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Original article

Structural and biological studies of mononuclear palladium(II) complexes containing *N*-substituted thiosemicarbazones

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Abstract

New complexes of Pd(II) with *N*-substituted thiosemicarbazone (**1**)–(**3**) have been synthesised and characterised by elemental analyses, IR, electronic, ^{1}H NMR spectroscopies. The electrochemical behaviour of the complexes has been tested by using cyclic voltammetry. The crystal structures of the complexes have been determined by single crystal X-ray diffraction technique. In all the complexes the thiosemicarbazone ligand is coordinated to palladium through ONS mode. The complex **1** crystallises in the monoclinic space group $P2_1/c$ with two molecules per unit cell, has the dimensions of $a = 9.4390(19)$ Å, $b = 10.645(2)$ Å, $c = 13.668(3)$ Å, $\alpha = 90°$, $\beta = 91.43°$ and $\gamma = 90°$. The complex **3** crystallises in the monoclinic space group $P2_1/c$ with four molecules per unit cell, has the dimensions of $a = 14.119(3)$ Å, $b = 11.155(2)$ Å, $c = 18.503(4)$ Å, $\alpha = 90°$, $\beta = 112.02°$ and $\gamma = 90°$. The new complexes have been tested for their antibacterial activity against various pathogenic bacteria. From this study, it was found out that the activity of the complex **2** almost reaches the effectiveness of the conventional bacteriocide *Streptomycin*.

Keywords: Palladium(II) complexes; Thiosemicarbazone ligands; IR; Electronic; ^{1}H NMR; Electrochemistry; X-ray crystallography; Cytotoxic studies

1. Introduction

A wide range of biological activities possessed by substituted thiosemicarbazones and their metal complexes include cytotoxic, antitumor and antileukemic properties [1–6]. They are well known chelating ligands coordinating to the metal ion through the sulphur and one of the hydrazinic nitrogen atoms (N2 or N1). Coordination through N2 results in an unusual four membered chelate ring [7–9] while with N1 hydrazinic nitrogen a more stable five membered chelate ring results [10–13]. However, on incorporation of an additional donor site into the thiosemicarbazones, their coordination behaviour becomes unpredictable. If there is intramolecular hydrogen bonding between either N2 nitrogen or N1 nitrogen and phenolic OH which reduces the availability of lone pair on the imine nitrogen preventing its coordination which might lead to the formation of either unusual four membered ring or more stable five membered ring. The steric hindrance created by the bulky ligands in six coordinated complexes is not present in four coordinated square planar complexes [10]. Though the versatility of thiosemicarbazone ligands for binding to the metal ion has been well established elsewhere, there remains an ambiguity in predicting the actual coordination mode of thiosemicarbazones. As a part of continuing interest in this area of research, we have investigated coordination behaviour of three *N*-substituted thiosemicarbazone ligands in palladium(II) complexes. The new complexes

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have been characterised by spectral, electrochemical and X-ray crystallography. With our keen interest in microbiological studies we have already reported the antimicrobial properties of many ruthenium complexes [14–16]. Herein, we have tested the cytotoxic activity of the ligands and their new Pd(II) complexes have been screened for their antibacterial activity against various pathogenic bacteria. The general structure of the ligands used in the present work is given below.

Ligand	Abbreviation
R= H; R' = C_6H_5	[H_2-Sal-ptsc]
R= C_4H_4 ; R' = C_6H_5	[H_2-Nap-ptsc]
R= C_4H_4 ; R' = CH_3	[H_2-Nap-mtsc]

2. Experimental

2.1. Materials

All the reagents used were of analar grade. Solvents were purified and dried according to the standard procedure [17]. The ligands and the starting complex $[PdCl_2(PPh_3)_2]$ used for the investigation were prepared according to the reported procedures [18–20].

