NEW AZO-SCHIFF BASE DERIVED WITH Ni(II), Co(II), Cu(II), Pd(II) AND Pt(II) COMPLEXES: PREPARATION, SPECTROSCOPIC INVESTIGATION, STRUCTURAL STUDIES AND BIOLOGICAL ACTIVITY

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ABSTRACT

The coordination ability of the azo-Schiff base 2-[1,5-Dimethyl-3-[2-(5-methyl-1H-indol-3-yl)-ethyl imino]-2-phenyl-2,3-dihydro-1H-pyrazol-4-ylazo]-5-hydroxy-benzoic acid has been proven in complexation reactions with Co(II), Ni(II), Cu(II), Pd(II) and Pt(II) ions. The free ligand (LH) and its complexes were characterized using elemental analysis, determination of metal concentration, magnetic susceptibility, molar conductivity, FTIR, UV-Vis, (1H, 13C) NMR spectra, mass spectra and thermal analysis (TGA). The results confirmed the coordination of the ligand through the nitrogen of the azomethine, Azo group (Azo) and the carboxylate ion with the metal ions. The activation thermodynamic parameters, such as ΔE^* , ΔH^* , ΔS^* , ΔG^* and K are calculated from the TGA curves using Coats-Redfern method. Hyper Chem-8 program has been used to predict structural geometries of compounds in the gas phase. The synthesized ligands and their metal complexes were screened for their biological activity against bacterial species, two Gram positive bacteria (*Bacillus subtilis* and *Staphylococcus aureus*) and two Gram negative bacteria (*Escherichia coli* and *Pseudomonas aeruginosa*).

Keywords: Azo- Schiff base ligand, Kinetics, Thermodynamic parameters, Antibacterial activity, Spectroscopic investigation

1. INTRODUCTION

Schiff base derivatives attract significant interest and occupy an important role in the development of coordination chemistry. Moreover, Schiff base complexes containing transition metals have been studied in several research areas such as structural chemistry¹. Azo compounds with two phenyl rings separated by an azo bond are very important in fundamental research area and applications². In addition, azo-Schiff base derivatives are known to be important in several classes of medicinal and pharmaceutical fields. Furthermore, some of them show biological activities such as antibacterial, antifungal, anticancer and herbicidal activities³⁻¹². However, the light induced interconversion allows systems incorporating azo group to be used as reversible control over a variety of chemical, electronic and mechanical applications^{2, 13, 14}. Azo compounds metal complexes have also been attracting much attention because of their applications in dyes, pigment, functional materials and optical computing¹⁵. As part of our research in the study of coordinating capabilities of Azo-schiff base derivatives and their coordination compounds¹⁶, we report herein the synthesis and spectroscopic studies as well as the thermal investigation of a novel Azo-schiff base derivative Ligand (LH) (L= 2-[1,5-Dimethyl-3-[2-(5-methyl-1H-indol-3-yl)-ethyl imino]-2-phenyl-2,3-dihydro-1H-pyrazol-4-ylazo]-5-hydroxy-benzoic acid with some transition metals such as Ni^{II}, Co^{II}, Cu^{II}, Pd^{II} and Pt^{II} complexes. (1H, 13C) NMR spectra were obtained to determine the structure of the ligand.

2. EXPERIMENTAL

2.1. Materials and measurements

All reagents were commercially available and used without further purification. Solvents were distilled from appropriate drying agents immediately prior to use.

Elemental analyses (C, H and N) were carried out on a Heraeus instrument (Vario EL). Melting points were obtained on a Buchi SMP-20 capillary melting point apparatus. IR spectra were recorded as KBr discs using a Shimadzu 8300 FTIR spectrophotometer in the range (4000-400) cm⁻¹. Electronic spectra were measured in the region (200-1100) nm using 10⁻³ M solutions in DMF at 25°C with a Shimadzu 160 spectrophotometer. NMR spectra (1H-, 13C-NMR) were recorded in DMSO-d₆ solution using Bruker AMX400 MHz spectrometer with tetramethylsilane (TMS) as an internal standard for 1H NMR analysis. Metals were determined using a Shimadzu (A.A) 680 G atomic absorption spectrophotometer. Chloride was determined using a potentiometric titration method on a 686-Titro processor-665Dosimat-Metrohm Swiss. Conductivity measurements were made with DMF solutions using a Jenway 4071 digital conductivity meter at room temperature. Electron impact mass spectra (70 eV) were recorded on a Finnegan-MAT model 8430 GC MS-DS spectrometer.

Magnetic moments were obtained using a magnetic susceptibility balance (Johnson Matthey Catalytic System Division). Thermal analysis studies of the ligand and complexes were performed on a Perkin-Elmer Pyris Diamond DTA/TG Thermal System under nitrogen atmosphere with a heating rate of 10°C/min from 30-700°C.

