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Palladium(II) complexes as biologically potent metallo-drugs: Synthesis, spectral characterization, DNA interaction studies and antibacterial activity

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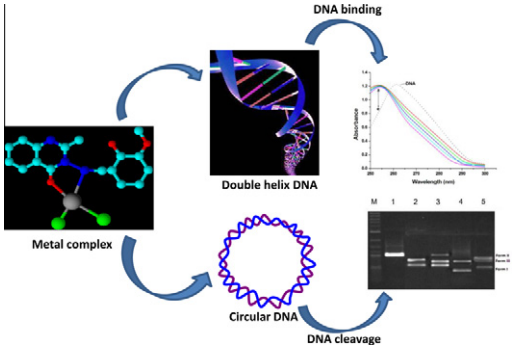
HIGHLIGHTS

- We synthesized four biologically potent palladium(II) complexes.
- The structures of synthesized complex were confirmed by spectral techniques.
- DNA binding studies show that complexes are avid binders to double helix CT-DNA.
- Palladium(II) complexes were able to cleave the supercoiled plasmid DNA even in the absence of an oxidant.

GRAPHICAL ABSTRACT

New Pd(II)-Schiff base complexes were synthesizes and characterized using spectral techniques. DNA interaction studies were performed using the synthesized Pd(II) complexes.



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ABSTRACT

Four novel mononuclear Pd(II) complexes have been synthesized with the biologically active Schiff base ligands (L_1–L_4) derived from 3-amino-2-methyl-4(*3H*)-quinazolinone. The structure of the complexes has been proposed by elemental analysis, molar conductance, IR, ^{1}H NMR, mass, UV–Vis spectrometric and thermal studies. The investigation of interaction of the complexes with calf thymus DNA (CT-DNA) has been performed with absorption and fluorescence spectroscopic studies. The nuclease activity was done using pUC19 supercoiled DNA by gel-electrophoresis. All the ligands and their Pd(II) complexes have also been screened for their antibacterial activity by discolor diffusion technique.

Introduction

Metals, in particular, transition metals offer potential advantages over the more common organic-based drugs. For example, a wide range of coordination numbers and geometries, accessible redox states, 'tune-ability' of the thermodynamics and kinetics of ligand substitution. On the basis of the structural and thermodynamic analogy between platinum(II) and palladium(II) complexes, there is also much interest in the study of palladium(II) derivatives as potential anticancer drugs [1–6].

Heterocyclic moieties can be found in a large number of compounds which display biological activity. The biological activity of the compounds is mainly dependent on their molecular

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structures [7]. Schiff bases are bimolecular condensation products of primary amines with aldehydes-represent valuable intermediates in organic synthesis and, at the same time, compounds with various applications [8]. Schiff bases resulted from aromatic aldehydes *ortho*-substituted with a hydroxyl group have initially arouse the researches interest because of their ability to act as bidentate ligands for transition metal ions [9]. Schiff bases are important class of compounds due to their flexibility, structural similarities with natural biological substances and also due to presence of imine (C=N), which imports in elucidating the mechanism of transformation and rasemination reaction in biological system [10]. These novel compounds could also act as valuable ligands whose biological activity has been shown to increase on complexation [11].

Very recently, we have reported the synthesis and biological activities of Schiff bases derived from 3-amino-2-methyl-4(*3H*)-quinazolinone [12]. In this work, we report the synthesis, DNA interaction studies and antimicrobial activity of new Pd(II) complexes with quinolin-4(*3H*)-one Schiff base ligands. To the best of our knowledge, Pd(II) complexes bearing 4(*3H*)-quinazolinone derived ligands have not been described to date.

Experimental

Materials and methods

The starting materials: 3-amino-2-methyl-4(*3H*)-quinazolinone and substituted aldehydes was obtained from Aldrich. Palladium(II) salts and solvents were commercially available of high purity and used as such. CT-DNA (calf thymus DNA) was obtained from *GENEI* laboratories, Bangalore. An elemental analysis was performed using a Perkin-Elmer 240 elemental analyzer. Infrared spectra were recorded with a JASCO FT-IR spectrophotometer from 4000 to 400 cm^{-1} using Nujol mulls technique. The UV–Visble spectra were recorded on Hitachi-3900 spectrophotometer. A Shimadzu TG-50H thermo analyzer was used to record simultaneous TGA and DTG curves in dynamic nitrogen atmosphere with a heating rate of 10 °C min^{-1}, in the temperature range 20–700 °C using platinum crucibles. ^1H NMR spectra were recorded using Varian-400 MHz spectrometer using DMSO-d_6 as a solvent. Chemical shifts are reported in parts per million downfield from tetramethylsilane. ESI-MS were determined on Varian-2000 mass spectrometer.

Antimicrobial activity

The *In vitro* antimicrobial activity of the test compounds were evaluated against three bacteria; *Bacillus subtilis* (MTCC 121) (Gram-positive), *Staphylococcus aureus* (MTCC 96) (Gram-positive) and *Escherichia coli* (MTCC 1652) (Gram-negative) by agar discolor diffusion method [13]. The test compounds were dissolved in dimethyl sulfoxide (DMSO) to a final concentration of 1 mg/mL.

