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Palladium(II) and zinc(II) complexes of neutral [N₂O₂] donor Schiff bases derived from furfuraldehyde: Synthesis, characterization, fluorescence and corrosion inhibitors of ligands



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HIGHLIGHTS

G R A P H I C A L A B S T R A C T

- The complexes are characterized by different spectroscopic techniques.
 The Schiff base ligands exhibited
- efficient corrosion inhibitors. • Zn(II) complexes may have potential
- uses as a Zn^{2+} sensor.
- The ligands and Zn(II) complexes exhibited strong fluorescence.



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ABSTRACT

Metal complexes of Schiff bases derived from furfuraldehyde and 4,5-dimethyl-1,2-phenylendiamine (L¹) or 4,5-dichloro-1,2-phenylendiamine (L²) have been reported and characterized based on elemental analyses, IR, ¹H NMR, UV–Vis, magnetic moment, molar conductance and thermal analysis. The complexes are found to have the formulae [PdL^{1–2}]Cl₂ and [ZnL^{1–2}](AcO)₂·H₂O. The molar conductance data reveal that Pd(II) and Zn(II) chelates are ionic in nature and are of the type 2:1 electrolytes. The spectral data are consistent with a square planar and tetrahedral geometry around Pd(II) and Zn(II), respectively, in which the ligands act as tetradentate ligands. The thermal behavior of some chelates is studied and the activation thermodynamic parameters are calculated using Coats–Redfern method. The corrosion inhibition of stainless steel types 410 and 304 in 1 M HCl using the synthesized Schiff bases as inhibitors have been studied by weight loss method. The obtained data considered these ligands as efficient corrosion inhibitors. The ligands and their metal complexes exhibited considerable antibacterial activity against *Staphylococcus aureus*, and *Escherichia coli* and antifungal activity against *Candida albicans*.

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Introduction

The Schiff bases are considered a very important class of ligands, which form complexes with many metals. These complexes have wide applications in some biological aspects [1–4],

* Tel.: +20 22344032. E-mail address: omaymaahmed92@yahoo.com analytical fields [5], organic catalysis [6], oxygen carriers [7] and as corrosion inhibitors in especially acidic environments for various alloys and metals [8–10]. Schiff base complexes derived from heterocyclic compounds have found an increased interest in the context of bioinorganic chemistry [11,12]. Various heterocyclic Schiff bases and their complexes having nitrogen and also oxygen donor atoms, have been reported by several scientists [13–15]. The furan ring, as a part in ligand, has been studied and has attracted great attention for a long time and significant progress has been made in understanding the structure of its complexes [13,16,17]. Complexes of some transition metal ions with Schiff bases derived from 2-furancarboxaldehyde and o-phenylenediamine [18–20], hydrazine hydrate [21], 3,3'-diaminobenzidene [22], 3aminodibenzofuran [23] and o-tolidine [24] were studied. Furaldehyde Schiff bases were found to show the selectivity towards anions and can act as anion-sensitive membrane electrodes [25], they also possess the nitrification inhibitory properties [26]. Moreover, luminescent compounds are attracting much current research interest because of their many applications including emitting materials for organic light emitting diodes, light harvesting materials for photocatalysis and fluorescent sensors for organic or inorganic analytes [27-29]. Indeed, Schiff bases derived from aromatic diamines have received much less attention and are considered. Here we report, the synthesis and characterization of heterocyclic Schiff base ligands. N.N'-bis-(2-furancarboxaldimine)-4,5-dimethyl-1,2-phenylenediamine (L¹), and N,N'-bis-(2-furancarboxaldimine)-4,5-dichloro-1,2-phenylenediamine (L²) and their complexes [M(N,N'-bis-(2-furancarboxaldimine)-4,5-dimethyl-1, 2-phenylenediamine)]Cl₂ and [M(N,N'-bis-(2-furancarboxaldimine)-4,5-dichloro-1,2-phenylenediamine)](AcO)₂·H₂O (M = Zn and Pd).