2.2. Preparation of new Pd(II) complexes

2.2.1. Preparation of [Pd(Sal-ptsc)(PPh_3)] (*1*)

An ethanolic (25 mL) solution of $[PdCl_2(PPh_3)_2]$ (0.200 g; 0.285 mmol) was slowly added to [H_2-Sal-ptsc] (0.077 g; 0.285 mmol) in dichloromethane (25 mL). The mixture was allowed to stand for 4 days at room temperature. Orange red crystals obtained were washed with *n*-hexane. Yield: (154.55 mg) 85%. M.p. 216–218 °C. FT-IR (KBr): 1602 cm^{-1} ($\nu_{C=N}$), 1324 cm^{-1} (ν_{C-O}), 756 cm^{-1} (ν_{C-S}), 3262 cm^{-1} (ν_{N-H}), 1438, 1096, 702 cm^{-1} (for PPh_3). UV–vis (CH_2Cl_2), λ_{max}: 322 (6, 250), 344 (7, 240) nm ($dm^3\,mol^{-1}\,cm^{-1}$) (intra-ligand transition); 408 (15.450) nm ($dm^3\,mol^{-1}\,cm^{-1}$) (LMCT s → d); ^1H NMR ($CDCl_3$); δ 6.6–8 (m, aromatic), δ 8.4–8.6 (d, CH=N), δ 9.4–9.6 (d, NH); elemental analyses calcd. for $C_{32}H_{26}N_3PdOPS$: C, 60.42; H, 4.11; N, 6.58; S, 5.02; found: C, 60.58; H, 4.06; N, 6.63; S, 5.20%.

2.2.2. Preparation of [Pd(Nap-ptsc)(PPh_3)] (*2*)

An ethanolic (25 mL) solution of $[PdCl_2(PPh_3)_2]$ (0.200 g; 0.285 mmol) was slowly added to [H_2-Nap-ptsc] (0.092 g; 0.285 mmol) in dichloromethane (25 mL). The mixture was allowed to stand for 4 days at room temperature. Orange red crystals obtained were washed with *n*-hexane. Yield: (166.67 mg) 92%. M.p. 260–262 °C. FT-IR (KBr): 1592 cm^{-1} ($\nu_{C=N}$), 1338 cm^{-1} (ν_{C-O}), 748 cm^{-1} (ν_{C-S}), 3274 cm^{-1} (ν_{N-H}), 1446, 1090, 706 cm^{-1} (for PPh_3). UV–vis (CH_2Cl_2), λ_{max}: 322 (6, 420) nm ($dm^3\,mol^{-1}\,cm^{-1}$) (intra-ligand transition); 421 (16, 580) nm ($dm^3\,mol^{-1}\,cm^{-1}$) (LMCT s → d); 443 (17, 260) nm ($dm^3\,mol^{-1}\,cm^{-1}$) (MLCT); ^1H NMR ($CDCl_3$); δ 6.7–7.9 (m, aromatic), δ 8.3–8.4 (d, CH=N), δ 9.6–9.7 (d, NH); elemental analyses calcd. for $C_{36}H_{28}N_3PdOPS$: C, 62.84; H, 4.10; N, 6.10; S, 4.66; found: C, 62.96; H, 4.16; N, 6.24; S, 4.72%.

2.2.3. Preparation of [Pd(Nap-mtsc)(PPh_3)] (*3*)

An ethanolic (25 mL) solution of $[PdCl_2(PPh_3)_2]$ (0.200 g; 0.285 mmol) was slowly added to [H_2-Nap-mtsc] (0.074 g; 0.285 mmol) in dichloromethane (25 mL). The mixture was allowed to stand for 4 days at room temperature. Orange red crystals obtained were washed with *n*-hexane. Yield: (151.40 mg) 90%. M.p. 271–273 °C. FT-IR (KBr): 1598 cm^{-1} ($\nu_{C=N}$), 1332 cm^{-1} (ν_{C-O}), 738 cm^{-1} (ν_{C-S}), 3292 cm^{-1} (ν_{N-H}), 1436, 1096, 698 cm^{-1} (for PPh_3). UV–vis (CH_2Cl_2), λ_{max}: 322 (6, 370) nm ($dm^3\,mol^{-1}\,cm^{-1}$) (intra-ligand transition); 413 (15, 780) nm ($dm^3\,mol^{-1}\,cm^{-1}$) (LMCT s → d); 437 (17, 150) nm ($dm^3\,mol^{-1}\,cm^{-1}$) (MLCT); ^1H NMR ($CDCl_3$); δ 2.9–3.1 (m, CH_3), δ 6.6–7.8 (m, aromatic), δ 8.1–8.2 (d, CH=N), δ 9.1–9.3 (d, NH); elemental analyses calcd. for $C_{31}H_{26}N_3PdOPS$: C, 61.50; H, 4.35; N, 6.72; S, 5.13; found: C, 61.82; H, 4.40; N, 6.58; S, 5.28%.