The bacteria were sub-cultured in nutrient agar medium, respectively. Gentamycine was used as standard antibacterial drug, under similar conditions for comparison. The inoculated Petri dishes were incubated for 24 h at 37 °C. During this period, the test solution diffused and the growth of the inoculated microorganisms was affected. Activity was determined by measuring the diameter of zone showing complete inhibition (mm). DMSO was used as control to clarify the ambiguity (no activity was observed). All the compounds were tested in triplicates and the average of three trails were reported.

DNA interaction studies

DNA binding

The DNA binding activity of complexes **2** and **3** with calf thymus DNA (CT-DNA) was performed by using electronic absorption spectroscopy in Tris–HCl/NaCl buffer (5 mMTris–HCl, 5 mMNaCl, pH 7.2). The purity of CT-DNA was checked by measuring the absorbance at 260 and 280 nm (A_{260}/A_{280}) which was found to be 1.81 in buffer solution [14].

Fluorescence spectral studies

In order to clarify the relative binding modes of complex with CT-DNA, fluorescence spectral studies were carried out at fixed complex concentration (3 μM) and increasing CT-DNA concentration (5, 10, 15, 20 and 25 μM) [15]. The binding of the complexes with CT-DNA is evaluated by the fluorescence emission intensity of ethidium bromide (EB) bound to DNA as a probe [16].

Viscosity measurements

Viscosity titration experiments were carried in buffer solution on an Ostwald's viscometer at room temperature by varying the complex concentration at constant CT-DNA concentration (40 μM). Flow time was measured with a digital stop watch. Each sample was measured at least three times and average flow time was calculated. Data were presented as $(\eta/\eta_0)^{1/3}$ vs binding ratio ([complex]/[DNA]) [17], where η was the viscosity value for DNA in presence of the complex and η_0 was the viscosity value of CT-DNA alone.

DNA cleavage

The cleavage of plasmid DNA was monitored using agarose gel electrophoresis: supercoiled pUC19 (0.5 μg) in Tris–HCl buffer (50 mM) with 50 mMNaCl (pH 7.2) was treated with metal complexes (10^{-3} M). The samples were incubated for 1 h at 37 °C. A loading buffer containing 25% bromophenol blue, 0.25% xylene cyanol and 25% glycerol were added and electrophoresis was performed at 70 V for 2 h in TBE buffer using 1.0% agarose gel containing 1.0 μg/mL ethidium bromide [18]. Bands were visualized using UV light and photographed. The cleavage efficiency was measured by determining the ability of the complex to convert the supercoiled DNA (Form I) to nicked circular form (Form II) or linear form (Form III).

Synthesis

Synthesis of ligands (L_1–L_4)

A volume of 25 mL methanolic solution of 3-amino-2-methyl-4(*3H*)-quinazolione (1.75 g, 10 mmol) was slowly added to a 15 mL of corresponding aldehyde (10 mmol in methanol). The reaction mixture was stirred for 30 min and then refluxed for 4 h. The completion of reaction was monitored by TLC. The solvent was removed by distillation. The solid product obtained was recrystallized from ethanol to yield respective ligand (L_1–L_4). The structures of ligands are given in Fig. 1.

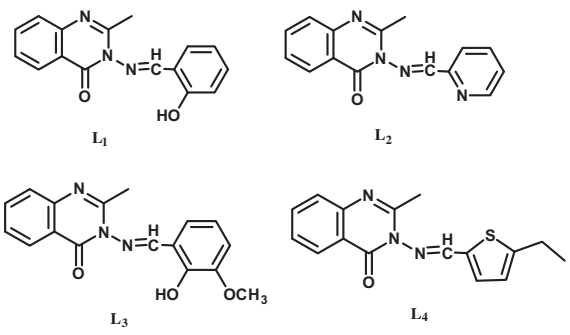


Fig. 1. Structures of Schiff base ligands.

Table 1
Elemental analysis of Pd(II) complexes.

Compound	Molecular formula	Yield (%)	Found (calcd) (%)			
			C	H	N	M
L_1	$C_{16}H_{13}N_3O_2$	71	68.43 (68.51)	4.58 (4.61)	14.9 (15.02)	–
L_2	$C_{15}H_{12}N_4O$	63	68.18 (68.27)	4.28 (4.31)	21.22 (21.32)	–
L_3	$C_{17}H_{15}N_3O_3$	61	66.01 (66.12)	4.93 (5.03)	13.58 (13.79)	–
L_4	$C_{16}H_{15}N_3OS$	79	64.62 (65.13)	5.08 (5.14)	14.13 (15.61)	–
1	$C_{16}H_{13}N_3O_2PdCl_2$	61	42.10 (42.31)	2.85 (2.97)	9.21 (9.35)	23.24 (23.42)
2	$C_{15}H_{12}N_4OPdCl_2$	67	40.90 (41.12)	2.72 (2.88)	12.72 (12.94)	24.09 (24.29)
3	$C_{17}H_{15}N_3O_3PdCl_2$	63	41.97 (42.09)	3.08 (3.19)	8.64 (8.79)	21.81 (21.97)
4	$C_{16}H_{15}N_3OSPdCl_2$	69	40.67 (40.86)	3.17 (3.29)	8.89 (9.02)	22.45 (22.64)

Table 2
The important infrared frequencies (in cm^{-1}) of Pd(II) complexes.

