Synthesis, Characterization and Antibacterial Activities of New Pd(II) And Pt(IV) Complexes of Some Unsymmetrical Tetradentate *Schiff* Bases

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Authors' contributions

Research Article

ABSTRACT

New palladium (II) and platinum (IV) complexes with a series of unsymmetrical tetradentate *Schiff* bases derived from aromatic 2-hydroxy aldehydes in an ethanolic medium were synthesized and characterized by elemental analyses, melting points, magnetic susceptibility, thermogravimetry, differential scanning calorimetry (*DSC*), infrared (*IR*), and electronic spectral measurements. The purity of the ligands and the metal complexes are confirmed by microanalysis, while the unsymmetrical nature of the ligands was further corroborated by ^{1}H-NMR spectroscopy. Comparison of the *IR* spectra of the *Schiff* bases and their metal complexes confirm that the *Schiff* bases act as tetradentate and coordinated *via* the two azomethine nitrogens and the two phenolic oxygens. Magnetic moments and electronic spectral data confirm square planar geometry for the Pd(II) and Pt(IV) complexes.
Thermal studies reveal a general decomposition pattern, whereby the complexes decomposed partially in a single step due to loss of part of the organic moiety. The *Schiff*

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bases and their complexes were screened in vitro against 10 human pathogenic bacteria.

1. INTRODUCTION

Metal complexes of *Schiff bases* occupy a central role in coordination chemistry for analytical, physical, and biochemical purposes (Desai and Thaker, 1990; Lamrani et al., 1995; Attari et al., 1997; Zhang et al., 1996; Li et al., 1997; Ibrahim et al., 1998; Levitin and Tsikalova, 1998; Pereira et al., 1998; Zhou et al., 1999; Anacona and Brito, 1999; Campos et al., 1999; Taha, 2001; Zhao and Yuan, 1993; Issa and Hegazy, 2001; Sengupta et al., 2006; El-Tabl et al., 2007, 2008; Gao-fei et al., 2007; Singh and Katiyar, 2008; Hegazy and Al-Motawaa, 2011; Hegazy, 2001). Coordination complexes with substituted salicylaldehydes have shown diverse structures and properties generating a variety of stereochemistries and a wide range of bonding interactions (Yoshida and Yamada, 1967; Elmali et al., 2000; Soliman and Linert, 1999; Zolezzi et al. 1999). The synthesis and characterization of symmetrical tetradentate *Schiff* base complexes have been thoroughly studied and reported in the literature (Yamada, 1999; Sallomi and Shaheen, 1998; Mahmoud khani et al., 2002; Ghames et al., 2006; Proetto et al., 2012), but only a few unsymmetrical complexes are available (Tan et al. 1990; Burke and McMillin, 1980; Kolawole and Osowole, 2009). Recently, oxovanadium(IV) complexes with a series of unsymmetrical *Schiff* bases were reported (Nejo et al., 2009). In this article, we report palladium (II) and platinum (IV) complexes of the unsymmetrical ligands and their antibacterial studies. Single crystal of the complexes could not be isolated from any solutions. However, analytical, spectroscopic, and magnetic data enable us to propose possible structures. The complexes investigated are reported for the first time.

2. EXPERIMENTAL

2.1 Materials and Methods

All reagents and solvents were of the spectroscopic grades and used as received. Ethanol, methanol, chloroform, *DMF*, *DMSO*, salicylaldehyde, 5-chlorosalicylaldehyde, 5-nitro-salicylaldehyde, 3-ethoxysalicyl-aldehyde, 2-hydroxy-1-naphthaldehyde, o-phenylene-diamine are from Aldrich-Sigma company. Anhydrous Palladium (II) chloride (59% -Merck) and anhydrous Platinum (IV) chloride (57.5% - Merck) were used. Elemental analyses were determined at the Microanalytical Centre, Cairo University, Egypt. *IR* spectra were recorded on Perkin Elmer (spectrum 1000) *FT-IR* spectrometer using KBr pellets at the chemistry department, College of Science, King Fahd University for Petroleum and Minerals Saudi Arabia. Conductance of the metal complexes was determined in *DMF* using a YSI-32 model conductometer. Magnetic measurements were done on solid complexes using the Gouy method. Melting points were recorded on a Gallenkamp apparatus and are uncorrected. Thermogravimetric analyses were measured under nitrogen flow rate: 30 cm^3 min^{-1} using a Shimadzu *TGA-60H* thermobalance from room temperature up to 700ºC at the Chemistry Department, College of Science and King Saud University, Saudi Arabia. The differential scanning calorimetry (*DSC*) analysis was carried out at 20ºC min^{-1} heating rate up to 450ºC using a Perkin Elmer *DSC* 4000 series, which was calibrated with indium metal.