Experimental

Materials and instrumentation

PdCl₂, Zn(CH₃COO)₂·2H₂O, 4,5-dimethyl-1,2-phenylendiamine and 4,5-dichloro-1,2-phenylendiamine and furfuraldehyde were supplied from Aldrich. All solvents were of analytical grade. IR measurements (KBr pellets) were carried out on a Shimadzu 8000 FT-IR spectrometer. Magnetic susceptibilities of the chelates were measured at room temperature using a magnetic susceptibility Cambridge England Sherwood Scientific. NMR measurements were performed on a Varian-Mercury 300 MHz spectrometer. Samples were dissolved in (CD₃)₂SO with TMS as internal reference. Mass spectra of the solid complexes (70 eV, EI) were carried out on a Finnigan MAT SSQ 7000 spectrometer. Thermogravimetric analyses (TG and DTG) were carried out under N2 atmosphere with a heating rate of 10 °C/min. using a Shimadzu DT-50 thermal analyzer. Microanalyses were performed using JEOL JMS-AX500 elemental analyzer. All conductivity measurements were performed in DMF (1×10^{-3} M) at 25 °C, by using Jenway 4010 conductivity meter. Ultraviolet spectra were recorded using a Shimadzu UV 1800 Spectrophotometer in the range of 200-800 nm. The photoluminescent properties of all compounds were studied using a Jenway 6270 Fluorimeter.

Preparation of Schiff base ligands

The ligands were obtained from the condensation of furfuraldehyde and 4,5-dimethyl-1,2-phenylendiamine or 4,5-dichloro-1,2phenylendiamine in 2:1 M ratio, in ethanol for 4 h. The yellow-orange precipitates obtained were filtered, washed with ethanol and dried in a vacuum. Recrystallization from ethanol afforded pure Schiff bases. The infrared and elemental analysis data of the obtained products were consistent very well with their formulae.

Preparation of Pd(II) complexes

A solution of [PdCl₂] (0.5 mmol) in ethanol (10 ml) was added to the solution of ligand (0.5 mmol) in ethanol (10 ml) while stirring. The resulting mixture was allowed to reflux on a water bath for 2 h in the presence of a few drops of concentrated HCl. The formed solid products were filtered, washing with ethanol and dried in vacuum desiccators. The complexes were purified by crystallization from ethanol.

Preparation of Zn(II) complexes

A solution of hydrated zinc acetate (1.0 mmol) in methanol (10 mL) was mixed with methanolic solution (10 mL) of each ligand (1.0 mmol) and the mixture was left under reflux for 3 h. The product was filtered off, washed with cold methanol and hot petroleum ether, recrystallized from ethanol and finally dried under vacuum.

Corrosion test

Gravimetric corrosion measurements (weight loss method) were carried out according to the ASTM standard procedure described in [30]. In brief, stainless steel specimens in triplicate were immersed for a period of 4 h in 100 ml 1 M HCl containing various concentrations of the studied inhibitors. The mass of the specimens before and after immersion was determined using an analytical balance accurate to 0.1 mg. Before measurements, the specimens were abraded with a sequence of emery papers of different grades (400, 800, 1000 and 1200), followed by washing with double distilled water and finally degreased with ethanol and dried at room temperature. The composition of the stainless steel types 410 and 304 are in wt.% 0.15C, 11Cr, 75Fe, 1Mn, 0.75Ni, 0.04P, 0.03S, 1Si and 0.08C, 18Cr, 66Fe, 2Mn, 8Ni, 0.04P, 0.03S, 1Si, respectively.

Antimicrobial activity

The in vitro activity of ligands and their metal complexes were tested against the bacterial species Staphylococcus aureus and Escherichia coli in Mueller Hinton-Agar medium. The antifungal activity was tested against the fungi Aspergillus flavus and Candida albicans cultured on YPD-agar medium. The test compounds were dissolved in DMSO at concentration 2 mg/mL. Antimicrobial activities of each compound were evaluated by the disc-diffusion method. The well (8 mm diameter) was then filled with the test solution and the plates were inoculated at 37 °C for 48 h (for bacteria) and 30 °C for 72 h (for fungi). During this period, the growth of the inoculated microorganisms was affected and then the inhibition zones developed on the plates were measured. The effectiveness of an antimicrobial agent was assessed by measuring the zones of inhibition around the well. The diameter of the zone is measured to the nearest millimeter (mm). The antibacterial activity of each compound was compared with that of standard antibiotics such as Streptomycin. The antifungal activity of the test compound was compared that of Chlorometazole as standard antifungal. DMSO was used as a control under the same conditions for each organism and no activity was found. The activity results were calculated as a mean of triplicates.