Compound	υ(C=O)	υ(C=N)	υ(M—N)	υ(M—O)
L_1	1603	1603	–	–
L_2	1597	1684	–	–
L_3	1586	1650	–	–
L_4	1574	1656	–	–
1	1647	1573	443	404
2	1653	1598	427	409
3	1656	1540	423	411
4	1651	1565	438	406

Synthesis of metal complexes

The Pd(II) complexes of Schiff base ligands were prepared in 1:1 ratio. To a hot methanolic solution of palladium chloride (0.170 g, 1 mmol) in 20 mL, an appropriate Schiff base ligand solution was added (L_1–L_4, 1 mmol) to obtain 1:1 complexes. The resulting mixture was stirred under reflux for 4 h, where upon the complexes were precipitated. They were collected by filtration, washed with hot water, then diethyl ether and dried in air. The analytical and physical data were reported in Table 1.

Result and discussion

The complexes [$PdCl_2$(L)] (where L = Schiff base ligands [L_1–L_4]) were obtained by reaction between the respective ligand (L_1–L_4) and the palladium salt in aqueous medium. The desired product is immediately formed as an amorphous precipitate upon addition of the ligand to the palladium salt.

The elemental analyses were in good agreement with the proposed formulas for the complexes. The reactions involved in the formation of palladium complexes are well-known substitution reactions of square-planar complexes which are favored by the *trans*-effect of the chloride ligands. The mass spectra of the complex **1** have molecular peaks; moreover, the peaks also provide support for the suggested composition and structure of the complex.

Infrared spectroscopy

The important IR bands of Schiff base ligands and their corresponding Pd(II) complexes are listed in Table 2.

The IR bands in the region 1682–1655 and 1655–1571 cm^{-1} in the Schiff bases are attributed to the ν(C=O) and ν(C=N), respectively. In the complexes **1**–**4**, these bands are shifted to lower frequencies at around 1656–1647 and 1602–1595 cm^{-1}, indicating the coordination of imine nitrogen and lactam oxygen atom to the metal ion [19]. In the IR spectra of complexes **1** and **3**, a very broad band at *ca.* 3414 and 3434 cm^{-1} were observed which is due to the OH group present in the Schiff bases L_1 and L_3, respectively (Fig. 2), reveals that the phenolic oxygen is not involved in the coordination [20].

Electronic spectra

The electronic absorption spectra of the Schiff base metal complexes in DMF were recorded at room temperature. Both the complexes exhibit an absorption band in the range 360–390 nm, which are assigned to charge transfer transition from the pπ-orbitals of the donor atoms to the d-orbitals of the metal. In addition, complexes exhibit d–d transition in the 617–724 nm range.

^{1}H NMR spectra

The ^{1}H NMR spectra of ligand L_3 and its complex **3** were recorded in DMSO-d_6 support the proposed structure of the compounds. The signal due to azomethine proton of L_3 at 8.71 ppm shows a downfield shift ca. 8.96 ppm [21] in the spectra of complex **3** suggesting the coordination of the azomethine nitrogen to the metal ion. This downfield shift is due to desheilding of

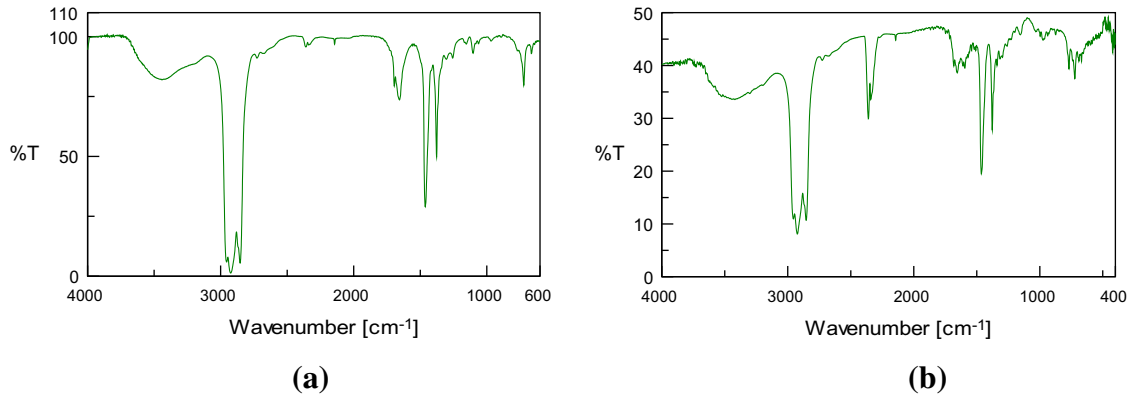


Fig. 2. IR spectra of (a) L_1 and (b) complex **1**.