2.2 Synthesis of the Compounds

The procedure for the preparation of the unsymmetrical *Schiff* bases was reported elsewhere (Nejo et al., 2009). The complexes were prepared easily and in good yield from an equimolar ratio of the ligands and the metal chloride. So, by the addition of (1.0 mmol) of $PdCl_2$ dissolved in 20 cm^3 ethanol and (1.0 mmol) $PtCl_4$ dissolved in 20 cm^3 acetone, to a magnetically stirred warmed (40ºC) solution of the ligand (1.0 mmol) in ethanol (20 cm^3). The color of the mixture changed instantly. The mixtures were refluxed for 2.5 h. The complexes were precipitated which, upon cooling, were filtered, washed several times with cold methanol, and allowed to dry in a desiccator over silica gel.

2.3 Biological Studies

2.3.1 Bacterial strains

The metal complexes and ligands were individually tested against a penal of microorganisms (Gram negative and Gram positive), namely *Enterobacter cloacae*, *Serratia marcescens*, *Acinetobacter calcaoceuticus*, *Acinetobacter calcaoceuticus anitratus*, *Salmonella spp.*, *Staphylococcus aureus*, *Bacillus pumilus*, *Bacillus subtilis*, *Staphylococcus epidermidis*, and *Micrococcus kristinae*. The organisms were obtained from the Department of Microbiology, National Research Centre, Egypt.

2.3.2 Disc diffusion assay

Antibacterial activity of the ligands and metal complexes were carried out using the disc diffusion method described by Bauer et al. (Bauer et al., 1966). Bacteria were maintained on Mueller–Hinton nutrient agar at 4ºC. Molten Mueller-Hinton agar was inoculated with a broth culture of the respective bacterial strains and poured over previously washed and sterilized 90 mm Petri dishes. Palladium (II) chloride, platinum (IV) chloride, metal complexes, and ligands were dissolved in *DMSO* to a final concentration of 10 mg cm^{-1} and sterile Whatman filter paper No. 1(6 mm) discs were separately impregnated with each sample to be tested at 5.0 mg cm^{-1} and placed on the inoculated agar. The plates were incubated at 37ºC for 24 h and the zones of inhibition were measured at the end of the incubation period. Chloramphenicol was used as the standard antibiotic for reference drug.

2.3.3 Minimum inhibitory concentration

The minimum inhibitory concentrations (*MICs*) of the ligands, metal complexes, and Palladium (II) chloride, platinum (IV) chloride that showed antibacterial activities were determined using the 96-well micro-plate dilution method described (Eloff , 1998). The serial plate concentrations were 5.0, 2.5, 1.25, 0.625, 0.313, 0.157, 0.078 and 0.039 mg cm^{-1} for the compounds. Standard antibiotic (chloramphenicol) was used as positive control. Bacteria were grown for 18 h in nutrient broth and cultures of 108 colony forming unit (cfu) cm^{-1} were used and incubated for 24 h at 37ºC. As an indicator of bacterial growth, 40 cm^3 of 0.2 mg cm^{-1} p-iodonitrotetrazolium (*INT*) solution was added to each well and incubated at 37ºC for 30-120 min. The colorless tetrazolium salt was reduced to a red-colored product by the biological activity of the organisms, thereby making the inhibition of bacterial growth visible as a clear well. *MICs* values were recorded as the lowest concentration in which there was no bacterial growth. Each treatment was repeated thrice.