Results and discussion

The complexes $[PdL^1]Cl_2$, $[PdL^2]Cl_2$, $[ZnL^1](AcO)_2 H_2O$, $[ZnL^2](AcO)_2 H_2O$ were synthesized by the reaction of ligands and metal salt in 1:1 M ratio. The results of the elemental analyses of the complexes, which are recorded in Table 1, are in good agreement with those required by the proposed formulae. All complexes were stable at room temperature. The molar conductivity data for 1 mM solutions of complexes (Table 1) suggest that these chelates are ionic in nature and they are of the type 2:1 electrolytes. All the prepared complexes are found in diamagnetic character. The solid

Table 1
Analytical and physical data of the Schiff bases and their metal chelates.

Compound	C% found (calc)	H% found (calc)	N% found (calc)	m/z	Color (% yield)	m.p (°C)	$\lambda_m (\Omega^{-1} \mathrm{mol}^{-1} \mathrm{cm}^2)$
L ¹	73.67 (73.96)	5.25 (5.51)	9.33 (9.58)	292	Yellow (55)	220	-
L ²	57.93 (57.68)	3.35 (3.02)	8.12 (8.41)	333	Yellow (65)	225	-
[PdL ¹]Cl ₂	46.43 (46.04)	3.12 (3.43)	5.67 (5.96)	469	Pale brown (70)	>300	219
[PdL ²]Cl ₂	37.25 (37.65)	2.21 (1.97)	5.13 (5.49)	510	Yellow (78)	>300	212
$[ZnL^1](AcO)_2 \cdot H_2O$	53.87 (53.51)	4.55 (4.89)	5.23 (5.67)	493	Pale yellow (60)	>300	228
$[ZnL^2](AcO)_2 \cdot H_2O$	44.63 (44.93)	3.12 (3.39)	5.47 (5.24)	534	Pale yellow (80)	>300	223

complexes are soluble in DMF and DMSO. The formation of Schiff base ligands and their complexes and bonding modes were inferred from characteristic band positions in FT-IR spectra and resonance signals in ¹H NMR spectra corresponding to coordinated Schiff base moiety. The geometry around Pd(II), Zn(II) ions in the complexes were deduced from the positions of absorption bands observed in the UV-vis spectra.

IR spectra and mode of bonding

In the absence of a powerful technique such as X-ray crystallography, IR spectra has proven to be the most suitable technique to give enough information to elucidate the way of bonding of the ligands to the metal ions. The main stretching frequencies of the IR spectra of the ligands $(L^1 \text{ and } L^2)$ and their metal complexes are tabulated in Table 2 The IR spectra of the complexes are compared with those of the free ligands in order to determine the coordination sites that may get involved in chelation. Spectra of ligands as well as their complexes showed absence of band at 1735 cm^{-1} due to vv(C=O) stretching frequency [22]. Upon comparison it was found that the v(C=N) stretching vibration is found in the free ligands L^1 and L^2 at 1625 and 1631 cm⁻¹, respectively. These bands were shifted to lower frequency in the complexes indicating the participation of azomethine nitrogen in the coordination to metal ion. This shift is due to the reduction of the double bond character of the C=N bond, which is caused by the coordination of nitrogen to the metal center and is in agreement with the results obtained from the other similar complexes described previously [31,32]. A medium intensity band due to v(C–O–C) stretching vibration of furan appeared at 1261 and 1294 cm⁻¹ in the ligands L¹ and L², respectively [19]. These bands shifted in metal complexes suggesting a coordination through oxygen of furan moiety. Appearance of new bands in the spectra of complexes in the regions 478-544 cm⁻¹ and 433-440 cm⁻¹ were assigned to v(M-O) and v(M-N) stretching vibration [33]. The bands appearing in the region 1522–1507 cm⁻¹, 1175–1143 cm⁻¹ and 758– 747 cm⁻¹ were usual modes of phenyl ring vibration. The infrared spectra of Zn(II) complexes exhibited a broad band in the region 3450–3395 cm⁻¹, confirming the presence of water molecules in complexes [34]. Fig. 1 shows the IR spectrum of [ZnL¹](AcO)₂·H₂O complex.