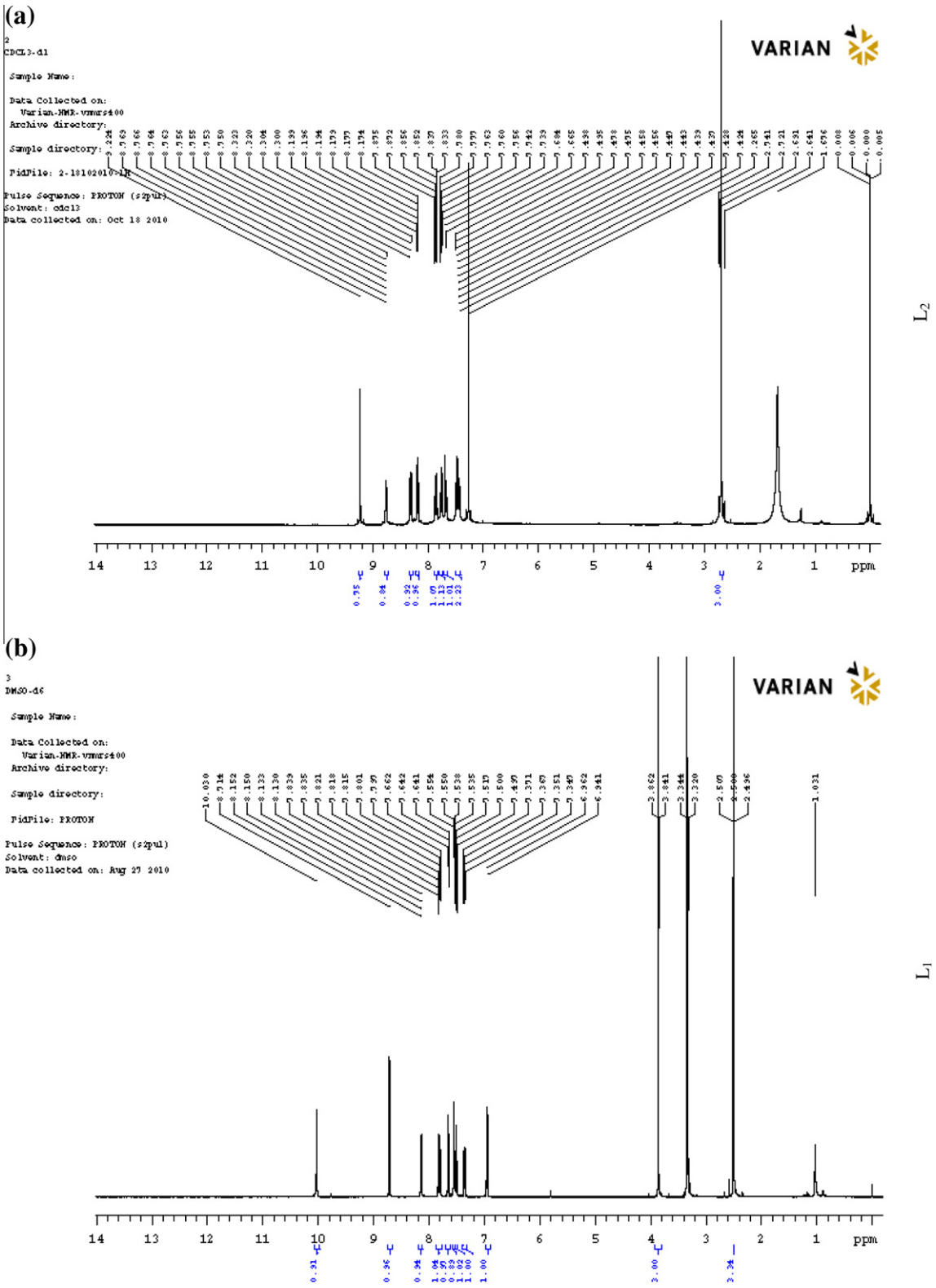


Fig. 3. ^{1}H NMR spectrum of L_1–L_4.

the = CH proton. In Fig. 3, the signal at 10.03 ppm is due to the phenolic OH group in L_3, which was found at same position in the complex **3**, indicating the non-involvement of phenolic oxygen atom in the coordination. In L_3, the multiplet *ca.* 7.0–8.2 ppm is due to the aromatic protons and signal around 3.86 ppm is due to the methoxy group.

Mass spectra

The representative mass spectrum of complex **3** is showed in Fig. 4. The molecular ion peak at m/z 486 corresponds to the molecular weight of the complex **3**. Also, the spectrum exhibited peaks for the fragments at m/z 451, 416, 310, 188, 176, 161, 147