3. RESULTS AND DISCUSSION

3.1 Synthesis

A series of new unsymmetrical tetradentate *Schiff* base complexes of Pd(II) and Pt(IV) were prepared by refluxing the relevant unsymmetrical *Schiff* bases with the corresponding metal chloride in methanol at 1:1 molar ratio as in the scheme presented in Fig. 1. All the metal complexes are stable, non-hygroscopic, insoluble in common organic solvents but partially soluble in chloroform and *DMSO*. The unsymmetrical *Schiff* base complexes did not melt or decompose when heated to 250⁰C. The purity of the *Schiff* bases and their metal complexes as formulated were established by microanalyses. Although crystal structures are not available, the proposed structures are consistent with all other evidence. The analytical data, color, percentage yields, melting points and magnetic moments of the compounds are presented in Table 1.
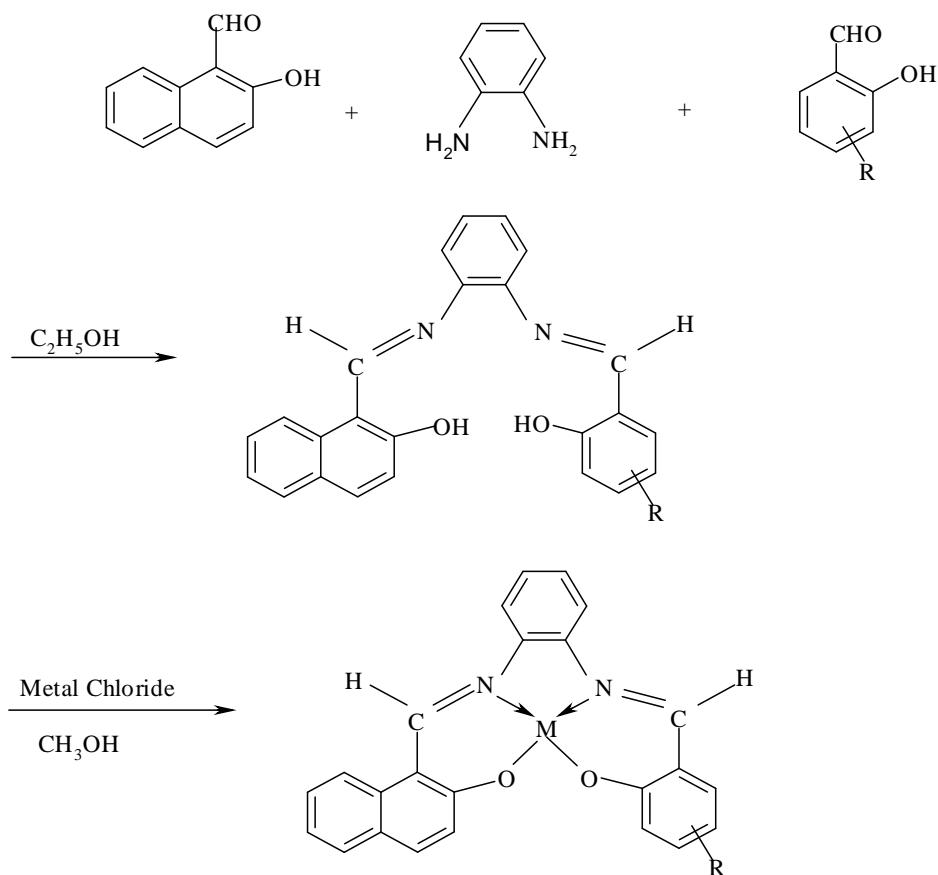
R=5-Cl, H_2L^1; R=5-NO_2, H_2L^2; R=3-OC_2H_5, H_2L^3; R=H, H_2L^4