2.2. Synthesis of the compound 1,5-dimethyl-3-[2-(5-methyl-1H-indol-3-yl)-ethylimino]-2-phenyl-2,3-dihydro-1H-pyrazol-4-ylamine (A)

An ethanolic solution (15 ml) of 5-methyltryptamine hydrochloride (1.036 g, 0.00492 mol) was added to a mixture containing an ethanolic solution (25 ml) of 4-amino-1,5-dimethyl-2-phenyl-3-pyrazol-5-one (1 g, 0.00492 mol). The reaction mixture was heated in a water bath at 40-50 °C for 14 h, in presence of K₂CO₃ after the addition of excess of ethanol (50 ml). The resulting mixture was refluxed under N₂. A white solid was formed, and then recrystallized from a water: ethanol (1:1) solvent mixture. The product was dried over anhydrous CaCl₂ under vacuum. Yield: 53.76 % (0.95 g); MP: 177 °C; 1H NMR (DMSO-d₆, ppm): δ 1.89 (s, =CCH₃), 2.10 (s, arom-CH₃), 3.43 (s, NCH₃), 3.30 (t, NCH₂), 2.74 (t, CCH₂), 7.64-8.08 (m, arom), 12.11 (s, NH), 4.10 (s, NH₂). 13C-NMR (100.622 MHz, DMSO-d₆): δ 16.39(C₂₀), 18.87(C₃), 38.79(C₁₃), 45.6(C₁₂), 58(C₁), 98(C₁₇), 100(C_{7,11,14}), 110(C₁₈), 111(C_{15,21}), 118(C₄), 123.77(C₉), 127(C₂₂), 129(C₁₉), 130(C_{8,10}), 140(C₆), 146(C₂), 151(C₅); MS, m/z 360, 164, 201.

2.3. Synthesis of the ligand (LH) 2-[1,5-Dimethyl-3-[2-(5-methyl-1H-indol-3-yl)-ethyl imino]-2-phenyl-2,3-dihydro-1H-pyrazol-4-ylazo]-5-hydroxy-benzoic acid

A solution of H₂SO₄ (18 M, 2 mL), ethanol (10 mL) and distilled water (10 mL), was used to dissolve (0.5 g, of (A) (1.39 mmol). An aqueous solution (2 mL) of NaNO₂ (0.0144 g, 1mmol) was added dropwise, while the temperature of the mixture was maintained between 0 and 5°C. After that, the diazonium chloride was added with constant stirring to a cold ethanolic solution of *m*-hydroxybenzoic acid (0.192 g, 1.39 mol), and then a solution of 1 M NaOH (25 mL) was added to the dark colored mixture. The mixture was stirred for 1 h at 0 °C and acidified with 1 mL of conc. HCl. The brown product formed was filtered off and recrystallized from an ethanol-water (1:1) solution and then dried. Yield: 62.2 % (0.44 g), mp 390°C as shown in Scheme 1.

1H NMR (DMSO-d₆, ppm): 1.89 (s, C-CH₃), 2.10 (s, arom-CH₃), 3.43 (s, NCH₃), 3.30 (t, NCH₂), 2.74 (t, CCH₂), 4.49 (s, O-H phenol), 7.00 (m, C_{8,10}-H), 7.23 (s, C₁₅-H), 7.36 (m, C_{7,11}-H), 7.44 (m, C_{9,18,21}-H), 7.85 (d, C₂₄-H), 7.90 (m, C₁₇-H), 8.08 (d, C₁₇-H), 12.11 (d, N-H), 13 (s, O-H carboxylic). 13C-NMR (100.622 MHz, DMSO-d₆) δ 16.39(C₂₀), 18.87(C₃), 38.79(C₁₃), 45.6(C₁₂), 58(C₁), 98(C₁₇), 100(C_{7,11,14}), 106(C₂₅), 110(C₁₈), 111(C₂₃), 111(C_{15,21}), 118(C₄), 123.77(C₉), 127(C₂₄), 128(C₂₆), 129(C₁₉), 130(C_{8,10}), 140(C₆), 144(C₂₇), 146(C₂₂), 146(C₁), 151(C₅), 152(C₂₆), 182(C₂₈), (MS) m/z 508 (C₂₉H₂₈N₆O₃), 345 (C₁₈H₁₅N₅O₃)²⁺, 159 (C₁₁H₁₃N).

Scheme 1. Synthesis of 2-[1, 5-dimethyl-3-[2-(5-methyl-1H-indol-3-yl)-ethyl imino]-2-phenyl-2,3-dihydro-1H-pyrazol-4-ylazo]-5-hydroxy-benzoic acid (LH)

2.4. Syntheses of metal complexes

Ni^{II}, Co^{II}, Cu^{II}, Pd^{II} and Pt^{II} complexes were prepared by adding 10 mL of an ethanolic metal salt (4 mmol) to an ethanol/chloroform (1:1 v/v) solution containing 8 mmol of the ligand (LH) and the mixture was refluxed for 6 h. The obtained solution was left at room temperature and the resulting precipitates were filtered off, washed with ethanol and then recrystallized from an ethanol/chloroform (1:3 v/v) solvent mixture.