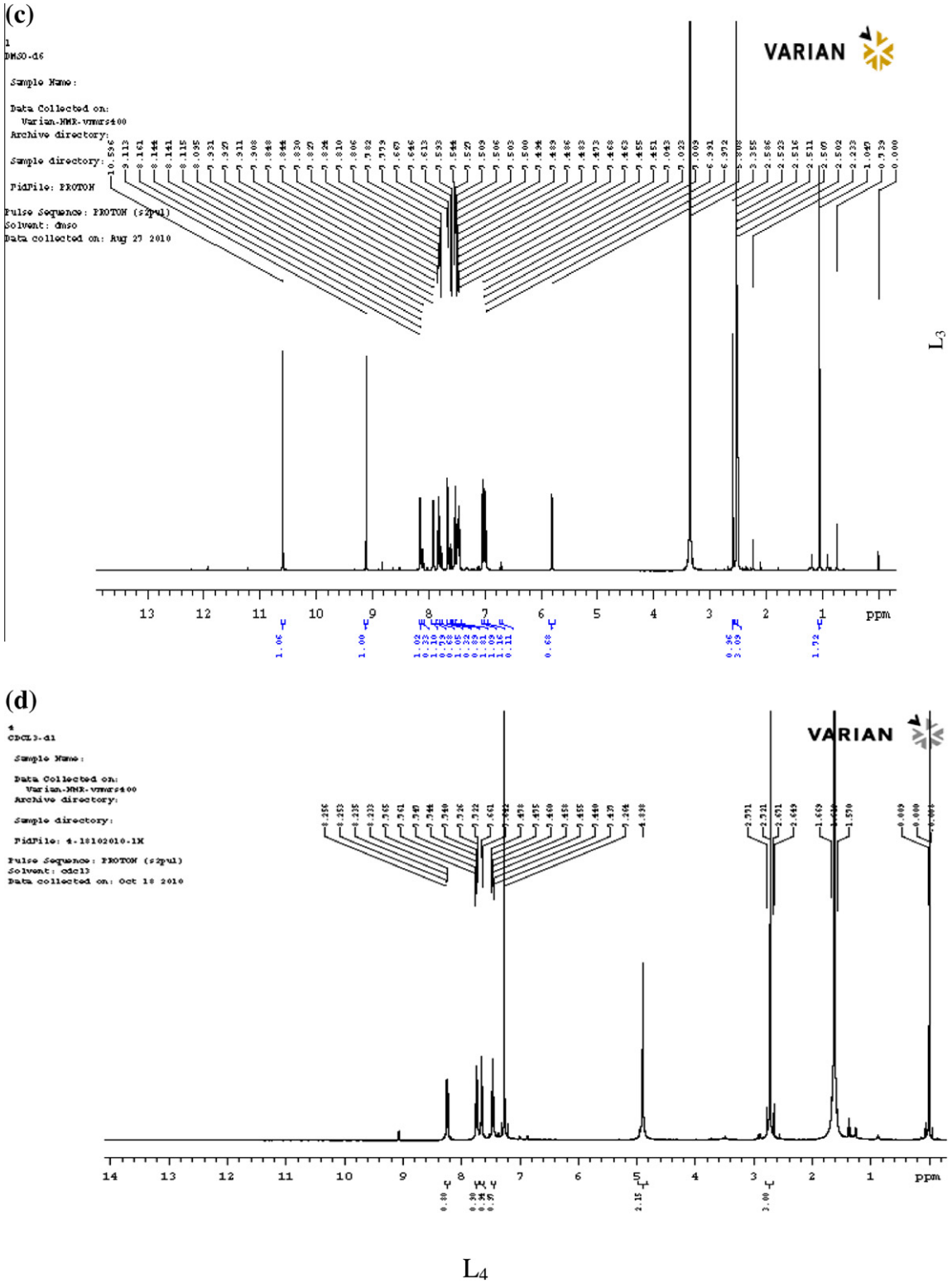


Fig. 3. (*continued*)

and 129 which are summarized in Scheme 1. Similar fragmentation pathway follows in all the complexes.

Thermal studies

The thermal decomposition behavior of complex **3** along with the% weight at different temperatures is recorded under N_2 atmosphere. Fig. 4 shows the TG and DTG curves of complex **3**. From Fig. 5, it is clear that the complex do not lose weight up to 310 °C, indicating the absence of coordinated or lattice water molecules and the same result was confirmed by spectral studies. Further rise in the temperature causes decomposition of complex in two steps. The first decomposition spans from 320 °C through 380 °C corresponds to the liberation of chloride ion as HCl [22]

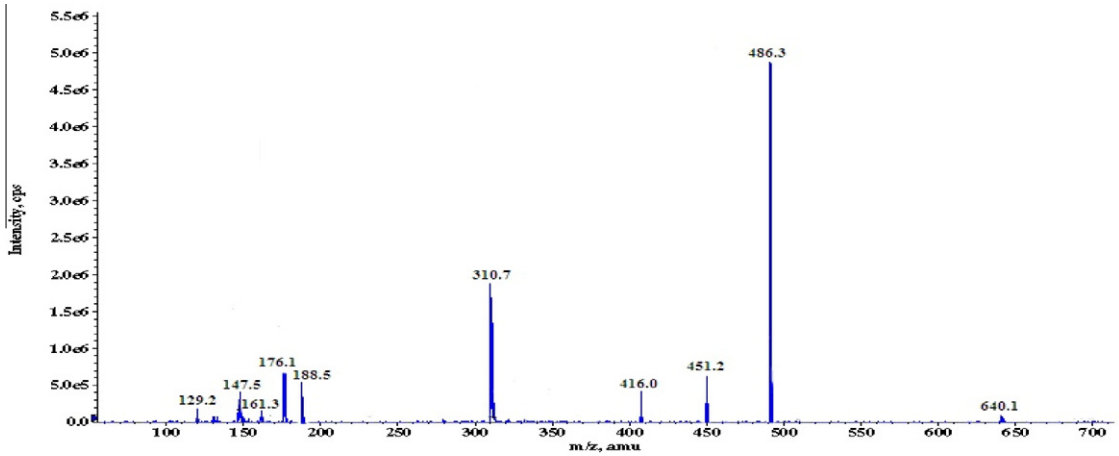
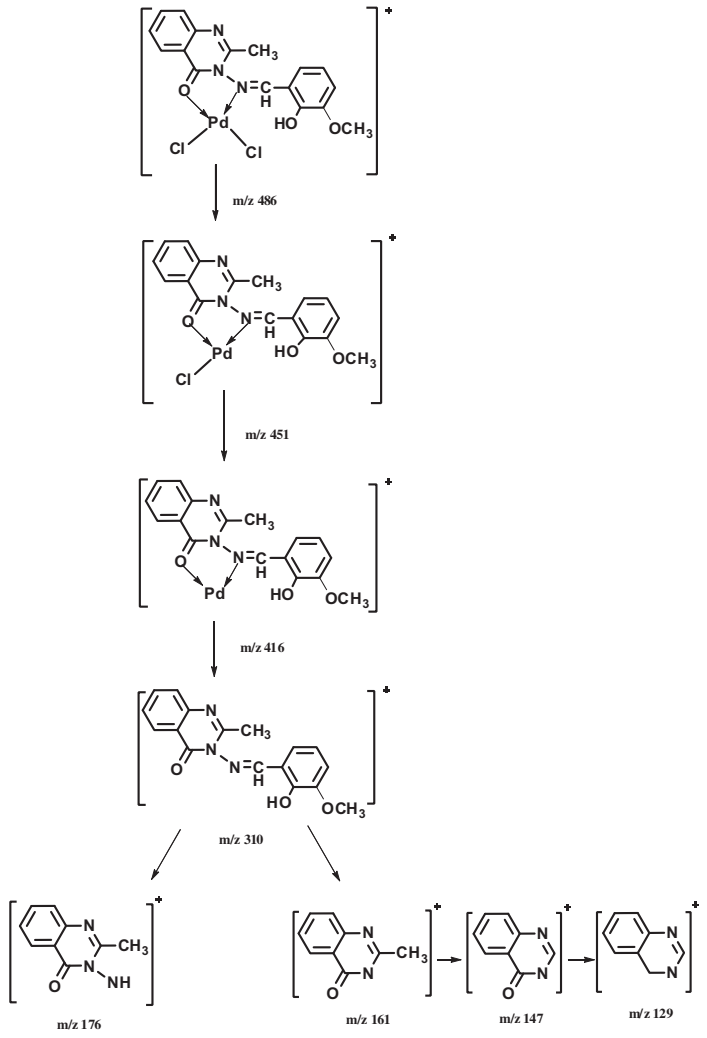