Table 2	
IR data of the Schiff bases and their metal chelates ($cm^{-1}).^{a}$



Fig. 1. The IR spectrum of $[ZnL^1](AcO)_2 \cdot H_2O$ complex.

¹H NMR spectra

Further evidence of the bonding mode of the ligands was also provided by the ¹H NMR spectra of the Schiff base ligands and their diamagnetic Pd(II) and Zn(II) complexes. The chemical shifts of the different types of protons in the ¹H NMR spectra of the N₂O₂ ligands and their metal complexes are listed in Table 3. The ¹H NMR spectra of L¹ and L² is shown in Figs. 2 and 3. The ¹H NMR spectra of the parent ligands L^{1-2} showed singlet in the region 7.95–8.12 ppm which was attributed to the azomethine (-CH=N-) protons. The ligands also revealed multiplets in the range 5.68–8.03 ppm which was attributed to aromatic and furan ring protons. On complexation, the position of azomethine signal was shifted to higher region 7.69-7.93 ppm in comparison with that of the free ligands, inferring coordination through the azomethine nitrogen atom of the ligand [35]. The multiplets, assigned to the aromatic and furan ring protons were displaced upper field around the region 5.58-7.83 ppm, indicating the involvement of oxygen of furan ring in the coordination [18].

Mass spectroscopy

Mass spectrometry is an effective method for investigation of molar weight and structure of the ligands and complexes. The

		. ,				
Compound	ν(OH)	$\nu(C=N)$	v(C—O—C)	v(M-O)	v(M—N)	Phenyl ring vibration
L^1	_	1625(m)	1261(w)	-	-	1507(s), 1143(m), 753(s)
L ²	-	1631(m)	1294(m)	-	-	1518(m), 1168(w), 750(s)
[PdL ¹]Cl ₂	-	1616(m)	1278(w)	544(w)	438(w)	1508(m), 1147(m), 750(s)
[PdL ²]Cl ₂	-	1612(s)	1302(m)	486(m)	435(m)	1516(s), 1175(w), 755(s)
$[ZnL^1](AcO)_2 \cdot H_2O$	3450(b)	1592(s)	1258(w)	521(w)	440(w)	1512(w), 1174(w), 758(m)
$[ZnL^2](AcO)_2 \cdot H_2O$	3395(b)	1583(s)	1298(w)	478(w)	433(w)	1522(sh), 1173(w), 747(m)
$[ZnL^2](AcO)_2 \cdot H_2O$	3395(b)	1583(s)	1298(w)	478(w)	433(w)	1522(sh), 1173(w), 747(m)

^a s, strong; m, medium; w, weak; b, broad.

 Table 3

 ¹H NMR spectral data of the Schiff bases and their metal chelates.

Compound	Chemical shift, (δ) ppm	Assignment
L ¹	7.95	(s, 2H, azomethine H)
	5.68-7.53	(m, 8H, 2ArH, 6 furan H)
	2.35	(s, 6H, methyl H)
L ²	8.12	(s, 2H, azomethine H)
	5.80-8.03	(m, 8H, 2ArH, 6 furan H)
[PdL ¹]Cl ₂	7.69	(s, 2H, azomethine H)
	5.58-7.58	(m, 8H, 2ArH, 6 furan H)
	2.31	(s, 6H, methyl H)
[PdL ²]Cl ₂	7.93	(s, 2H, azomethine H)
	5.77-7.83	(m, 8H, 2ArH, 6 furan H)
$[ZnL^{1}](AcO)_{2} \cdot H_{2}O$	7.88	(s, 2H, azomethine H)
	5.65-7.45	(m, 8H, 2ArH, 6 furan H)
	2.31	(s, 6H, methyl H)
	1.81	(s, 6H, CH₃COO)
$[ZnL^2](AcO)_2 \cdot H_2O$	7.80	(s, 2H, azomethine H)
	5.60-7.78	(m, 8H, 2ArH, 6 furan H)
	1.79	(s, 6H, CH ₃ COO)



Fig. 3. ¹H NMR spectrum of L² ligand.