2.3. Measurements

Elemental analyses of the complexes were performed with Vario EL III CHNS at the Department of Chemistry, Bharathiar University, Coimbatore, India. IR spectra of the ligands and complexes have been recorded in KBr pellets with Shimadzu/Nicolet instruments in the 400–4000 cm^{-1} range. The cyclic voltammetric studies were carried out on CH instruments. The electronic spectra of the complexes have been recorded in dichloromethane using an Analytic Jena Specord 200 spectrophotometer in 200–800 nm range. Proton NMR studies have been carried out in $CDCl_3$ by using Bruker Instrument with TMS as standard. Melting points were recorded in a Boetius micro heating table.

2.4. X-ray crystallography

Single crystal data collections of [Pd(Sal-ptsc)(PPh_3)] were done with a Nonius Kappa CCD diffractometer using graphite monochromated Mo Kα ($\lambda = 0.71073$ Å) radiation and the data were collected and processed by using the crystal clear software package SHELXL-97 [21]. The structures were solved by direct methods and refined by full matrix least squares on F^2 using SHELXL-97. The data collection for [Pd(Nap-mtsc)(PPh_3)] was done at 173 K with Bruker smart 1000 CCD diffractometer using monochromated Mo Kα ($\lambda = 0.71073$ Å) radiation. The data were collected and processed using software Saint and the structures solved were refined by full matrix least squares on package F^2 using SHELXL-97 [21].

2.5. Cytotoxic studies

The Schiff base ligands and their new palladium(II) complexes have been screened for their antibacterial activities against various pathogenic bacteria *Escherichia coli*, *Staphylococcus aureus*, *Pseudomonas aeruginosa* and *Vibrio cholerae* by Kirby Bauer method [22]. The test solutions have been prepared in DMSO. The test organisms were grown on nutrient agar medium in Petri plates. The compounds to be tested were dissolved in DMSO and soaked in filter paper disc of 5 mm diameter and 1 mm thickness. The concentrations used in this study were 0.25, 0.5, 1 and 2%. The discs were placed on the previously seeded plates and incubated at 37 °C for 24 h. The diameter of inhibition zone around each disc was measured after 24 h. *Streptomycin* was used as standard.

3. Results and discussion

3.1. IR spectra

The IR spectra of the free Schiff base ligands showed a strong absorption at around 1622–1595 cm^{-1} due to the azomethine $\nu_{(C=N)}$ group. This absorption has been shifted to lower frequency in all the complexes indicating the coordination of the azomethine nitrogen to palladium ion [23,24]. The medium intensity band which appeared around 3300–3400 cm^{-1} due to $\nu_{(O-H)}$ in the free Schiff bases disappeared upon complexation showing deprotonation prior to coordination through oxygen atoms in complexes. A band that appeared at 1263–1275 cm^{-1} due to phenolic $\nu_{(C-O)}$ stretching in the free Schiff bases has been shifted to higher frequency by 69–71 cm^{-1} in the complexes indicating the coordination through the phenolic oxygen atom in the complexes [25]. The $\nu_{(C-S)}$ band that appeared at around 815 cm^{-1} in the free Schiff bases disappeared completely and a new band appeared in the region 738–756 cm^{-1}. This observation may be attributed to the enolisation of NH–C=S group and subsequent coordination through the sulphur atom [26,27]. In all the complexes the characteristic absorption bands for triphenylphosphine were also present in the expected region [28].

3.2. Electronic spectra

All the palladium complexes have been found to be diamagnetic indicating +2 oxidation state for palladium. The electronic spectra of the complexes have been recorded in CH_2Cl_2 and they displayed three bands in the region around 320–470 nm. The bands that appeared below 470 nm have been reported as due to both distorted square planar and undistorted square planar Pd(II) complexes [29,30]. The bands that appeared around 322, 400 and 440 nm have been assigned to intra-ligand transition [31,32], LMCT [31,33] and MLCT [34,35], respectively.