Fig. 4. Mass spectrum of complex **3**.



Scheme 1. Mass fragmentation pattern of complex **3**.

(found ~15%). The second decomposition step starts at 380 °C and terminates at about 490 °C, corresponding to the decomposition of Schiff base ligand (found 64%) leaving behind metal oxide as the end product [23]. Stepwise thermal degradation data of all complexes were presented in Table 3.

Antibacterial activity

The contribution to the field of bioinorganic chemistry is important, consequently, the synthesized Pd(II) complexes have been evaluated for their antibacterial actions. The results of the bacteri-

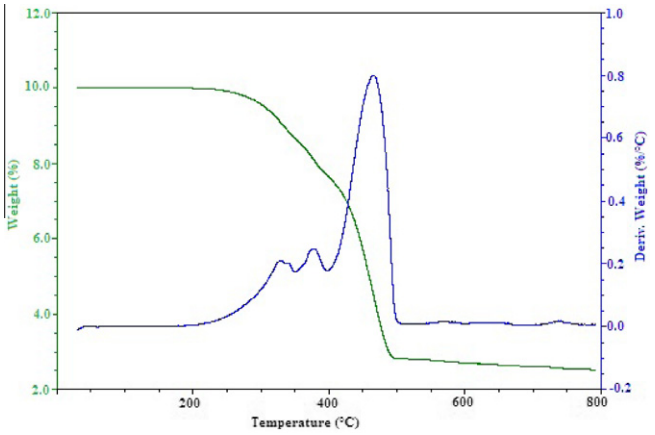


Fig. 5. Thermogravimetric curve of complex **3**.

cidal study of the synthesized compounds are reported in Table 4. Further, the antibacterial action of ligands may be significantly enhanced on chelation with metal ions. From the bactericidal activity, it is apparent that the complexes were more toxic towards gram positive strains than gram negative strains. The reason is the difference in the structure of the cell walls [24]. The walls of gram negative cells are more complex than those of gram positive cells. Further to it, the ligands showed moderate, and the complexes showed moderate to high activities and were compared with standard drug towards the entire organism.

DNA binding experiments

Fig. 6 shows the titration of the palladium(II) complex (**2** and **3**) samples in the aqueous buffer solution (50 mM NaCl/5 mM Tris–HCl, pH 7.1). The studies were performed by using a fixed complex concentration (12 μM) with increasing amounts of DNA over a range of 0.5–2 μM. The intrinsic binding constants (K_b) of complexes **2** and **3** were found to be 2.36×10^3 and 2.21×10^3 M^{-1}, respectively. The results indicate the binding obtained here are lower than that reported for classical intercalator [25]. Thus, complexes are weak binders and they bind in an intercalative stacking manner to the double helix [26].

Viscosity measurements

In order to confirm the interactions between the prepared complexes and DNA, viscosity measurements were carried out in Tris-buffer solution. A stacking intercalation model results in the lengthening the DNA helix as base pairs were separated to accommodate the complex, leading to the increase of DNA viscosity. The effects of complexes **2** and **3** on the viscosity of CT-DNA at 25 °C are shown in Fig. 7. Viscosity experimental results clearly show that Pd(II) complex can stack between adjacent DNA base pairs, causing an extension in the helix, and increase the viscosity of DNA.

Table 4
In vitro antibacterial activity of the Schiff base ligands and their Pd(II) complexes.