2.5. Microbiological investigations

The filter paper disc method was applied according to Gupta et al.¹⁷. The test bacteria were seeded in tubes with nutrient broth (NB). The seeded NB (1 mL) was homogenized at 45°C in the tubes with 9 mL of melted nutrient agar (NA) and the homogeneous suspensions were poured into Petri dishes. The discs of filter paper (diameter 4 mm) were ranged on the cooled medium. After cooling the formed solid medium of the investigated compounds were applied using a micropipette. After incubation for 24 h in a thermostat at 25–27 °C, the inhibition (sterile) zone diameters of the discs were measured and expressed in mm. An inhibition zone diameter over 7 mm indicates that the tested compound is active against the bacteria under investigation. The antibacterial activities of the investigated compounds were tested against *Escherichia coli* and *Pseudomonas aeruginosa* as Gram negative, *Bacillus subtilis* and *Staphylococcus aureus* as Gram positive. The concentration of each solution

was 10⁻³ M, commercial DMSO was employed to dissolve the tested samples.

2.6. Programs used in theoretical calculation

Hyper Chem-8 program is a sophisticated molecular modeler, editor and powerful computational package that are known for its quality, flexibility and ease of use, uniting 2D visualization and animation with quantum chemical calculations, molecular mechanics and dynamic. PM3 is more popular than other semi-empirical methods due to the availability of algorithms and more accurate than with other methods. PM3/TM is an extension of the PM3 method to include orbital's for use with transition metals. It has parameterized primarily for organic molecules and selected transition metals. In the present work, parameterization method 3 (PM3) was used for the calculation of heat of formation and binding energy for all metal complexes.

3. RESULTS AND DISCUSSION

All the prepared complexes in this paper were insoluble in water but soluble in dimethyl formamide. The range of conductance values in DMF which are listed in table 1 indicates that all the metal complexes have a non-electrolyte nature. Thus, the molar conductance value indicate that the Cl anion is in the first coordination sphere of the metal^{15, 17, 18}. The physical properties and elemental analysis data are listed in Table 1.

Table 1. Physical properties, conductivity and analytical data of the free ligands and its complexes

Compound Formula	Yield %	Color	M.P. °C	Elemental Analysis Calculated (Found) %					Molar conductivity Ohm ⁻¹ cm ² mol ⁻¹
				C	H	N	M	Cl	
A C ₂₂ H ₂₅ N ₅	62.2	White	177	73.51 (75.55)	7.01 (6.87)	19.48 (21.23)	-	-	-
L C ₂₉ H ₂₈ N ₆ O ₃	62.2	Brown Yellow	>390	(68.4) 67.76	(5.55) 5.83	(16.52) 16.56	-	-	-
[CoL(H ₂ O) ₂ Cl] C ₂₉ H ₃₁ N ₆ O ₅ ClCo	66	Brown reddish	220d	(54.60) 54.83	(4.90) 3.99	(13.17) 14.31	(9.24) 10.12	(5.56) 4.78	15
[NiL(H ₂ O) ₂ Cl] C ₂₉ H ₃₁ N ₆ O ₅ ClNi	68	Yellow- green	235d	(54.62) 55.07	(4.90) 4.47	(13.18) 13.01	(9.20) 8.53	(5.56) 4.27	25
[CuL(H ₂ O) ₂ Cl] C ₂₉ H ₃₁ N ₆ O ₅ ClCu	71	Dark red	300d	(54.20) 55.07	(4.86) 5.55	(13.08) 14.01	(9.89) 8.79	(5.52) 4.79	18
[PdLCl] C ₂₉ H ₂₇ N ₆ O ₃ ClPd	55	Brown reddish	280d	(53.63) 54.05	(4.19) 3.85	(12.94) 13.52	(16.39) 15.76	(5.46) 4.87	23
[PtLCl ₃] C ₂₉ H ₂₇ N ₆ O ₃ Cl ₃ Pt	59	Brown	280d	(43.05) 44.22	(3.36) 3.88	(10.39) 11.05	(24.11) 23.97	(13.15) 12.12	30

d= decomposes

3.1. Electronic spectra and magnetic moments

The electronic spectrum of the free ligand (LH) shows two bands at 275 nm and 300 nm which are attributed to $\pi \rightarrow \pi^*$ and $n \rightarrow \pi^*$ transitions respectively. The electronic spectrum of the Co^{II} complex exhibits three absorption bands at 400, 500 and 648 nm which were attributed to ${}^4\text{T}_{1\text{g}(\text{F})} \rightarrow {}^4\text{A}_{2\text{g}(\text{F})}$, ${}^4\text{T}_{1\text{g}(\text{F})} \rightarrow {}^4\text{T}_{1\text{g}(\text{P})}$ and ${}^4\text{T}_{1\text{g}(\text{F})} \rightarrow {}^4\text{T}_{2\text{g}(\text{F})}$ respectively. Furthermore, the magnetic moment of the Co^{II} (d^7) complex was found to be 5.01 B.M., which is higher than the spin only calculated value, difference that can be attributed to the orbital contribution. All the above mentioned data correspond to an octahedral geometry¹⁹⁻²².