3.3. ^{1}H NMR studies

The d^8 square planar palladium(II) complexes are all diamagnetic and give well resolved NMR spectra which confirm the nature of the binding. The ^{1}H NMR spectra of **1** showed a series of overlapping multiplet for aromatic protons at δ 6.6–8.0 ppm [8,10]. The NH resonance is split into a doublet due to nuclear quadrupolar effect occurring at δ 9.6–9.7 ppm [26]. One more doublet occurring at δ 8.4–8.6 ppm corresponding to azomethine protons may be due to the splitting of CH resonance by phenyl group of protons. In the complex **2**, a multiplet at δ 6.7–6.9 ppm and two doublets at δ 9.6–9.7 ppm and δ 8.4–8.6 ppm appeared corresponding to aromatic, NH and azomethine protons. The reason for the appearance of the doublets may be the splitting of NH and CH resonance by nuclear quadrupolar effect [36]. The complex **3** showed a multiplet at δ 6.6–7.8 ppm corresponding to aromatic protons. An extra multiplet appeared at δ 2.9–3.1 ppm corresponding to methyl group of protons [26]. The NH and CH resonances were split into doublet because of nuclear quadrupolar effect at δ 9.1–9.3 ppm and 8.1–8.3 ppm [36].

3.4. X-ray crystallography

3.4.1. Description of molecular structures of *1* and *3*

The reactions of $[PdCl_2(PPh_3)_2]$ with $[H_2$-(Sal-ptsc)], $[H_2$-(Nap-ptsc)], $[H_2$-(Nap-mtsc)] in 1:1 molar ratio afforded complexes of the type [Pd(L)(PPh_3)] (where L = tridentate dibasic *N*-substituted thiosemicarbazone ligands). In all the three complexes the ligands coordinated to palladium metal as ONS chelating donor by forming one stable five membered ring and another six membered ring. The remaining coordination site is occupied by triphenylphosphine. The single crystals of **1** and **3** suitable for X-ray diffraction studies were obtained from $CHCl_3$/*n*-hexane at room temperature. A summary of data, crystallographic parameters for **1** and **3** are given in Table 1. The relevant bond lengths, bond angles are given in Table 2. The ORTEP diagrams of the complexes are shown in Figs. 1 and 2.

In the complex [Pd(Sal-ptsc)(PPh_3)] (**1**), the Pd–O, Pd–P, Pd–S bond lengths of 2.003(4) Å, 2.2651(15) Å,

Table 1
Crystallographic data of palladium(II) thiosemicarbazone complexes

	[Pd(Sal-ptsc)(PPh_3)] (**1**)	[Pd(Nap-mtsc)(PPh_3)] (**3**)
Empirical formula	$C_{32}H_{26}N_3OPSPd$	$C_{32}H_{27}N_3OPSPd$
Formula weight	637.990	624.99
Crystal dimensions	2.00 × 1.50 × 0.50 mm	0.4 × 0.2 × 0.1 mm
Crystal system	Monoclinic	Monoclinic
a	9.4390 Å	14.119 Å
b	10.645 Å	11.155 Å
c	13.668 Å	18.503 Å
α	90°	90°
β	91.43(3)°	112.02°
γ	90°	90°
V	1372.9(5) $Å^3$	2701.7(9) $Å^3$
Space group	*P*2(1)	*P*2(1)
Z value	2	4
D_{calc}	1.543 g cm^{-3}	1.537 g cm^{-3}
F_{000}	648	1272
R indices (all data)	$R1 = 0.0566$, $wR2 = 0.1571$	$R1 = 0.0418$, $wR2 = 1105$
μ (Mo Kα)	8.42 cm^{-1}	0.853 mm^{-1}
$2\theta_{max}$	27.49	28.26

Table 2
Selected bond lengths (Å) and angles (°) for palladium(II) thiosemicarbazone complexes