Fig. 1. Preparation of the *Schiff* bases and their metal complexes

Table 1. Physical properties of the prepared compounds

Compound	Molecular Formula (Formula Weight)	Yield (%)	Color	M. p. °C	Microanalysis (Calc.)			μ eff. *B.M.*
					% C	%H	%N	
H_2L^1	$C_{24}H_{17}N_2O_2Cl$ (400.58)	89.6	Orange-yellow	195	71.60 (71.94)	4.73 (4.29)	6.60 (6.81)	-
PdL^1	$C_{24}H_{17}N_2O_2ClPd$ (504.99)	91.3	Brown	> 250°C	56.88 (57.08)	3.34 (3.39)	5.43 (5.55)	0
PtL^1	$C_{24}H_{17}N_2O_2ClPt$ (595.94)	90.9	Brown	> 250°C	48.42 (48.37)	2.82 (2.88)	4.71 (4.70)	0
H_2L^2	$C_{24}H_{17}N_3O_4$ (411.12)	84.7	Orange-yellow	135	69.69 (70.06)	4.23 (4.21)	10.12 (10.12)	-
PdL^2	$C_{24}H_{17}N_3O_4Pd$ (515.53)	84.1	Brown	> 250°C	55.80 (55.92)	3.23 (3.32)	8.57 (8.15)	0
PtL^2	$C_{24}H_{17}N_3O_4Pt$ (604.21)	86.9	Brown	> 250°C	48.59 (47.71)	2.25 (2.24)	7.11 (6.96)	0
H_2L^3	$C_{26}H_{22}N_2O_3$ (410.16)	76.6	Orange-yellow	136	76.34 (76.07)	5.51 (5.37)	6.79 (6.84)	-
PdL^3	$C_{26}H_{22}N_2O_3Pd$ (514.57)	81.4	Brown	> 250°C	61.23 (60.69)	4.28 (4.31)	5.43 (5.44)	0
PtL^3	$C_{26}H_{22}N_2O_3Pt$ (603.25)	79.1	Brown	> 250°C	52.06 (51.77)	3.63 (3.68)	4.55 (4.64)	0
H_2L^4	$C_{24}H_{18}N_2O_2$ (366.14)	82.5	Orange-yellow	188	78.41 (78.54)	4.81 (4.91)	7.62 (7.77)	-
PdL^4	$C_{24}H_{18}N_2O_2Pd$ (470.54)	84.2	Brown	> 250°C	61.81 (61.26)	3.72 (3.86)	5.52 (5.95)	0
PtL^4	$C_{24}H_{18}N_2O_2Pt$ (559.22)	87.5	Brown	> 250°C	52.01 (51.55)	3.22 (3.25)	5.12 (5.01)	0

3.2 IR Spectra

The positions of the important bands of the compounds are shown in Table 2. Tentative assignments of the observed bands for the compounds were made by comparing spectra of the metal complexes with those of the *Schiff* bases. Due to the unsymmetrical nature of the ligands and the complexes two bands were observed for each of the following bonds, (C=N), (C-O), (M-N), and (M-O) taking their origin from the different aldehydes (Nejo et al., 2009) The ligands exhibited characteristic C=N stretching frequency at 1610-1621 and 1567-1583 cm^{-1}, which shift to lower frequencies at 1603-1609 and 1557-1572 cm^{-1}, respectively, upon complexation. This indicates participation of the azomethine nitrogen in bonding (Aranha et al., 2007). The corresponding phenolic C-O stretching frequency occurs at 1313-1333 and 1276-1289 cm^{-1} for the ligands and at 1325-1366 and 1287-1317 cm^{-1} for the complexes. The shift confirms participation of the phenolic O in C-O-M bond formation (Abd-Elzaher, 2001). Thus, it can be concluded that the *Schiff* bases are tetradentate, coordinating via the azomethine N and the phenolic O. It has also been reported that the metal-ligand vibrational modes are very sensitive to substituent effects from isotopic labeling studies (Hancock and Thornton, 1969; Percy and Thornton, 1972). The substituent effects were based on the position of substitution rather than the nature of the substituents. The (M-O) bands are observed to exhibit higher vibrational frequencies than the (M-N) bands for the meta-substituents, while the order is reversed for para-substituents regardless of the nature of the substituents. The substituents in the complexes reported in this study are located in the 3- and 5-positions on the salicylaldehyde ring and it is expected that (M-O) bands would be greater than (M-N) bands, as shown in Table 2. For ML_1-ML_3, assignments of (M-O) bands in the meta-substituted complexes are located at 501-554 and 545-577 cm^{-1}, while (M-N) bands are at 421-467 and 457-498 cm^{-1}. Corresponding assignments for ML_4 are at 415-431 and 460-463 cm^{-1}, for (M-O) and 509-554 and 570-583 cm^{-1}, for (M-N).