The electronic spectrum of the yellow-green Ni^{II} complex shows bands in the visible region at 394, 490 and 650 nm, which are assigned to the d-d electronic transitions ${}^3\text{A}_{2\text{g}(\text{F})} \rightarrow {}^3\text{T}_{1\text{g}(\text{P})}$, ${}^3\text{A}_{2\text{g}(\text{F})} \rightarrow {}^3\text{T}_{2\text{g}(\text{F})}$ and ${}^3\text{A}_{2\text{g}(\text{F})} \rightarrow {}^3\text{T}_{1\text{g}(\text{F})}$ respectively. The value of μ_{eff} of the Ni^{II} complex d^8 is 2.82 B.M.; this value is in agreement with the spin-only value. All these results for the Ni^{II} complex confirm an octahedral geometry²⁰.

The copper complex exhibits absorption bands at 289 and 385 nm which are assigned to charge transfer transition ($\text{M} \rightarrow \text{L}$). Besides, the complex shows a band in the visible region at 590 nm which can be assigned to $2\text{Eg} \rightarrow {}^2\text{T}_{2\text{g}(\text{D})}$. The μ_{eff} of the Cu^{II} complex d^9 was found to be 1.82 B. M within the expected value for one electron²³.

The diamagnetic Pd^{II} d^8 low spin complex exhibits absorption bands at 410 and 492 nm which assigned to ${}^1\text{A}_{1\text{g}} \rightarrow {}^1\text{A}_{2\text{g}}$ and another band at 790 nm which can be assigned to ${}^1\text{A}_{1\text{g}} \rightarrow {}^1\text{B}_{1\text{g}}$. These assignments correspond to a square planar Pd^{II} complex^{20, 24}.

Finally, the spectrum of brown Pt^{II} complex show electronic transitions of ${}^1\text{A}_{1\text{g}} \rightarrow {}^1\text{T}_{2\text{g}}$ and ${}^1\text{A}_{1\text{g}} \rightarrow {}^1\text{T}_{1\text{g}}$ at 495 and 792 nm respectively. Table 2 gives the electronic spectral bands and the magnetic moments of the ligand and its complexes.

Table 2. Magnetic susceptibility and electronic spectra of the ligand and the reported complexes

Compound	λ_{max} nm	Wave number cm^{-1}	ϵ_{max} $\text{L mol}^{-1}\text{cm}^{-1}$	Assignment	μ_{eff} Calc. (found) B.M
A	280	35714	35000	$\pi \rightarrow \pi^*$	-
	300	33333	36900	$\text{n} \rightarrow \pi^*$	
LH	275	36363	30000	$\pi \rightarrow \pi^*$	-
	300	33333	34500	$\text{n} \rightarrow \pi^*$	
[CoL(H ₂ O) ₂ Cl]	346	28901	520	M→L (C.T)	3.872 (5.01)
	400	25000	650	${}^4\text{T}_{1\text{g}(\text{F})} \rightarrow {}^4\text{A}_{2\text{g}(\text{F})}$	
	500	20000	190	${}^4\text{T}_{1\text{g}(\text{F})} \rightarrow {}^4\text{T}_{1\text{g}(\text{P})}$	
	648	15432	185	${}^4\text{T}_{1\text{g}(\text{F})} \rightarrow {}^4\text{T}_{2\text{g}(\text{F})}$	
[NiL(H ₂ O) ₂ Cl]	340	29411	110	M⊗L (C.T)	2.828 (2.82)
	394	25380	120	${}^3\text{A}_{2\text{g}(\text{F})} \rightarrow {}^3\text{T}_{1\text{g}(\text{P})}$	
	490	20408	36	${}^3\text{A}_{2\text{g}(\text{F})} \rightarrow {}^3\text{T}_{2\text{g}(\text{F})}$	
	650	15384	40	${}^3\text{A}_{2\text{g}(\text{F})} \rightarrow {}^3\text{T}_{1\text{g}(\text{F})}$	
[CuL(H ₂ O) ₂ Cl]	289	34602	140	M→L (C.T)	1.732 (1.82)
	385	25974	140	$\text{n} \rightarrow \pi^*$	
	590	16949	24	${}^2\text{Eg}_{(\text{D})} \rightarrow {}^2\text{T}_{2\text{g}(\text{D})}$	
[PdLCl]	380	26315	2150	M→L (C.T)	Diamagnetic
	410	24390	3200	${}^1\text{A}_1\text{g} \rightarrow {}^1\text{A}_2\text{g}$	
	492	20325	390		
	790	12658	400	${}^1\text{A}_1\text{g} \rightarrow {}^1\text{B}_1\text{g}$	
[PtLCl ₃]	289	34602	780	$\pi \rightarrow \pi^*$	(0.90)
	495	20202	160	${}^1\text{A}_1\text{g} \rightarrow {}^1\text{T}_2\text{g}$	
	792	12626	120	${}^1\text{A}_1\text{g} \rightarrow {}^1\text{T}_1\text{g}$	