Atoms	[Pd(Sal-ptsc)(PPh_3)] (**1**)	[Pd(Nap-mtsc)(PPh_3)] (**3**)
Pd–S(1)	2.2273(15)	2.2408(8)
Pd–P(1)	2.2651(15)	2.2835(8)
Pd–O(1)	2.003(4)	2.027(2)
Pd–N(1)	2.010(5)	2.018(2)
S(1)–Pd(1)–P(1)	92.28(6)	92.92(3)
S(1)–Pd(1)–O(1)	178.05(13)	175.81(5)
S(1)–Pd(1)–N(1)	84.50(12)	84.60(6)
P(1)–Pd(1)–O(1)	89.65(13)	91.23(6)
P(1)–Pd(1)–N(1)	175.21(13)	177.18(6)
O(1)–Pd(1)–N(1)	93.55(18)	91.24(8)

2.2273(15) Å, respectively, are well in the reported region for square planar palladium(II) complexes [37–43] but Pd–N bond length of 2.010(5) Å was found to be slightly higher than that of the reported value for other palladium(II) complexes [39–41].

In the complex [Pd(Nap-mtsc)(PPh_3)] (**3**), the Pd–O, Pd–P, Pd–S bond lengths of 2.027(2) Å, 2.2835(8) Å, 2.2408(8) Å, respectively, are slightly higher than that observed for (**1**). Pd–N bond length of 2.018(4) Å was found to be slightly higher than that of the reported palladium(II) complexes [39–41]. The slight increase in Pd–N bond lengths in these two complexes may be due to trans-influence of PPh_3 ligand. The variations in bond lengths and bond angles in all the complexes indicate considerable distortion around palladium from its square planar geometry.

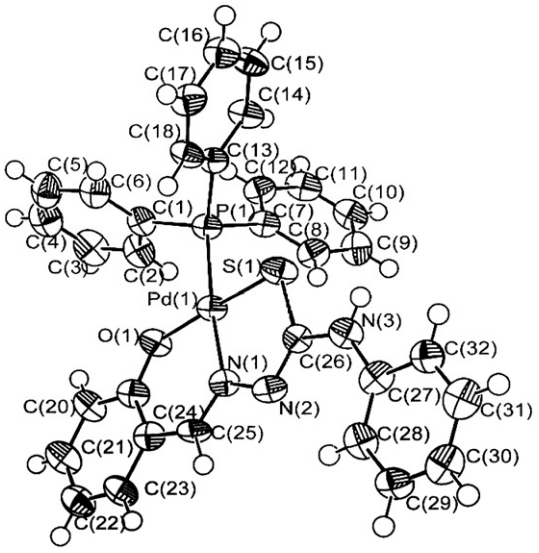
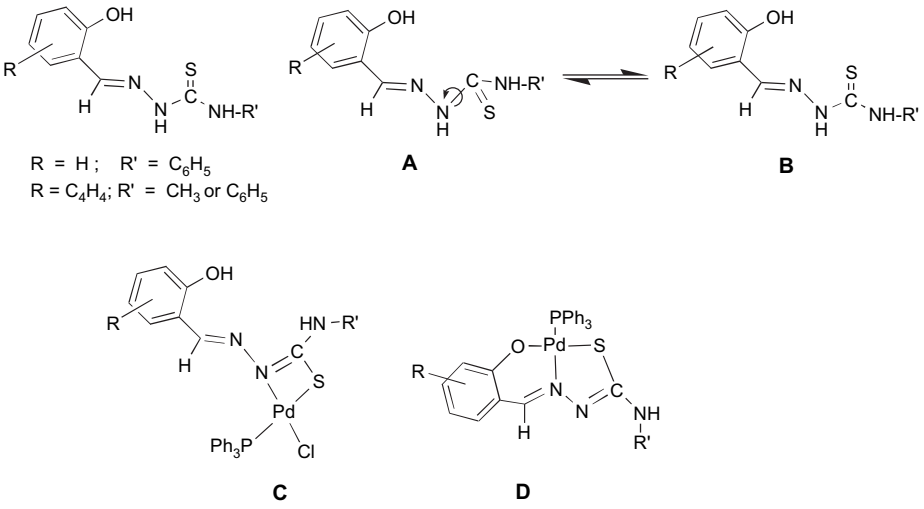


Fig.1. ORTEP diagram of [Pd(Sal-ptsc)(PPh3)] (**1**).