Compound	Concentration (μg mL^{-1})	Antibacterial activity (zone of inhibition in%)*		
		B. subtilis	*E. coli*	*S. aureus*
L_1	100	45	48	44
L_2	100	33	39	37
L_3	100	54	52	51
L_4	100	35	40	38
1	100	78	81	78
2	100	67	72	77
3	100	80	83	81
4	100	67	66	71
Gentamycine	100	100	100	100

* Average of three replicates.

Fluorescence spectra

The fluorescence spectra of complexes **2** and **3** interacting with CT-DNA were studied according to previously developed procedures [27]. The spectra are shown in Fig. 8. The fluorescence intensity of ethidium bromide (EtBr) [28] itself is very faint, but it was shown to emit intense fluorescence light in the presence of DNA due to its intercalation into DNA between base pairs. Upon addition of a second molecule, which binds to DNA more strongly than EtBr, the DNA-induced EtBr emission would be quenched [29], indicating the replacement of EtBr by the second molecule intercalated into DNA [30]. The binding isotherm of complexes **2** and **3** is again indicative of non-intercalative binding of the complexes to DNA.

Nuclease activity

The degree to which the four complexes could function as DNA cleavage agents was examined using supercoiled pUC19 plasmid DNA as the target. The efficiency of cleavage of these molecules was probed using agarose gel electrophoresis [31]. Complexes **2** and **3** were found to promote the cleavage of pUC19 plasmid DNA from supercoiled Form (I) to the nicked Form (II) or linear Form (III) (Fig. 9). A little DNA-cleavage was observed for the control in which metal complex was absent. The complexes can induce the obvious cleavage of the plasmid DNA at the concentration of 10^{-3} M in the presence and absence of an oxidant (H_2O_2).The different DNA-cleavage efficiency of the complexes may be due to the different binding affinity of the complexes to DNA.

Table 3
Stepwise thermal degradation data obtained from TGA curves and their composition.

Complex	Process	Temp. range (°C)	Products	% Weight loss		No. of moles	% Residue		Nature
				Calcd	Expt		Calcd	Expt	
$C_{16}H_{13}N_3O_2PdCl_2$	I	300–360	2HCl	15.78	15.52	2	26.75	26.37	PdO
	II	470–510	$C_{16}H_{15}N_3O_2$	61.14	60.86	1			
$C_{15}H_{12}N_4OPdCl_2$	I	290–350	2HCl	16.36	16.12	2	27.72	27.29	PdO
	II	460–520	$C_{15}H_{12}N_4O_2$	60.00	59.49	1			
$C_{17}H_{15}N_3O_3PdCl_2$	I	310–390	2HCl	14.40	13.91	2	25.10	24.77	PdO
	II	450–500	$C_{17}H_{15}N_3O_3$	63.78	62.69	1			
$C_{16}H_{15}N_3OSPdCl_2$	I	280–370	2HCl	14.83	14.18	2	25.84	25.12	PdO
	II	470–520	$C_{16}H_{15}N_3OS$	62.71	61.93	1			

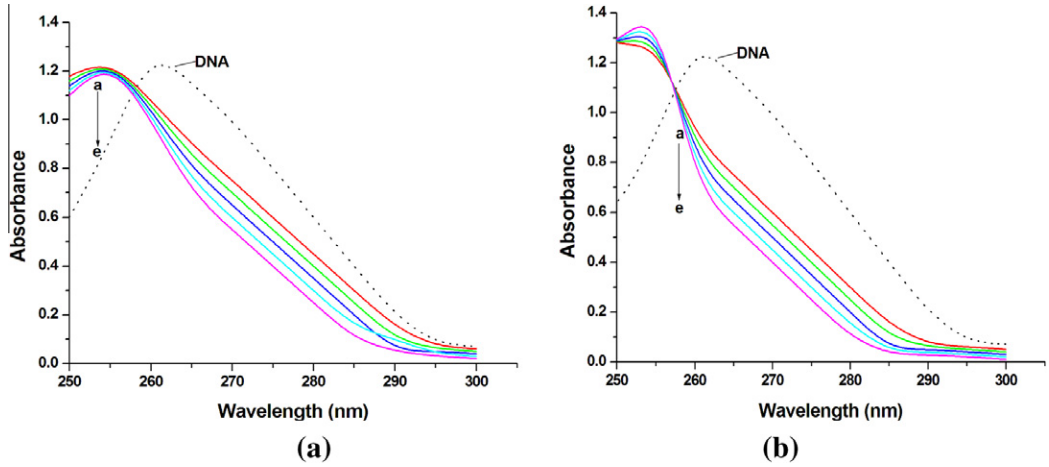


Fig. 6. Absorption spectra of (a) complex **2** and (b) complex **3**, in Tris–HCl buffer upon addition of DNA = 1×10^{-4} M, 0–25 μl. Arrow shows the absorbance changing upon increasing the concentration of DNA.