Table 2. Selected IR spectral bands of the compounds (cm^{-1})

Compound	(C=N)		(C-O)		(M-N)		(M-O)	
H_2L^1	1611	1583	1313	1276	-	-	-	-
PdL^1	1609	1572	1352	1280	457	431	545	510
PtL^1	1606	1564	1364	1282	459	421	563	501
H_2L^2	1621	1567	1333	1289	-	-	-	-
PdL^2	1604	1557	1361	1314	460	431	560	507
PtL^2	1603	1558	1359	1298	471	453	561	542
H_2L^3	1610	1569	1316	1283	-	-	-	-
PdL^3	1606	1562	1366	1288	498	433	577	554
PtL^3	1605	1558	1358	1306	488	467	574	548
H_2L^4	1615	1568	1313	1286	-	-	-	-
PdL^4	1603	1557	1353	1292	570	554	463	431
PtL^4	1606	1561	1360	1317	583	509	460	415

3.3 ^{1}H-NMR Spectroscopy

The ligands display signals at 6.54, 6.87-7.78 and 9.67 ppm due to -CH=N, aromatic, and -OH protons, respectively. The presence of the phenolic (OH) protons at 9.67 ppm that

vanished in the spectra of the metal complexes suggested deprotonation and subsequent participation in complexation.

3.4 Electronic Spectra

Electronic absorption spectra of the Pd(II) and Pt(IV) complexes were recorded in 10^{-5} mol L^{-1} solutions of each complex in *DMSO* from 11111.11 to 52631.58 cm^{-1} at room temperature and their results are presented in Table 3. Solution spectra of all the Pd(II) complexes in *DMSO* show two bands at 20619-20877 and 25974-26178 cm^{-1}. These two transitions are assignable to square-planar geometry (Kolawole and Osowole, 2009; Boghaei and Lashanizadegan, 2000). At higher energy, two more intense absorptions are observed in the range 30395-39063 cm^{-1}, which are likely due to charge transfer or intra-ligand transitions. The assignment of square-planar geometry is supported by the diamagnetism of the complexes. The electronic spectra of Pt(IV) complexes consist of two energy bands at 20106-20713 cm^{-1} and 26654-26821 cm^{-1} which is assignable to square-planar geometry of Pt(IV) complexes. One strong high energy band at 30211-34961 cm^{-1} is also observed, assigned to metal-ligand charge transfer. The electronic spectral data are given in Table 3.

Table 3. Electronic spectral data of the complexes

Complex	d-d Transition/cm^{-1} (cm^{-1} mol^{-1})	C. T.	Ligand[a]
PdL[1]	20786 (161), 25974 (375)	30581 (195)	39063 (658)
PdL[2]	20877 (155), 25840 (404)	30395 (232)	31250 (216)
PdL[3]	20619 (150), 26178 (340)	30675 (217)	38168 (638)
PdL[4]	20746 (172), 26117 (340)	30303 (234)	38155 (820)
PtL[1]	20213 (151), 26654 (345)		32250 (262)
PtL[2]	20106 (177), 26691 (340)		34314 (901)
PtL[3]	20666 (103), 26821 (375)	30211 (231)	
PtL[4]	20713 (187), 26816 (400)	30455 (236)	34961 (482)

[a] *The spectra were noisy in the UV region and some of the bands could not be extracted*

3.5 Magnetic Susceptibility Measurements

Pd(II) complexes have $4d^8$ electronic configuration and should exhibit a magnetic moment higher than expected for two unpaired electrons in octahedral (2.8-3.2 *B.M.*) and tetrahedral (3.4-4.2 *B.M.*) complexes. Deviations from spin-only moment of 2.83 B.M. is due to two unpaired electrons are attributed to orbital contributions. However, Pd(II) square-planar complexes are diamagnetic (Boghaei and Lashanizadegan, 2000). The observed diamagnetism confirms the square planar environment for the Pd(II) complexes, Table 1. At room temperature Pt(IV) complexes observe diamagnetism. These results, Table 1 support the square planar geometry for Pt(IV) complexes.

