm NH adjacent to the C=O group; a doublet signal 4.45 ppm (NH_2 group)	
L	a singlet at 8.59 ppm -NH of triazole ring; 3.5 ppm NH_2 group closer to the N-triazole ring; multiples signal at (1.19 ppm) ethyl group	174, 154 and 145 ppm -C=S thione moiety; -C=N- of triazole ring (124–120) ppm of aromatic carbon atoms; 39 and 59 ppm (CH_3 , CH_2)
Ni-L	6.22 ppm NH protons	
Zn-L	6.23 ppm NH proton close to triazole ring	
Pd-L	6.28 ppm NH proton close to triazole ring	
Pt-L	6.28 ppm NH proton close to triazole ring	

and -C=N- of triazole ring, at 124–120 ppm of aromatic carbon atoms, and 39 and 59 ppm from methyl and methylene groups, respectively.

^1H -NMR of complexes

A comparison between ^1H -NMR spectra of complexes and with the corresponding ligand clearly indicated the coordination of ligands to metals. The ^1H -NMR spectrum of Ni(II) complexes in $\text{DMSO-}d_6$ showed the chemical shift of amino protons at 6.22 ppm. Whereas these signals appear at 6.23 ppm in Zn(II) complex and 6.28 ppm in both Pd(II), Pt(IV) complex, respectively. These chemical shifts indicate the amino protons close to the triazole ring in the metal complexes are located in different chemical environments and confirm the contribution of the NH_2 group with metal ions. Also, the ^1H -NMR spectrum of these complexes showed a small shift to the downfield in the aromatic regions, which refers to the coordination of ligands to metals. The ^1H -NMR spectrum of complexes illustrated that the peak at 2.8 ppm corresponding to methyl group also appeared in the spectrum of complexes without any change (Fig. S3).

Mass Spectra (MS)

The mass spectral of Ni(II) complexes exhibited main molecular ions plus H_2O bands at m/z 700 [$\text{M}+\text{H}_2\text{O}$] with other bands at 551, 530, 445, and 288 which correspond to the fragmentation of complexes as shown in Fig. 6.

The mass spectra of the Pd(II) complex displayed a mother peak at 739 [M] m/z , which indicated the molecular ion of the Pd(II) complex with many other

peaks at 513, 397, 355, and 288 corresponding to the fractions of Pd(II) complex. While the mass spectral of Pt(IV) complex showed a main peak at 930 [$\text{M}+2\text{H}_2\text{O}$] m/z attributed to a molecular weight of Pt(IV) complex and two molecules of H_2O , a variety of fractions at 712, 515, and 353 m/z correspond to another component of Pt(IV) complex. The mass spectrum of the ligand exhibited the main peak at 281 m/z , which agreed with elemental analyses and confirmed the formation of the ligand (Fig. S4).

FT-IR Spectrum for Ligand and Its Complexes

The main bands of the FTIR spectrum of the ligand and its complexes are presented in Table 3. The free ligand shows strong bands at 1280 and 1620 cm^{-1} assigning to the vibrations of thioamide -C=S and -C=N- of the triazole ring (Fig. S5). The chelation of Ni(II), Zn(II), Pd(II) and Pt(IV) ions to the active sites -C=S and - NH_2 groups have been observed from the lowering in their absorptions to the regions of 3100–3250 and 1250–1275 cm^{-1} . As well as the weak to medium bands at around 520–422 and 389–320 cm^{-1} are associated with the coordination bonds of M-N and M-S, respectively [17-19]. The Zn-L and Pt-L complexes exhibit weak bands at 250–290 cm^{-1} , revealing the presence of M-Cl moieties in the structure of complexes [20-21].

Electronic Spectra and Magnetic Susceptibility of Complexes

The UV-Vis absorption data of triazole ligand were carried out in absolute ethanol at room temp. This study