In general, thiosemicarbazone ligands can exist as **A** or **B**. Earlier reports with ruthenium and osmium metals showed that the formation of four membered ring **C** and the ONS five membered ring **D** is unusual for complexes containing triphenylphosphine [7,8]. In order to find out the real driving force which directs the different mode of coordination, we have changed the metal ruthenium by palladium. In all the three palladium(II) thiosemicarbazone complexes, we have found that the ligands coordinate through ONS mode and form complexes of the type **D**. From our investigation we have concluded that the coordination mode of the ligands to metals is decided not only by the formation of intramolecular hydrogen bonding, bulkiness of co-ligand or thiosemicarbazone ligand itself but also by the metal atom [44].



4. Eletrochemistry

Electrochemical studies of new Pd(II) thiosemicarbazone complexes have been carried out by cyclic voltammetry in acetonitrile solution using platinum disc working electrode and Pt wire counter electrode. All the potentials were referenced to Ag/AgCl reference electrode. The cyclic voltammetric data are given in Table 3. Among the three complexes, the complex **1** showed reversible oxidation potential at 0.9605 V with a peak to peak separation of 87 mV and quasi reversible

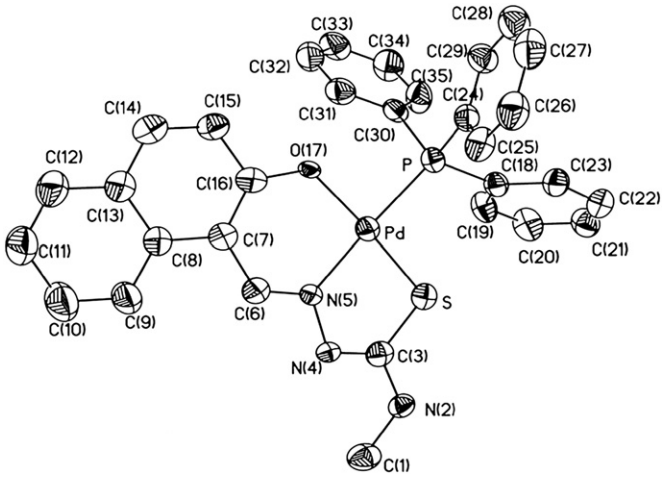


Fig. 2. ORTEP diagram of [Pd(Nap-mtsc)(PPh3] (**3**).

reduction potential at −0.760 V with a peak to peak separation of 140 mV [45]. In addition to this, the ligand oxidation was observed at 1.125 V. The complex **2** showed only quasi reversible oxidation at 0.5749 V with a peak to peak separation of 470 mV. The complex **3** showed both quasi reversible oxidation and reduction at 0.824 V and −0.898 V with the peak to peak separation of 199 and 195 mV, respectively. The reason for the quasi reversible electron transfer process may be the adsorption of the complex on to the electrode surface [46]. The variation in the electron donating ability of the ligands affects the redox potentials of the complexes.

5. Antibacterial studies

The antibacterial activities that have been shown by the complexes are given in Table 4. The increased activity of the complexes has been explained by Tweed's chelation theory [11]. Among the three complexes, [Pd(Nap-ptsc)(PPh_3)] (**2**) exhibited higher activity than that of the other two complexes. The activity increases in the order of [Pd(Nap-mtsc)(PPh_3)] (**3**) < [Pd(Sal-ptsc)(PPh_3)] (**1**) < [Pd(Nap-ptsc)(PPh_3)] (**2**). The changes that have been done on the ligands are only the substitution of alkyl and aryl groups on the phenolic ring and on thioamido nitrogen. This change only should be responsible for exhibiting different activity on the pathogenic bacteria. In the complex [Pd(Nap-ptsc)(PPh_3)] (**2**), the presence of two electron withdrawing groups (napthyl and phenyl) pulls out more electrons from the metal ion compared to two electron withdrawing (phenyl and phenyl) groups in **1** or one electron withdrawing napthyl and one electron donating methyl groups in **3**. Chelation of the ligands considerably reduces the polarity of the metal ion because of the partial sharing of its positive charge with the donor groups and possible π-electron delocalisation over the chelate ring. Such chelation could increase the lipophilic character of the central metal atom, which subsequently favours the permeation through the lipid layer of cell membrane. The mode of action of the complexes may involve the formation of the hydrogen bond through the azomethine group (>C═N) with the active centres of the cell constituents resulting in the interference with normal cell process [25]. In the complex **2**, the electron density deficiency on Pd(II) metal ion is comparatively higher than that of the other two complexes. This increases the permeability of the complex on the cells of microbes. Based on the study, the following observations have been made.