Mass spectrum of the L¹ exhibited a molecular ion peak at m/2 292 which is equivalent to its molecular mass (Fig. 4). The ion peaks at 225, 120, 80 and 68 referred to the ions $[C_{14}H_{13}N_2O]^+$, $[C_8H_{10}N]^+$, $[C_5H_4O]^+$ and $[C_4H_4O]^+$, respectively. The mass spectrum of the

ligand L² displayed the parent molecular ion $[M]^+$ at m/z = 333 which is an agreement with the formula $C_{16}H_{10}N_2O_2Cl_2$ and is equivalent to its molecular weight, Fig. 5. The ligand L² shows some important peaks at m/z 266 corresponding to $[C_{12}H_7N_2OCl_2]^+$ (obtained by loss a furfural molecule $[C_4H_3O]$), at m/z 158 belongs to $[C_7H_3Cl_2]^+$ and at m/z 79 corresponding to $[C_5H_3O]^+$. The mass spectra of the complexes showed a peak at m/z value corresponding to their molecular weight, Table 1.

Magnetic measurements and electronic absorption spectra

Magnetic susceptibility measurements showed diamagnetic properties for Pd(II) and Zn(II) complexes. In addition, these complexes gave ¹H NMR signals (Table 3) confirming its diamagnetism. So, no molar magnetic susceptibility data were recorded for diamagnetic complexes whereas that for paramagnetic complexes were recorded. The electronic absorption spectra of the Schiff base ligands and their complexes were explored in DMF solution $(1 \times 10^{-5} \text{ M})$. The data are summarized in Table 4. The UV-Vis absorption spectra of the ligands and their complexes are shown in Figs. 6 and 7. The absorption spectra of the two ligands (L^1) and L²) exhibited four bands. The first two bands around 230-244 and 256–264 nm may be attributed to π – π * transitions and the second two bands observed at 318-320 nm and 332-334 nm are assigned to $n-\pi^*$ transitions, for the electrons localized on the C=N chromophore. The shift of these bands in the spectra of complexes indicated the formation of their metal complexes. As expected for the diamagnetic Zn(II) (d¹⁰) configurations, ligand field band due to d-d electronic transitions is not expected [36] and the trends observed for the ligands were maintained after coordination. The electronic absorption spectra of the Pd(II) complexes exhibited broad bands at about 408-422 nm assignable to the transition (${}^{1}B_{1g} \leftarrow {}^{1}A_{1g}$). These data and the diamagnetic nature of the complexes are in accordance with square planar geometry for the Pd(II) complexes [37,38].

Fluorescence spectra studies

The fluorescence properties of the Schiff base ligands and their complexes were studied at room temperature in DMF solutions (Figs. 8 and 9). The L¹ and L² ligands displayed the maximum emission bands at 359 and 356 nm when excited at 318 and 334 nm, respectively. [PdL¹]Cl₂ complex upon excitation at 308 nm displayed a maximum emission band at 361 nm and a weak broad band at 463 nm with fluorescence intensity 21.7 and 1.23, respectively. Also, [PdL²]Cl₂ complex exhibited a maximum emission band at 359 nm and a weak broad band at 359 nm and a weak broad band at 481 nm upon excitation at 324 nm. The intensity of the emission bands in Pd(II) complexes is decreased in comparison with ligands. The emission spectral shapes of the Zn(II) complexes closely resembled that of the ligands (Table 5). The emission intensity of the Zn(II) complexes is stronger than that of the ligands [39]. These results suggest that



Fig. 4. Mass spectrum of the ligand L¹.



Fig. 5. Mass spectrum of the ligand L².

Table 4UV-Vis data of the Schiff bases and their metal chelates.

Compound	$\lambda_{\rm max} ({\rm nm})^{\rm a}$			
	$\pi - \pi^*$	$n-\pi^*$	d–d transition	
L^1	230, 256	318, 332(sh)	-	
L ²	244, 264	320, 334	-	
[PdL ¹]Cl ₂	236, 262(sh)	308	408(b)	
[PdL ²]Cl ₂	236	324, 338(sh)	374(sh, b), 422(b)	
$[ZnL^1](AcO)_2 \cdot H_2O$	252	318, 334(sh)	-	
$[ZnL^1](AcO)_2 \cdot H_2O$	246	324, 334	-	

^a sh, shoulder; b, broad.