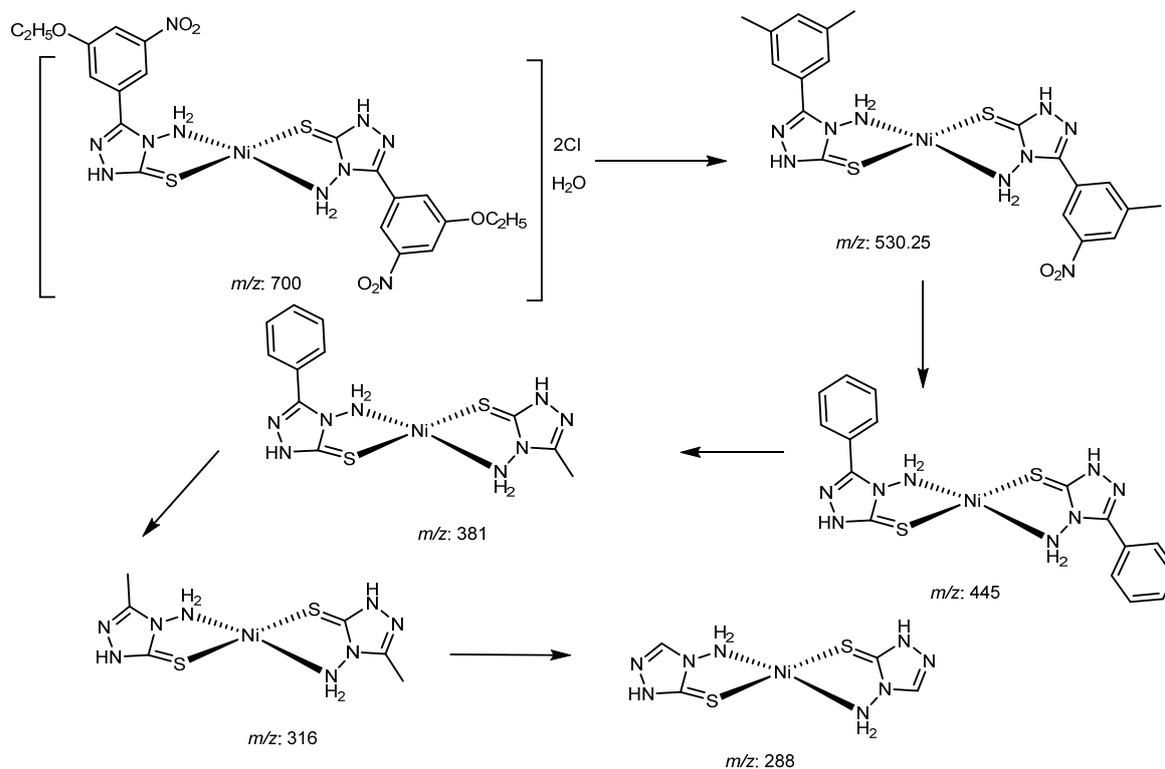


Fig 6. Fragmentation pattern of Ni(II) complexes

Table 3. IR spectrum of triazole ligand and its corresponding metal complexes

No.	Compound	$\nu\text{NH}_{2\text{asy}}, \text{NH}_{2\text{sym}}$	νNH	$\nu\text{C}=\text{S}$	$\nu\text{N}-\text{NH}_2$	M-N	M-S	M-Cl
1	L	3290, 3300	3190	1280	1620			
2	Ni-L	3200(br)	3150	1275	1610(s)	490(m)	389	-
3	Zn-L	3300	3200	1268	1590(s)	422(w)	350(w)	275, 290(w)
4	Pd-L	3400(br)	3120	1250	1566(sh)	520(m)	320(w)	-
5	Pt-L	3360(br)	3209	1269	1605(s)	488(m)	370(w)	250, 288(w)

exhibited three absorption bands, two bands at (210 nm, 47619 cm^{-1}) and (275 nm, 36080 cm^{-1}) were indicated to $\pi-\pi^*$ transition and observed at (380 nm, 26315 cm^{-1}), which is assigned to L-M C.T transition [19]. The solutions of NiL, PdL and PtL complexes in ethanol (10^{-3} M) displayed weak absorptions at (400–800) nm assigning to d-d spectra. The square planar complexes of Ni(II) and Pd(II) recorded weak bands at 450–380 and 350–310 nm, which are mainly attributed to $^1\text{A}_{1g}\rightarrow^1\text{B}_{1g}$ and $^1\text{A}_{1g}\rightarrow^1\text{E}_g$ transitions, respectively (Fig. S6). Furthermore, the diamagnetic properties of all complexes are in well-agreement of low-spin state of the Pd(II) complex having a d^8 configuration favors the formation of complexes with square planar geometry and d^6

configuration with a strong field of the triazole ligand [21].

Molar Conductance for Synthesized Complexes

The molar conductivity of complexes was recorded at 298 K temperature (0.001 M) in DMF solution. The finding suggested that the complexes with a 2:1 ratio are electrolytes due to the presence of two chloride ions in the outer sphere of the complexes structure except for Zn(II) complex, which showed a different manner as a neutral complex with the chemical formula ZnLCl_2 . The following Fig. 7 represents the octahedral geometry of the Pt(IV) complex, square-planar of Ni(II) and Pd(II) complexes, whereas the tetrahedral environment around Zn(II) ions was adopted.