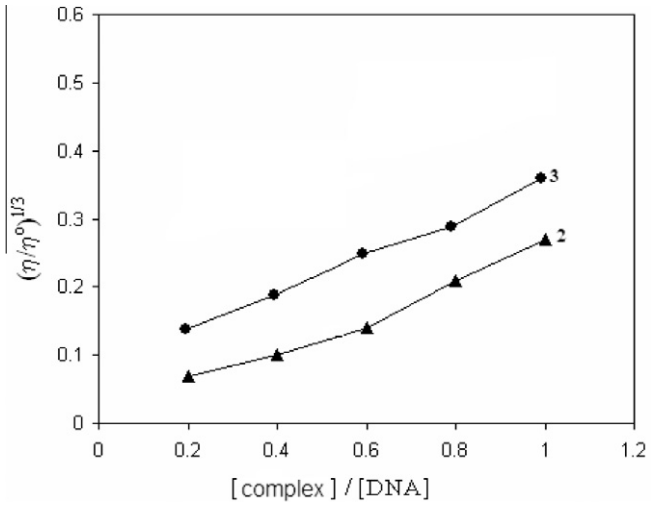


Fig. 7. Effect of increasing amount of complexes **2** and **3** on the relative viscosity of CT-DNA.

Conclusions

The synthesized palladium(II) complexes with 4(*3H*)-quinazolinone derived Schiff base ligands have been characterized using different analytical, physical and spectroscopic techniques. The above studies confirmed that the bonding of Schiff base ligands to metal ion was through azomethine nitrogen and lactonyl oxygen atom. The electronic spectral data suggested the square-planar geometry for the complexes. The DNA binding propensity of the palladium(II) complexes was determined by an electronic absorption spectroscopy, fluorescence spectroscopy and viscometric studies. The data obtained by binding studies revealed that the complexes bind in stacking manner to the double helical DNA and thus, acts as weak binding agents. The oxidative damage study of supercoiled pUC19 DNA with the complexes in the presence and absence of H_2O_2 revealed that complexes acts as good cleaving agents both in the presence and absence of an oxidant. The antimicrobial results of the Schiff bases and their Pd(II) complexes show promising activity against the selected microorganisms. In particular, ligands L_1 and L_3 and their corresponding complexes **1** and **3** showed very potent activity compared to other compounds, respectively.

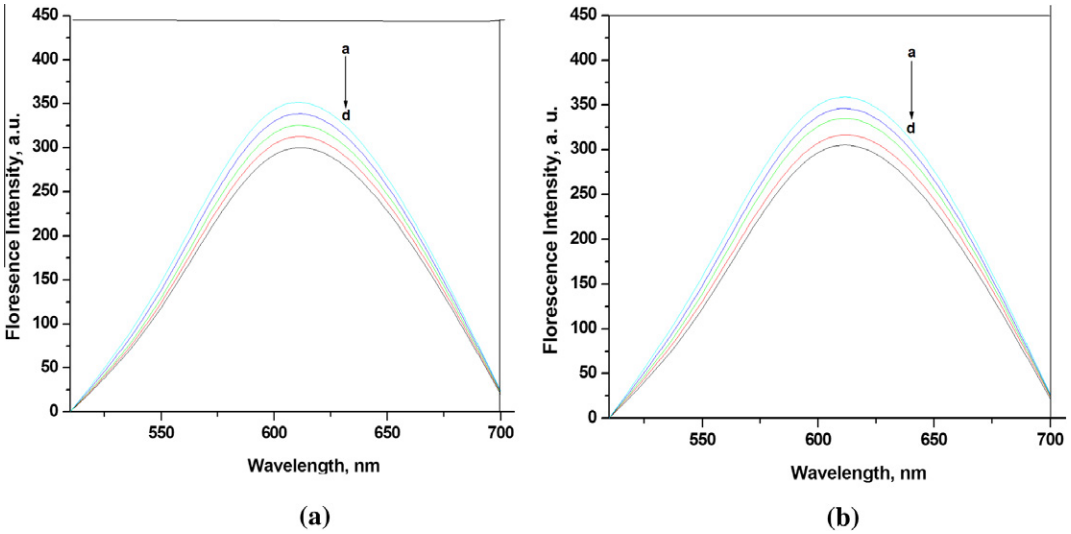


Fig. 8. Emission spectra of the complexes (a) **2** and (b) **3** inTris–HCl buffer upon addition of calf-thymus DNA. [complex] = 1×10^{-5} M, [DNA] = $(0–5) \times 10^{-5}$ M. Arrow shows the intensity changing upon increasing DNA concentrations.

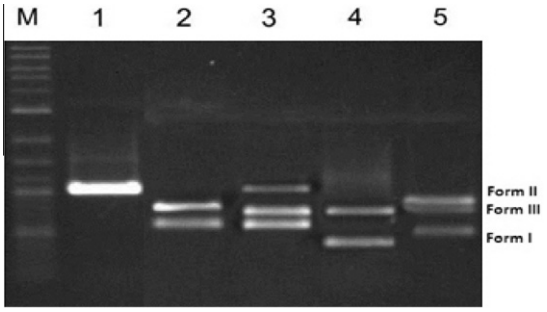


Fig. 9. Cleavage of supercoiled pUC19 DNA (0.5 μg) by the Pd(II) complexes **2** and **3** in a buffer containing 50 mM Tris–HCl at 37 °C (30 min): lane M: marker. lane 1: DNA control. lane 2: complex **2** (10^{-3} M) + DNA. lane 3: complex **2** (10^{-3} M) + DNA + H_2O_2. lane 4: complex **3** (10^{-3} M) + DNA. lane 5: complex **3** (10^{-3} M) + DNA + H_2O_2.

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Appendix A. Supplementary material

Supplementary data associated with this article can be found, in the online version, at http://dx.doi.org/10.1016/j.saa.2013.01.013.

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