3.2. Infrared spectra studies

The main vibrational bands of the FTIR spectrum were assigned to the functional groups of the Azo-Schiff base ligand LH. The spectrum of the ligand shows strong bands at 3699, 3429, 3234, 1728, 1601, 1444, 1342 and 1288 cm^{-1} that are assigned to the $\nu(\text{OH})$ carboxyl, $\nu(\text{OH})$ phenolic, $\nu(\text{NH})$, $\nu(\text{C}=\text{N})$, $\nu(\text{COO})$ asymmetrical, $\nu(\text{N}=\text{N})$, $\nu(\text{COO})$ symmetrical and $\nu(\text{CO})$ phenolic respectively²⁵⁻²⁷. On complex formation the bands of $\nu(\text{C}=\text{N})$, $\nu(\text{N}=\text{N})$ and $\nu(\text{COO})$ are shifted to lower frequencies by (39 to 44), (8 to 18) and (3 to 8) cm^{-1} respectively; these shifts confirm the coordination of the ligand through

the nitrogen of the azomethine group, and the azo group and the carboxylate ion with the metal ions. Moreover, the spectra of the complexes exhibited weak bands between (534-553) cm^{-1} and (437-454) cm^{-1} which are attributed to $\nu(\text{M}-\text{N})$ and $\nu(\text{M}-\text{O})$ respectively. This indicates that the ligand is coordinated to the metal ions through the N and O atoms. Besides, the spectra of the complexes present weak bands between 407-412 cm^{-1} which can be assigned to $\nu(\text{M}-\text{Cl})$ ²⁸. Characteristic vibrations and assignments of free the ligand and its complexes are reported in Table 3.

Table 3. The IR spectra bands (cm⁻¹) of the free ligand and its complexes

Compound	$\nu(\text{OH})_{\text{ca}}$	$\nu(\text{OH})_{\text{ph}}$ $\nu(\text{CO})_{\text{ph}}$	$\nu(\text{NH})$	$\nu(\text{C}=\text{N})$	$\nu(\text{N}=\text{N}), \nu(\text{C}-\text{N}=\text{N}-\text{C})$	$\nu(\text{COO})_{\text{as}}$ $\nu(\text{COO})_{\text{s}}$	$\nu(\text{M}-\text{N})$ $\nu(\text{M}-\text{O})$	$\nu(\text{M}-\text{Cl})$	$\nu(\text{H}_2\text{O})$
L	3699	3492 1288	3234	1728	1444, 1124	1601 1342	-		-
[CoL(H ₂ O) ₂ Cl]	-	3420 1281	3229	1688	1434, 1124	1586 1337	534 437	412	3534
[NiL(H ₂ O) ₂ Cl]	-	3429 1280	3239	1687	1427, 1120	1598 1333	540 440	407	3539
[CuL(H ₂ O) ₂ Cl]	-	3425 1283	3226	1689	1434, 1124	1586 1333	548 450	411	3533
[PdLCl]	-	3425 1289	3231	1685	1437, 1124	1584 1336	540 454	410	-
[PtLCl ₃]	-	3426 1289	3239	1684	1434, 1124	1583 1337	553 443	411	-

Ph=phenolic, ca=carboxylic, as=asymmetric, s=symmetric

3.3. Thermal analysis TGA

To understand the thermal decomposition processes of the studied compounds, the azo-Schiff base ligand and its metal complexes were examined by thermo gravimetric analysis in the temperature range of 30–700 °C. The obtained results from the TG curves for all these compounds are given in Table 4. The decomposition was complete at 693 °C for all the complexes. The comparison of the thermograms of the ligand and the complexes shows that the complexes are more thermally stable than the Azo-Schiff base (10–35 °C). The final decomposition products were metal Pd complex in (600°C), metal oxide CoO in the 696 °C, NiO 698 °C and PtO 598 °C) and metal mixture formed above 600 °C for the Cu complex

The thermal data have been analyzed for thermodynamic parameters by using Coats- Redfern method. From the half decomposition temperature, the relative thermal stability of the compounds is: NiL > CoL > PdL > CuL > PtL > L
(L)=C₂₉H₂₇N₆O₃ [101.131% Found (99.999% Cal) (158-348°C) → C₂₃H₂₃N₅O₃ [82.648%Found (82.085% Cal)] (348-598 °C) → C₆H₃N [18.483% Found (17.914%Cal); C₂₉H₂₇N₆O₃ClCu (642.59) (35-142°C) → 2H₂O [4.931% Found (5.607%Cal)]; C₂₉H₂₇N₆O₃ClCu (606.59) (142-435°C) → C₉H₁₁N [22.003% Found (20.716% Cal)]; C₂₀H₁₆N₅O₃ClCu (473.59) (435-600°C) → C₁₃H₁₂N₃Cl [38.174% found (38.239% Cal); C₇H₄CuN₂O₃ [35.438% Found (35.358% Cal)].