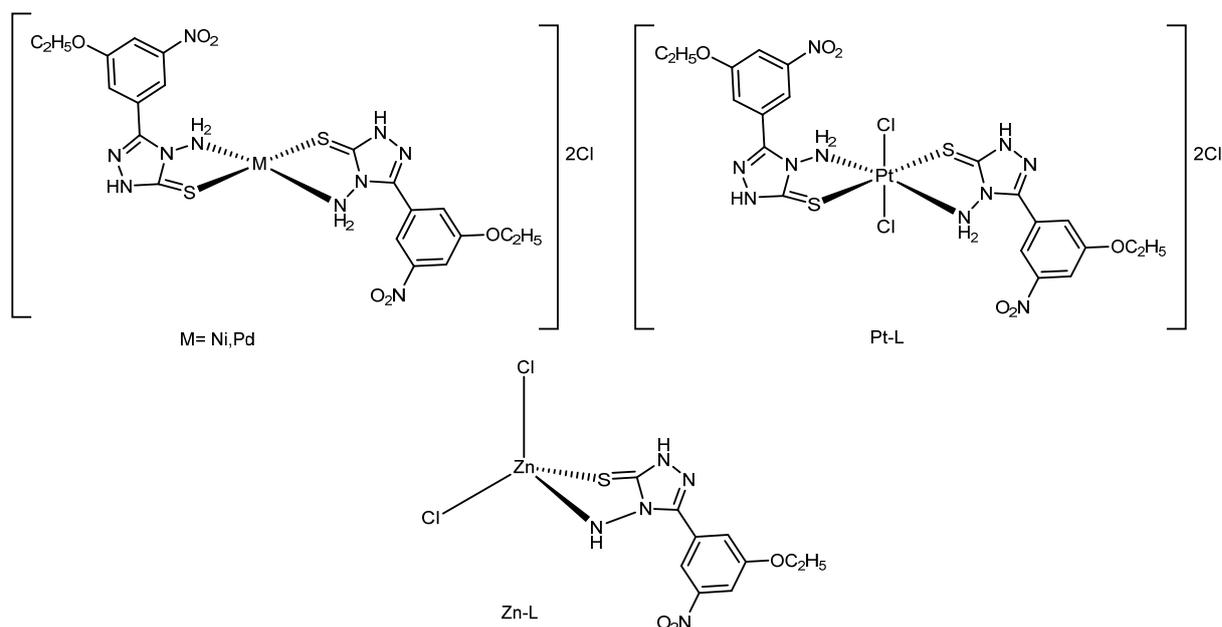


Fig 7. Suggested geometry of the prepared metal complexes

Antimicrobial Study

The inhibition zones (mm) of DMSO solutions of triazole ligand and metal complexes are shown in Table 4. The observed data revealed that Pd(II) and Pt(IV) complexes showed the highest activity against all microorganisms due to the high penetration of the lipoprotein of the bacteria and fungi [20-21]. As well as the free ligand solution in blank DMSO exhibits medium inhibition zones (10–17) mm toward *Staphylococcus aureus* and *Escherichia coli* bacteria, whereas no remarkable antifungal, which may be reasonable in high

polarity of the triazole structure [22]. Furthermore, the solutions of Ni(II) and Zn(II) displayed the lowest activity toward the *E. coli* and *S. aureus* bacteria compared with the control drug of azithromycin (10 ppm), which mainly resulted from the ionic character of chloride ions in the outer sphere of their chemical structures [10,21]. It is observed that the solutions of Pt(IV) and Pd(II) showed greater activity against *Candida albicans* and *Aspergillums favus* which are close to the activity of control Miconazole antifungal drug of 10 ppm concentration. These data on biological

Table 4. Biological activity of the ligand and its metal complexes

Compound		Zone of Inhibition in mm			
		<i>S. aureus</i>	<i>E. Coli</i>	<i>C. albicans</i>	<i>A. favus</i>
L	10 µg/mL	8	8	-	-
	20 µg/mL	10	12	-	-
[NiL ₂]Cl ₂	10 µg/mL	6	8	-	-
	20 µg/mL	8	12	-	-
[ZnCl ₂]	10 µg/mL	4	5	5	-
	20 µg/mL	6	8	7	-
[PdL ₂]Cl ₂	10 µg/mL	12	11	13	18
	20 µg/mL	17	18	17	20
Azithromycin	10 µg/mL	18	22	-	-
	20 µg/mL	25	30	-	-
Miconazole	10 µg/mL	-	-	17	23

activity would have encouraged us in the future to do a wide spectrum of *in vivo* studies for the new complexes.

■ CONCLUSION

In conclusion, the new derivative of 1,2,4-triazole ligand was synthesized, and fully characterized, and its complexes Ni(II), Zn(II), Pd(II) and Pt(IV) complexes were synthesized and characterization via different spectroscopic techniques. It was found that ligand coordinate with metals *via* S and N to form Ni(II) and Pd(II) complexes with square planer geometry and Pt(IV) complex show octahedral geometry while Zn(II) different exhibit shapes by forming tetrahedral geometry. This study suggested that the ligand and its complexes showed moderate activity against bacteria and had the potential as antimicrobial. The PdL and PtL complexes are in good agreement with the antimicrobial activity of expectations due to their *cis*-platinum structures compared with other Ni(II) and square planer NiL complexes. The inhibition zones (mm) of Pt(IV) and Pd(II) complexes in blank DMSO exhibited great antifungal against the two fungi studied, and they are so close to the Miconazole control drug.

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