3.6 Thermal Analysis

The thermal decomposition characteristics of the Pd(II) and Pt(IV) complexes were studied using thermal analytical techniques (*TGA* and *DSC*) under nitrogen. Transition temperatures, enthalpy changes, and decomposition temperatures of complexes are tabulated in Table 4.

The results show good agreement with the formulas suggested from the analytical data, Table 1. The *TGA* data indicate that H_2L^1, H_2L^2, H_2L^3, and H_2L^4 start decomposition at 244ºC, 239ºC, 266ºC and 246ºC, respectively, indicating H_2L^3 has the greatest stability. The thermograms of the Pd(II) and Pt(IV) complexes exhibited no mass loss up to 362.4ºC, indicating the absence of coordinated solvent and high thermal stability of the complexes. A single decomposition step which involved partial loss of the same set of organic moieties was observed for the metal complexes.

In the *TGA* curve of the PdL^1 complex an estimated mass loss of 25.64% (Calc.=25.72%) was observed at 402.5ºC, attributed to the loss of C_6H_4 and HCN from the organic moiety. The decomposition curve of PdL^2 showed single-step degradation with an onset temperature of 382ºC and an estimated mass loss of 20.4% (Calc.=20.26%). The weight loss is attributed to loss of C_6H_4 and HCN. For this step, an exothermic peak with t_{max}=428.6ºC in the *DSC* was observed. The PdL^3 complex was stable up to 362.4ºC where the decomposition began. The thermogram of the PdL^3 complex showed a mass loss of 30.93% (Calc.=31.04%), which corresponds to the loss of C_6H_4, 2HCN, and C_2H_5. The onset of decomposition of the PdL^4 complex occurs at 385.5ºC with an estimated mass loss of 21.99% (Calc.=21.89%), which may be attributed to the loss of C_6H_4 and HCN. The order of thermal stability of the Pd(II) complexes, PdL^1 > PdL^2 > PdL^4 > PdL^3, showed that the complexes with electron-withdrawing substituents on the salicylaldehyde were more stable than the other complexes.

In the *TGA* curve of the PtL^1 complex proceeded with a single degradation step. The onset degradation temperature begins at 422.9ºC with an estimated mass loss of 22.03% (Calc.=21.82%), accompanied by an exothermic peak with t_{max}=432.9ºC on the *DSC* curve which reasonably accounted for the combined loss of C_6H_4 and 2HCN groups. The thermogram of the PtL^2 complex showed a mass loss of 13.18% (Calc.=12.60%) at the onset degradation temperature of 415.4ºC and an exothermic *DSC* peak in this region, t_{max}=430.8ºC, which also corresponds the loss of C_6H_4. The thermogram of the PtL^3 complex shows an estimated mass loss of 17.24% (Calc.=17.08%) with a corresponding exothermic peak with t_{max}=423.3ºC on the *DSC* curve which could be attributed to the loss of C_6H_4 and HCN. The *TGA* curve of the PtL^4 complex showed single-step decomposition. The onset decomposition temperature begins at 413.2ºC with an estimated mass loss of 13.86% (Calc.=13.61%), attributed to the loss of C_6H_4. An exothermic peak with t_{max}=418.1ºC on the *DSC* curve was observed for this step. The order of thermal stability of the Pt(IV) complexes, PtL^2 > PtL^1 > PtL^4 > PtL^3, corresponds to the reverse order for that of the free ligands, thus coordination seemed to have stabilized the ligands.

DSC studies presented a melting process (endothermic peaks) at 381.5°C, 265.3°C, 313.4ºC, 439.3ºC, 256.2ºC, and 348.8ºC for PdL^1, PdL^3, PdL^4, PtL^1, PtL^3, and PtL^4, respectively, which confirmed that these complexes did not melt below 250ºC. The complexes with the nitro substituent (PdL^2 and PtL^2) decomposed (exothermic peaks) without melting. All complexes investigated decomposed (exothermic peaks) with H values ranging from as low as -74.3 J g^{-1} to as high as -368.4 J g^{-1} for, Table 4.