Total wt. loos= 65.003% Found (64.562% Cal) and final residue: 34.997% Found (35.438% Cal)

C₂₉H₂₇N₆O₃ClPd (649.44) (35-412°C) → C₁₈H₁₇N₃ [42.814% Found (42.344 %Cal)]; C₁₁H₁₀N₃O₂ClPd (390.44) (412-600°C) → C₁₁H₁₀N₃O₂Cl [44.124% Found (41.19 %Cal)]; Pd [13.062% Found (16.387%Cal)]

Total wt. loos= 86.938% Found (83.534% Cal) and final residue: 13.062 % Found (16.466 % Cal)

C₂₉H₂₇N₆O₃ClNi (637.74) (45-170°C) → 2H₂O + CH₇ClO [16.823% Found (16.707%Cal)]; C₂₈H₁₈N₆O₂Ni (567.24) (170-355°C) → C₇H₁₀N₂ [20.175% Found (19.156% Cal)]; C₂₁H₈N₄O₂ (348) (355-698°C) → C₂₁H₈N₄O [52.903% Found (54.004% Cal); NiO [10.099% Found (11.712% Cal)]

Total wt. loos= 89.901% Found (89.867% Cal) and final residue: 10.099% Found (10.133% Cal)

C₂₉H₂₇N₆O₃ClCo (637.98) (45-150°C) → 2H₂O + C [7.647% Found (7.528%Cal)]; C₂₈H₁₈N₆O₂CoCl (589.95) (150-430°C) → C₇H₁₀N₂ClO₂ [31.601% Found (29.725% Cal)]; C₂₁H₁₇N₄O (341) (430-696°C) → C₂₁H₁₇N₄ [52.310% Found (50.942% Cal); CoO [8.442% Found (9.237% Cal)]

Total wt. loos= 91.558% Found (88.195% Cal) and final residue: 8.442% Found (11.745% Cal)

1-C₂₉H₂₇N₆O₃ClPt (809) (45-145°C) → C₃H₆ [4.931% Found (50.191%Cal)]; C₂₈H₂₁N₆O₃ClPt (767) (145-445°C) → C₆H₁₀Cl₂ [22.003% Found (21.867%Cal)]; C₁₈H₁₁N₆O₃ClPt (590.096) (445-598°C) → C₂₂H₁₇N₅ [47.166% Found (47.213%Cal)]; PtO [25.906% Found (25.729%Cal)]; Total wt. loos= 74.094% Found (74.271% Cal) and final residue: 25.906% Found (25.729% Cal)

Table 4. Thermal analysis data of the metal complexes derived from L.

Com	TG range (°C)	DTG _{max} (°C)	%Estimated (calculated)		Assignment
			Mass Loss	Total mass Loss	
L	158-348 348-598	290.36 513.87	82.648 (82.085) 18.483 (17.914)	101.131 (99.999)	C ₂₃ H ₂₃ N ₅ O ₃ C ₆ H ₃ N-
[CoL(H ₂ O) ₂ Cl]	45-150 150430 430-696	72.03 359.39 476.91	7.64 (7.528) 31.601(29.725) 52.310(50.942) 8.442 (9.237)	91.558 (88.195)	2H ₂ O C ₇ H ₁₀ N ₂ ClO ₂ C ₂₁ H ₁₇ N ₄ CoO
[NiL(H ₂ O) ₂ Cl]	45-170 170-355 355-698	75.35 263.96 477.38	16.823(16.707) 20.175(19.156) 52.903(54.004) 10.099(11.712)	89.901 (89.867)	2H ₂ O + CH ₇ ClO C ₇ H ₁₀ N ₂ C ₂₁ H ₈ N ₄ O NiO
[CuL(H ₂ O) ₂ Cl]	35-142 142-435 435-600	68.22 339.60 552.20	4.931 (5.607) 22.003(20.716) 38.174(38.239) 35.438(35.358)	65.003 (64.562)	2H ₂ O C ₉ H ₁₁ N C ₁₃ H ₁₂ N ₃ Cl C ₇ H ₄ CuN ₂ O ₃
[PdLCl]	35-412 412-600	313.97 497.47	42.814(42.344) 44.124 (41.19) 13.062(16.387)	86.938 (83.534)	C ₁₈ H ₁₇ N ₃ C ₁₁ H ₁₀ N ₃ O ₂ Cl Pd
[PtLCl ₃]	45-145 145-445 445-598	70.42 357.8 554.4	4.931 (4.902) 22.003(21.843) 47.166(47.417) 24.873(25.838)	75.127 (74.162)	C ₃ H ₄ C ₆ N ₄ H ₁₄ Cl ₃ C ₁₆ N ₃ H ₁₁ PtO

3.4. Kinetic study

Coats–Red fern is the method mentioned in the literature related to decomposition kinetics studies; this method is applied in this study²⁹. From the TG curves, the activation energy, E, preexponential factor, A, entropies, ΔS , enthalpy, ΔH , and Gibbs free energy, ΔG , were calculated by Coats–Redfern method; where:

$$\Delta H = E - RT \text{ and } \Delta G = \Delta H - T\Delta S$$

The linearization curves of Coats–Red fern method. Kinetic parameters are calculated by employing the Coats–Red fern equations, are summarized in Table 5. The Coats–Red fern equation²⁹ may be written in the form:

$$\log \left[\frac{1-(1-\alpha)^{1-n}}{T^2(1-n)} \right] = \log \frac{ZR}{qE} \left[1 - \frac{2RT}{E} \right] - \frac{E}{2.303RT} \quad \dots n \neq 1 \dots \dots \dots 1 \text{ for complexes}$$

$$\log \left[\frac{-\log(1-\alpha)}{T^2} \right] = \log \left[\frac{AR}{\beta E} \left(1 - \frac{2RT}{E} \right) \right] - \frac{E}{2.303RT} \quad n=1 \dots \dots \dots 2 \text{ for ligand}$$