1. All the complexes are active against the four pathogenic bacteria.
2. The complexes have shown more activity than their parent ligands.
3. The activity of the complex **2** against *E. coli*, almost reaches the effectiveness of the conventional bacteriocide *Streptomycin*.

6. Conclusion

New palladium(II) complexes have been synthesised, characterised by spectral, electrochemical and X-ray crystallography. In these square planar complexes the three *N*-substituted thiosemicarbazone ligands are coordinated in ONS fashion, the fourth coordination site is filled with triphenylphosphine group. Though several reasons have been offered for the display of variable coordination modes of thiosemicarbazone ligands, still chemists have not yet come out with any concrete reason for that. Detailed investigation is underway with different *N*-substituted thiosemicarbazones with various transition metal ions to find out the real driving force which influences the coordination modes of thiosemicarbazones. The new complexes exhibited enhanced antibacterial activity over corresponding ligands and activities are compared with the standard *Streptomycin*.

6.1. Supplementary material

Crystallographic data for **1** and **3** have been deposited at the Cambridge Crystallographic Data Centre as supplementary publication (CCDC No. 284721 and CCDC No. 290485). These

Table 3
Electrochemical data of new palladium(II) thiosemicarbazone complexes

Complex	Pd^{II}–Pd^{III} (oxidation)				Pd^{II}–Pd^{I} (reduction)			
	Ep_a (V)	Ep_c (V)	$E_{1/2}$ (V)	ΔEp (mV)	Ep_a (V)	Ep_c (V)	$E_{1/2}$ (V)	ΔEp (mV)
1	1.004	0.9169	0.9605	87	−0.830	−0.690	−0.760	140
2	0.8098	0.340	0.5749	470	–	–	–	–
3	0.923	0.724	0.824	199	−0.800	−0.995	−0.898	195

Table 4
Antibacterial activity of new palladium(II) thiosemicarbazone complexes

Compound	Diameter of inhibition zone (mm)															
	Escherichia coli (%)				*Staphylococcus aureus* (%)				*Pseudomonas aeruginosa* (%)				*Vibrio cholerae* (%)			
	0.25	0.5	1.0	2.0	0.25	0.5	1.0	2.0	0.25	0.5	1.0	2.0	0.25	0.5	1.0	2.0
[H_2-Sal-ptsc]	5	7	8	–	–	6	8	9	–	5	7	9	4	6	8	9
[H_2-Nap-ptsc]	4	6	8	9	5	6	8	10	6	8	–	9	5	6	7	9
[H_2-Nap-mtsc]	5	5	7	8	6	7	9	11	7	7	8	9	–	–	6	8
1	11	17	–	–	10	12	15	17	11	11	12	13	12	13	15	17
2	15	17	20	23	–	12	16	19	10	12	18	21	11	12	15	18
3	10	12	12	19	11	13	14	16	12	13	14	–	11	12	13	15
Streptomycin	*18*	*20*	*22*	*25*	*17*	*19*	*23*	*25*	*18*	*21*	*23*	*24*	*14*	*17*	*20*	*22*

data can be obtained free of charge at www.ccdc.cam.ac.uk/conts/retrieving.html or from the Cambridge Crystallographic Data Centre, 12, Union Road, Cambridge CB2 1EZ, UK [fax: +44-1223/336-033; e-mail: deposit@ccdc.cam.ac.uk].

Supplementary data

Supplementary data associated with this article can be found in the online version, at doi: 10.1016/j.ejmech.2007.03.006.

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