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Table 4. Thermoanalytical results (*TGA, DSC*) of the complexes

Complex	T^a ºC	Weight Loss[a] (Calc.) %	Endothermic		Exothermic		Decomposition Assignment
			t_{min}^b, ºC	H^b, Jg^{-1}	t_{max}^b, ºC	H^b, Jg^{-1}	
PdL[1]	397.5	25.64 (25.72)	381.5	15.4	402.5	- 235.2	C_6H_4, HCN
PdL[2]	382.0	20.40 (20.26)	-	-	428.6	- 184.4	C_6H_4, HCN
PdL[3]	362.4	30.93 (31.04)	265.3	32.1	382.6	- 74.3	C_6H_4, 2HCN, C_2H_5
PdL[4]	385.5	21.99 (21.89)	313.4	80.3	417.1	- 206.6	C_6H_4, HCN
PtL[1]	422.9	22.03 (21.82)	439.3	94.3	432.9	- 146.4	C_6H_4, 2HCN
PtL[2]	415.4	13.18 (12.60)	-	-	430.8	- 344.6	C_6H_4
PtL[3]	406.3	17.24 (17.08)	256.2	44.2	423.3	- 212.7	C_6H_4, HCN
PtL[4]	413.2	13.86 (13.61)	348.8	86.4	418.1	- 368.4	C_6H_4

T^a: Onset decomposition temperature from TGA; [a]: Data obtained from TGA; 15ºC min^{-1} under N_2; [b]: Data obtained from DSC; 20ºC min^{-1} under N_2

3.7 Biological Properties

Antibacterial activity of the ligands and complexes were tested in vitro against 10 human pathogenic bacteria. The activities were compared with that of chloramphenicol, a standard broad-spectrum antibiotic for bacterial strains. The compounds were tested at a concentration of 5 mg cm^{-1} in *DMSO* using the paper disc diffusion method. The growth inhibition zones were measured in diameter (mm) and the results are reproduced in Table 5. The susceptibility zones measured were clear zones around the discs killing the bacteria. All the *Schiff* bases and their complexes exhibit varying degrees of inhibitory effects on the growth of the tested bacterial species.

H_2L^1 and H_2L^2 were effective against all the bacteria, with inhibitory zones of 8-12 and 9-14 mm, respectively. H_2L^3 was effective against eight organisms, with inhibitory zones of 8-10 mm, whereas H_2L^4 was effective against five organisms with inhibitory zones of 9-10 mm. The Pd(II) and Pt(IV) complexes of all the *Schiff* bases were highly effective against all the bacterial strains with zones of inhibition of 10-24 mm. The increased activity of the metal complexes can be explained on the basis of Overtones concept (Dharmaraj et al., 2001) and Tweedy's chelation theory (Tweedy, 1964). Metal complexes also disturb the respiration process of the cell and thus block the synthesis of proteins, which restricts further growth of the organism (Dharmaraj et al., 2001). A general observation is that the Pt(IV) complexes were more active than the Pd(II) complexes while the standard drug, chloramphenicol, exhibited higher antimicrobial activity than the *Schiff* bases and their metal complexes, with inhibitory zone of 18-30 mm.

MICs values of the 10 bacteria strains used in this study are presented in Table 6. Antibacterial *MICs* less than 1 mg cm^{-1} is considered to be an acceptable antibacterial activity (Aligiannis et al., 2001). When the *Schiff* bases and the corresponding complexes have the same *MICs*, the complexes are considered to be more active because of the lower molar concentration of the complexes due to higher molecular mass. The free ligands and metal complexes exhibit pronounced antibacterial activities against some bacterial strains, in a number of cases comparable or even higher with that of chloramphenicol. In general, the antibacterial results show that the majority of the metal complexes were more active than their respective *Schiff* bases. Chloramphenicol showed the lowest *MICs* value of less than 0.0098 mg cm^{-1} against eight bacterial strains used in this study and was more active than all the compounds tested when their *MICs* values are compared.