where α is the mass loss at the completion of the reaction, R the gas constant, Ea the activation energy in J mol⁻¹ and q is the heating rate. Since $1-2RT/Ea \approx 1$, a plot of the left-hand side of the above equation against ΔE^* was calculated from the slope and A (Arrhenius constant) was found from the intercept. The activation entropy ΔS^* , the activation enthalpy ΔH^* and the free energy of activation ΔG^* were calculated using the following equations:

$$S^* = 2.303 (\log Ah / KT) R; \quad H^* = E^* - RT; \quad G^* = H^* - TS^*$$

Where K and h are the Boltzmann's and Plank's constants, respectively. The calculated values of ΔE^* , ΔS^* , ΔH^* and ΔG^* for the dehydration and the decomposition steps are given in Table 5. The activation energies of the decomposition were found to be in the range 134–208 J mol⁻¹. According to the kinetic data obtained from TGA curves, the negative values of activation entropies ΔS^* indicate a more ordered activated complexes than the reactants and/or the reactions are slow³⁰.

Table 5. Thermodynamic parameters of the ligand and metal complexes.

Sam (step)	Trange °C	n	R ²	T _{max} °K	Ea K.J mol ⁻¹	ΔH^* KJ mol ⁻¹	A Sec ⁻¹ x10 ⁵	ΔS^* J mol ⁻¹ K ⁻¹	ΔG^* KJ mol ⁻¹	K x 10 ⁻⁶
L(1)	158-348	1	0.99	563.51	7.6669	2.982	425.5	-104.171	61.983	1.7958
L(2)	348-598	1	0.99	786.85	12.2404	5.6986	830.9	-101.378	85.467	2.1189
CuL ₌₁	25-145	0.9	0.97	341.37	4.57425	1.736	124.3	-117.54	41.86	3.9316
CuL ₌₂	145-435	0.9	0.99	612.75	9.60396	4.509	479.0	-103.878	68.160	15.4668
CuL ₌₃	435- 600	0.9	0.99	825.35	12.68103	7.174	410.0	-107.65	96.022	8.37053
PdL ₌₁	35-412	0.9	0.98	587.12	7.442325	2.56101	505.41	-103.0818	68.4756	8.0847
PdL ₌₂	412-600	0.9	0.99	770.62	11.90189	5.49496	794.69	-101.5799	83.77449	20.9573
Ni L=1	45-170	0.9	0.99	348.5	6.609926	3.7215	1087.817	-92.370	35.9035	41.5445
Ni L=2	170-355	0.9	0.99	537.11	9.66478	5.19925	359.8129	-105.167	61.6855	10.011818
Ni L=3	355-698	0.9	0.99	750.53	16.21645	9.97655	646.665	-103.074	87.336	8.3455
CoL=1	45-150	0.9	0.99	345.18	3.083122	.2133	102.215	-111.9558	38.8582	13.1695
CoL=2	150-430	0.9	0.99	632.54	10.34927	5.09033	497.5594	-103.8282	70.7658	14.3221
CoL=3	430-696	0.9	0.99	750.06	14.9008	8.6648	648.66152	-103.04	85.95	10.3317
ptL ₌₁	45-145	0.9	0.99	341.37	5.792853	2.9547	146.04	-108.8958	40.12847	7.2377
ptL ₌₂	145-445	0.9	0.99	632.75	12.11535	6.85467	477.78	-104.1716	72.76927	9.8303
ptL ₌₃	445-598	0.9	0.99	827.55	12.7574	5.8772	936.7026	-100.80124	96.17546	8.496

3.5. Microbiological Investigation

The biological activity of ligand L and its complexes were tested against bacteria, we used more than one test organism to increase the chance of detecting antibiotic principles in tested materials. The organisms used in the present investigation included two Gram positive bacteria (*Bacillus subtilis* and *Staphylococcus aureus*) and two Gram negative bacteria (*Escherichia coli*

and *Pseudomonas aeruginosa*). The results of the bactericidal screening of the synthesized compounds are recorded in Table 6. An influence of the central ion of the complexes in the antibacterial activity against the tested Gram positive and Gram negative organisms show that the complexes have an enhanced activity compared to the ligands itself

Table 6. Antibacterial activity data of ligands and its complexes inhibition zone (mm).

compound	Bacillus subtilis G ⁺	Staphylococcus aureus G ⁺	Escherichia Coli G ⁻	Pseudomonas aeruginosa G ⁻
L	20	17	19	16
[CoL(H ₂ O) ₂ Cl]	22	20	12	12
[NiL(H ₂ O) ₂ Cl]	24	23	15	14
[CuL(H ₂ O) ₂ Cl]	28	24	19	11
[PdLCl]	22	24	12	17
[PtLCl ₃]	30	21	28	25

Key to interpretation: less than 10 mm=inactive, 10-15 mm= weakly active, 15-20 mm=moderately active, more than 20 mm=highly active.