 L^1 and L^2 may be a suitable agent to detect zinc ion. Therefore, this kind of compounds may have potential uses as a Zn^{2+} sensor [40]. The Zn(II) complexes exhibited strong fluorescence in comparison



Thermal analysis (TGA and DrTGA)

The presence of water and thermal behavior of the complexes was further investigated by thermal analysis. The thermal analysis data for $[PdL^1]Cl_2$ and $[ZnL^1](AcO)_2 \cdot H_2O$ complexes are listed in Table 6 and the calculated thermodynamic parameters from DrTGA are listed in Table 7. One of the features in TGA data concerning the associated water molecules within the complexes supports the elemental analyses. The TGA curve of $[PdL^1]Cl_2$ (Fig. 10) showed a decomposition step within the temperature range of 194–490 °C



Fig. 6. Electronic absorption spectra of: (a) Schiff base ligand L¹; (b) [ZnL¹](AcO)₂·H₂O; and (c) [PdL¹]Cl₂ complexes in 10⁻⁴ M DMF.



Fig. 7. Electronic absorption spectra of: (a) Schiff base ligand L²; (b) [ZnL²](AcO)₂·H₂O; and (c) [PdL²]Cl₂ complexes in 10⁻⁴ M DMF.



Fig. 8. Emission spectra of:(a) Schiff base ligand L¹; (b) [PdL¹]Cl₂; and (c) [ZnL¹](AcO)₂·H₂O complexes in 10⁻⁴ M DMF solution.



Fig. 9. Emission spectra of:(a) Schiff base ligand L²; (b) [ZnL²](AcO)₂·H₂O; and (c) [PdL²]Cl₂ complexes in 10⁻⁴ M DMF solution.

 Table 5

 Fluorescence data of the Schiff bases and their metal chelates.

Compound	$\lambda_{\text{excitation}}$	$\lambda_{emission}$
L ¹	318	359, 378(sh)
L ²	334	356, 373(sh)
[PdL ¹]Cl	308	361, 377(sh), 463(b)
[PdL ²]Cl ₂	324	359, 376(sh), 481(sh, b)
$[ZnL^1](AcO)_2 \cdot H_2O$	318	358, 373(sh)
$[ZnL^2](AcO)_2 \cdot H_2O$	334	353, 371(sh)

with a mass loss of 73.20%; (calculated 73.06%) leaving the metal oxide (PdO) as a residue. The thermal decomposition of $[ZnL^1]$ (AcO)₂·H₂O (Fig. 11) complex proceeds with three main degradation steps. The first stage of decomposition occurred in the temperature range 33–128 °C with a net weight loss of 3.90% (Calc. 3.66%) which is consistent with the elimination of H₂O molecule. The second decomposition step occurred in the temperature range 128–290 °C with a net weight loss of 63.00% (Calc. 63.22%). This decomposition step could be assigned to the elimination of two

acetate moieties and $C_{13}H_8NO$ species. The third step involved removal of organic ligand moiety to give finally ZnO residue with a net weight loss of 16.33% (Calc. 16.63%).

Kinetic data

The kinetic and thermodynamic activation parameters of decomposition processes of complexes namely activation energy (E^*) , enthalpy (H^*) , entropy (S^*) and Gibbs free energy change of the decomposition (G^*) were evaluated graphically by employing the Coats–Redfern relation [43].

$$\log\left[\frac{\log(W_{\infty}/(W_{\infty}-W))}{T^{2}}\right] = \log\left[\frac{AR}{\phi E^{*}}\left(1-\frac{2RT}{E^{*}}\right)\right] - \frac{E^{*}}{2.303RT} \quad (1)$$

where W_{∞} is the mass loss at the completion of the decomposition reaction, W is the mass loss up to temperature T, R is the gas constant and ϕ is the heating rate. Since $1-2RT/E^* \cong 1$, the plot of the left-hand side of Eq. (1) against 1/T would give a straight line. E^* was then calculated from the slope and the Arrhenius constant, A, was obtained from the intercept. The other kinetic parameters;

Table 6

Thermogravimetric data of [PdL¹]Cl₂ and [ZnL¹](AcO)₂·H₂O complexes.