Table 5. The antibacterial activities of the *Schiff* bases and their metal complexes

Bacterial Strains	Diameter of the Inhibition Zone of Bacteria in Different Compounds												
	H_2L^1	PdL^1	PtL^1	H_2L^2	PdL^2	PtL^2	H_2L^3	PdL^3	PtL^3	H_2L^4	PdL^4	PtL^4	Chloram-phenicol
E. cloacae	9.0	19.4	20.0	11.6	13.2	18.8	8.4	10.1	16.0	9.4	15.6	21.4	20.4
S. marcescens	12.6	16.2	20.1	14.2	14.2	22.1	8.1	15.2	17.3	0.0	13.2	21.1	29.1
A. calcaoceuticus	12.4	14.4	17.4	11.8	16.1	16.4	0.0	12.3	15.6	10.7	12.1	14.2	18.5
A. calcaoceuticus anitratus	12.1	16.3	16.8	12.1	13.7	15.8	8.5	7.8	14.5	0.0	12.2	15.5	23.4
Salmonella spp.	10.2	14.5	15.4	17.4	18.1	21.2	10.1	11.6	20.0	10.1	14.7	20.2	24.1
S. aureus	12.7	15.2	18.8	15.5	16.2	18.4	0.0	12.2	18.1	0.0	15.8	16.5	26.5
B. pumilus	10.5	17.7	17.9	16.2	16.0	18.9	9.2	13.4	15.0	9.4	11.4	17.2	22.4
B. subtilis	10.2	15.1	18.1	12.0	14.5	16.4	10.4	14.4	21.2	0.0	13.4	16.7	23.1
S. epidermidis	10.1	19.4	20.2	10.2	12.2	14.5	15.1	17.9	22.1	10.3	18.7	24.2	20.2
M. kristinae	8.8	21.1	22.2	9.1	17.3	18.0	9.1	9.5	12.2	0.0	10.9	19.1	24.5

Table 6. Antibacterial *mics* ($mmol\ cm^{-1}$) of the compounds

Bacterial Strains	H_2L^1 10^{-3}	PdL^1 10^{-3}	PtL^1 10^{-3}	H_2L^2 10^{-3}	PdL^2 10^{-3}	PtL^2 10^{-3}	H_2L^3 10^{-3}	PdL^3 10^{-3}	PtL^3 10^{-3}	H_2L^4 10^{-3}	PdL^4 10^{-3}	PtL^4 10^{-3}	Chloramphenicol 10^{-3}
E. cloacae	0.40	0.35	0.34	0.39	0.09	0.08	0.76	1.35	1.10	0.11	0.09	0.09	3.87
S. marcescens	1.57	0.68	0.51	1.53	0.67	0.65	1.54	0.69	0.68	0.85	0.73	0.66	< 0.03
A. calcaoceuticus	3.12	0.68	0.65	3.04	0.67	0.65	Resist.	0.34	0.32	0.85	0.73	0.72	< 0.03
A. calcaoceuticus anitratus	1.57	1.38	1.35	1.53	0.66	0.65	0.76	0.66	0.65	0.85	1.50	1.32	< 0.03
Salmonella spp.	3.12	1.38	1.35	1.53	0.68	0.60	3.05	1.35	1.35	3.69	1.50	1.30	< 0.03
S. aureus	1.57	1.38	1.30	1.53	1.36	1.35	0.78	0.70	0.70	1.72	1.50	1.12	< 0.30
B. pumilus	0.20	0.70	0.66	0.39	1.34	1.35	0.10	1.35	1.35	0.22	1.32	1.30	3.87
B. subtilis	1.57	2.73	1.75	1.53	1.35	1.35	1.54	1.35	1.30	1.72	0.75	0.70	< 0.03
S. epidermidis	0.40	1.38	1.35	0.78	1.35	1.20	1.54	1.30	1.22	0.87	2.95	1.11	< 0.03
M. kristinae	1.57	1.38	1.35	3.04	1.38	1.28	3.29	1.35	1.35	3.41	2.55	1.85	0.06

4. CONCLUSION

Four unsymmetrical tetradentate Schiff bases and their Pd(II) and Pt(IV) complexes were prepared, characterized and were screened in vitro against 10 human pathogenic bacteria. The free ligands and the metal complexes exhibit antibacterial activities against some strains of the microorganisms, which in a number of cases were comparable with that of chloramphenicol. In the future, this might open the door to their use as vital and effective antibiotics.

COMPETING INTERESTS

Authors have declared that no competing interests exist.

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