3.6. Theoretical study

The vibration spectra of the A and Azo -Schiff base L was calculated by using a semi-empirical (PM3) method. The results obtained for wave numbers are presented in Table 7, and the comparisons with the experimental values indicate some deviations. These deviations may be due to the harmonic oscillator approximation and lack of electron correlation. It was reported Chamberlain, *et al.* that frequencies coupled with Hartree- Fock Theory (HFT) approximation and quantum harmonic oscillator approximations tend to be 10% too high^{31,32}.

3.6.1. Optimized Geometries Energy of metal complexes for A and Azo-Schiff base

Theoretically probable structures of metal complexes with (A) and Azo-Schiff base were calculated to search for the most probable model building stable structure, these shapes, show the calculated optima geometries for L and their metal complexes as shown in Figs. 1 and 2. The results of PM3 method of calculation in gas phase for the binding energies and heat of formation of Co(II), Ni(II), Cu(II) and Pd(II) complexes, are described in Table 7 and 8.

Table 7. Conformation energetic in (K J.Mol⁻¹) for the starting material (A), L and metal complexes.

Conformation	ΔH_f°	ΔE_b
A	143.0217934	-5484.108206
L	44.0793240	-7227.2636760
CoL	-284.4905433	-8081.4355433
CuL	-74.4882040	-7849.7332040
NiL	-204.0042712	-8001.3492712
PdL	103.0683621	-7353.9506379

Table 8. Comparison of experimental and theoretical vibration frequencies for ligands

Com	$\nu(\text{NH}_2)_{\text{as}}$	$\nu(\text{NH}_2)_s$	$\nu(\text{C}=\text{N})$	$\nu(\text{C}-\text{N})$	$\nu(\text{N}=\text{N})$	$\nu(\text{C}=\text{C})$	$\nu(\text{NH})$	$\delta(\text{NH}_2)$	$\nu(\text{OH})$ phenol	$\nu(\text{OH})$ carboxylic	$\nu(\text{C}-\text{O})$ phenol
A	3485* 3504** 0***	3305* 3382** 0***	1641- 1633* 1867** -0.001***	1243* 1249** 0***		1591-1556* 1832** -0.001***	3271* 3452** 0***	1612* 1021** 0.003***			
L	- -	-	1728* 1891** 0***	1276* 1341** 0***	1072* 1874** -0.007***	1589-1554* 1779** -0.001***	3234* 3456** 0***	-	3699* 3890** 0***	3429* 3885** -0.001***	1288* 1412** 0***

*: Experimental frequency, **: Theoretical frequency, ***: Error % due to main difference in the experimental measurements and theoretical treatments of vibration spectrum.

3.6.2. Electrostatic Potential (E.P)

Electron distribution governs the electrostatic potential of molecules and describes the interaction of energy of the molecular system with a positive point charge, so it is useful for finding sites of reaction in a molecular positive charged species tend to attack a molecule where the E.P. is strongly negative electrophilic attack³¹. The E.P. of free ligand was calculated and plotted as 2D contour to investigate the reactive sites of the molecules, and one can interpret the stereochemistry and rates of many reactions involving soft electrophiles and nucleophiles in terms of the properties of frontier orbitals (HOMO and LUMO). Overlap between the HOMO and LUMO values were plotted as 2D contour to get more information about these molecules. The results of calculation showed that the LUMO of transition metal ion prefers to react with the HOMO of nitrogen atoms of Azo- Schiff base ligand as shown in Fig. 3.

4. CONCLUSION

New Co^{II}, Ni^{II}, Cu^{II}, Pd^{II} and Pt^{II} metal complexes with Azo-Schiff base derived L₁ from reaction *m*-hydroxy benzoic acid with 1,5-Dimethyl-3-[2-(5-methyl-1*H*-indol-3-yl)-ethylimino]-2-phenyl-2,3-dihydro-1*H*-pyrazol-4-ylamine have been synthesized. All the complexes are insoluble in water but soluble in DMF, as well as all of them are non-electrolyte. The structure of the complexes based on Uv-Vis, IR, mass spectroscopy were proposed that the

Azo-Schiff base Ligand L behave as tridentate which coordinated with the metal ions through N, N, O atoms. It can be suggested that the geometry of the Co(II), Ni(II) and Cu(II) have octahedral geometry as shown in Fig. 4, Pd(II) and Pt(II) complexes have square planer geometry as shown in Fig. 5 (a and b). Hyper Chem-8 program was used to predict structural geometries of compounds in gas phase. The heat of formation (ΔH_f°) and binding energy (ΔE_b) at 298°K for the free ligands and its vanadyl complexes was calculated by PM3 method. The synthesized ligands and its metal complexes were screened for their biological activity against bacterial species, two Gram positive bacteria (*Bacillus subtilis* and *Staphylococcus aureus*) and two Gram negative bacteria (*Escherichia coli* and *Pseudomonas aeruginosa*)

Fig.1. Conformational Structure of A, ligand and their Complexes

Fig. 2. The calculated vibrational frequencies of starting material A(a) and ligand L (b)

Fig. 3. HOMO and Electrostatic Potential as for starting material and L

Fig.4. Structure of octahedral complexes

Fig.5. (a) Structure of the $[PtLCl_3]$ complex and (b) Structure of the $[PdLCl]$ complex

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