Complex	TG range (°C)	DTG (°C)	Mass loss%		Assignment	Metallic residue
			Calcd	Found		
[PdL ¹]Cl ₂	194-490	316	73.20	73.06	Loss of $Cl_2 + L^1$	PdO
$[ZnL^1](AcO)_2 \cdot H_2O$	33-128	84	3.90	3.66	Loss of H ₂ O	ZnO
	128-290	241	63.00	63.22	Loss of 2 (CH ₃ COO) + $C_{13}H_8ON$	
	290-492	417	16.33	16.33	Loss of C ₅ H ₈ N	

Table 7

The thermodynamic data of the thermal decompositions of [PdL¹]Cl₂ and [ZnL¹](AcO)₂·H₂O complexes.

Complex	Decomposition range (°C)	E^* (kJ mol ⁻¹)	$A(S^{-1})$	$S^* (K^{-1} \operatorname{Jmol}^{-1})$	H^* (kJ mol ⁻¹)	G^* (kJ mol ⁻¹)
$[PdL^{1}]Cl_{2}$ $[ZnL^{1}](AcO)_{2} \cdot H_{2}O$	194–490 128–290 366–492	109.67 72.98 185.27	$\begin{array}{l} 7.1\times 10^8 \\ 2.8\times 10^6 \\ 5.95\times 10^{12} \end{array}$	75.85 119.55 3.32	107.04 70.975 181.72	131.01 99.78 183.14



Fig. 10. TG and DTG curves of [PdL¹].



Fig. 11. TG and DTG curves of $[ZnL^1](AcO)_2 \cdot H_2O$.

the entropy of activation (S^*), enthalpy of activation (H^*) and the free energy change of activation (G^*) were calculated using the following equations:

$$S^* = 2303 \left(\log \frac{Ah}{KT} \right) R \tag{2}$$

$$H^* = E^* - RT \tag{3}$$

$$G^* = H^* - TS^* \tag{4}$$

where (k) and (h) are the Boltzman and Planck constants, respectively. The kinetic parameters are listed in Table 7. From the obtained results, it is apparent that G^* values of the complexes acquire highly positive magnitudes. The high value of the energy of activation of the complexes revealed the high stability of the investigated complexes due to their covalent character [44]. The negative values of S^* for the degradation process indicates that more ordered activated complex than the reactants and the decomposition reaction is slow [45].

Structural interpretation

The structures of the complexes of Schiff bases L^1 and L^2 , with Pd(II) and Zn(II) ions were confirmed by elemental analyses, IR, NMR, molar conductance, magnetic, UV–Vis, mass, and thermal analysis data. Therefore, from the IR spectra, it is concluded that L^1 and L^2 ligands behave as a neutral tetradentate ligand, coordinated to the metal ions via azomethine N and furan O. From the molar conductance data, it was found that all complexes are ionic in nature and they are of the type 2:1 electrolytes. On the basis of the above observations square planar and tetrahedral geometries are suggested for Pd(II) and Zn(II) complexes (Scheme 1).

Corrosion inhibition

The weight loss method for monitoring corrosion rate is useful because of its simple application and reliability. The values of corrosion rate (R_{corr}) obtained from weight loss measurements at different concentrations of Schiff bases at 25 °C (Tables 8 and 9). From the weight loss values, the inhibition efficiency (θ) and percentage inhibition efficiency η of each concentration was calculated using the following equations [8]:

$$\theta = \frac{R_1 - R_2}{R_1}$$

$$\eta = \theta \times 100$$

where R_1 and R_2 are the corrosion rates in the absence and presence of inhibitors, respectively. It has been found that the inhibition efficiency of all of these compounds increases with increasing of concentration of inhibitors. The maximum efficiencies for L¹ ligand is 91% for the concentration of 1×10^{-4} M on SS410 and 92% for the concentration of 1×10^{-4} M on SS304. Also, the maximum efficiencies for L² ligand is 83% for the concentration of 1×10^{-3} M on



Scheme 1. The proposed structure of Pd(II) and Zn(II) complexes.

Table 8 Corrosition parameters of stainless steel 410 in 1 M HCl at different L^1 and L^2 concentrations.

Inhibitor	Conc. (M)	$R (m mg cm^{-2} h^{-1})$	θ	η (%)
Blank	-	0.73	-	-
L	1×10^{-5}	0.45	0.38	38
	$5 imes 10^{-5}$	0.09	0.86	86
	$1 imes 10^{-4}$	0.06	0.91	91
L^2	$1 imes 10^{-5}$	0.32	0.56	56
	$1 imes 10^{-4}$	0.21	0.70	70
	$1 imes 10^{-3}$	0.12	0.83	83

Table 9 Corrosion parameters of stainless steel 304 in 1 M HCl at different L^1 and L^2 concentrations.

Inhibitor	Conc. (M)	$R_{\rm Corr} ({ m mg}{ m cm}^{-2}{ m h}^{-1})$	θ	η (%)
Blank	-	4.28	-	-
L	$5 imes 10^{-6}$	2.99	0.30	30
	$1 imes 10^{-5}$	1.35	68	0.68
	$1 imes 10^{-4}$	0.34	92	0.92
L ²	$1 imes 10^{-5}$	2.7	36	0.36
	$2 imes 10^{-5}$	2.46	42	0.42
	5×10^{-5}	0.38	90	0.90

SS410 and 90% for the concentration of 5×10^{-5} M on SS304. This indicates a good corrosion inhibition for stainless steel 410 and 304. The inhibition efficiencies of all ligands seem to be comparable

to a large extent and this may be due to the similarity of all utilized ligands in their chemical compositions, the number of donor atoms (nitrogen and oxygen) and structures. The inhibition efficiency of the ligands can be illustrated on the basis of their larger molecular sizes and electron donating nature lead to a larger surface coverage of the metal and a high bond strength between the molecule and the metal surface. This was indicated from the fact that, by increasing the inhibitor concentration, both (θ) and (η %) were increased while (R) was reduced. So, the dissolution of stainless steel in the presence of the investigated inhibitors can be interpreted on the basis of interface inhibition mode, the inhibitors act effectively at the metal solution interface [10].

Biological activity

The in vitro biological screening effects of the investigated compounds were tested against two bacterial strains; *Escherichia coli* (*E. coli*) as Gram-negative and *Staphylococcus aureus* (*S. aureus*) as Gram-positive and also antifungal screening was studied against two species, *C. albicans* and *A. flavus* microorganisms. The antibacterial and antifungal activities obtained for the prepared compounds are listed in Table 10. The ligands and Pd complexes show a moderate activity against Gram-negative and Gram-positive microorganisms while Zn complexes have higher antibacterial effect than Schiff bases. This enhancement in the activity can be explained on the basis of chelation theory [46]. On the other hand, the ligands and the tested complexes show a moderate activity against *C. albicans* fungi and no antifungal activity against *A. flavus*.

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Table 10					
Biological	activities	of ligand	s and	their	complexes.

Compound	Diameter of inhibition zone (mm)					
	Escherichia coli (G–)	Staphylococcus aureus (G+)	Aspergillus flavus (Fungus)	Candida albicans (Fungus)		
L ¹	10	12	0.0	10		
L ²	11	10	0.0	9		
[PdL ¹]Cl	10	11	0.0	10		
$[PdL^2]Cl_2$	9	9	0.0	9		
$[ZnL^1](AcO)_2 \cdot H_2O$	16	19	0.0	10		
$[ZnL^2](AcO)_2 \cdot H_2O$	18	17	0.0	9		
Streptomycin antibacterial agent	21	24	_	_		
Chlorometazole antifungal agent	-	-	23	20		

Conclusion

Zn(II) and Pd(II) complexes of the Schiff bases derived from furfuraldehyde and 4,5-dimethyl-1,2-phenylendiamine or 4,5dichloro-1,2-phenylendiamine were prepared and characterized. The study reveals that the formation of 1:1 Schiff base/metal ion complexes in all cases. The Schiff bases behave as a neutral tetradentate ligand and are coordinated to the central metal ion through the azomethine N and furan O. Pd(II) complexes have square planar geometry while Zn(II) complexes have tetrahedral geometry. The zinc(II) complexes with these ligands present interesting fluorescence properties. The corrosion inhibition data considered these ligands as efficient corrosion inhibitors. The ligands and their metal complexes show a biological activity against bacterial species and *C. albicans* fungi.

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