Synthesis, Physicochemical Properties, and *in vitro* Antibacterial Screening of Palladium(II) Complexes Derived from Thiosemicarbazone

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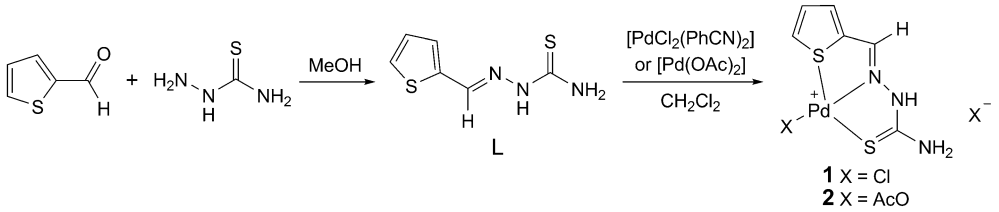
A new series of Pd^{II} complexes derived from thiosemicarbazone has been synthesized. The synthesized Pd^{II} complexes have been characterized on the basis of elemental analyses, FT-IR, ^{1}H- and ^{13}C-NMR, UV/VIS, and thermal studies. A square-planar geometry has been assigned around Pd^{II} ions on the basis of results obtained from UV/VIS studies. The thiosemicarbazone ligand and its Pd^{II} complexes have been screened against *Gram*-positive (*Bacillus subtilis* and *Staphylococcus aureus*) and *Gram*-negative (*Escherichia coli* and *Pseudomonas aeruginosa*) bacteria *in vitro* as growth-inhibiting agents, and the results revealed significant antibacterial activities.

Introduction. – Thiosemicarbarbazones (TSCs) are very promising molecules in coordination chemistry because of their pharmacological features, which include notably their antibacterial, antiviral, antimalarial, antileprotic, and anticancer activities [1–3]. Among TSCs, heterocyclic TSCs have received considerable attention due to their potential biological activities [4]. TSCs, being well-known chelating ligands, coordinate to the metal ion through S- and one of the hydrazine N-atoms (N(2) or N(1)). Coordination through N(2) results in an unusual four-membered chelating ring, while that through the hydrazine N(1)-atom leads to a more stable five-membered chelate [4][5]. TSCs possess the ability to adopt various coordination modes, leading to a rich structural diversity of these complexes [6–8]. It has been reported that the biological activity of TSCs is due to their ability to form tetradentate chelates with essential heavy metal ions bonded to S- and two N-atoms. Structural alterations that hinder a TSC to act as a chelating agent with metal ions tend to destroy or reduce its medicinal activity [1][9]. In view of the wide spectrum of biological applications of TSCs, including activity against diseases such as TB, leprosy, malaria, as well as a range of bacterial infections, the chemistry of TSCs and their complexes has attracted prolific attention over the past decade [10][11]. It has been reported that several metal complexes of TSCs, particularly with Cu, Pt, Pd, Re, and Ru, exhibited marked and diverse biological activities [12][13]. Among them, Pd^{II} and Pt^{II} complexes with TSC are active against cisplatin-resistant human tumor cell lines, probably because their mode of action involves *inter*strand cross-links with DNA instead of *intra*strand cross-links, which is the major coordination mode of cisplatin [14]. Moreover, Pd^{II} complexes with N-containing ligands have been the subject of intensive biological evaluation in the search for less toxic and more selective anticancer therapies [15][16]. However,

Pd^{II} *N,S*-chelates with inert ligands (*e.g.*, S or N) were suggested to be more effective antitumor agents than those of other metals because of their proper lability to bring the metal to the target (DNA) and allow their interaction. In this respect, Pt^{II} chelates are kinetically inert, while those of other metals such as Ni^{II}, Zn^{II}, and Cu^{II} do not have sufficient thermodynamic stability [17]. The N,S-donor ligands used to prepare antitumor and antimicrobial Pd^{II} complexes were mostly TSCs and dithiocarbazates, and possess antiviral, antimalarial, antifungal, antimicrobial, and antitumor activities, and their mechanisms of action, most probably involve the inhibition of ribonucleotide reductase, converting ribonucleotides to deoxyribonucleotides [18][19]. Herein, we report the synthesis, structural characterization of Pd^{II} complexes derived from thiosemicarbazone, followed by their *in vitro* antibacterial screening against *Gram*-positive (*Bacillus subtilis* and *Staphylococcus aureus*) and *Gram*-negative (*Escherichia coli* and *Pseudomonas aeroginosa*) bacteria.

Result and Discussion. – *Synthesis.* Targeted Pd^{II} complexes were synthesized by the reaction of TSC ligand with $[PdCl_2(PhCN)_2]$ and $[Pd(OAc)_2]$ in 1: 1 molar ratio (*Scheme*). The formation of Pd^{II} complexes were ascertained by elemental analyses, ^{1}H- and ^{13}C-NMR, FT-IR, and thermal studies. The complexes so formed are soluble in common organic solvents. The overall geometry around Pd^{II} ions has been assigned on the basis of bands observed in electronic spectra.

Scheme. *Synthesis of Ligand (L), and Its Pd^{II} Complexes* **1** *and* **2**



IR-Spectral Investigations. The IR spectrum of the free ligand showed a strong absorption band at 1585 cm^{-1} assigned to ν(C=N) which was shifted to lower wave number of *ca.* 1475 cm^{-1} in the spectra of complexes, indicating the coordination of azomethine N-atom to Pd ion (*Fig. 1*) [20][21]. The moderate strong band at 1250 cm^{-1} assigned to ν(C=S) in the free ligand disappeared completely and, instead, a new band appeared at 785 cm^{-1} attributed to the enolization of NH–C=S group [22][23]. The missing of S–H band between 2600–2800 cm^{-1} indicated that the ligand remained in its thione form [24]. The spectrum of ligand showed three bands at 3190, 3395, and 3310 cm^{-1} assignable to asymmetric and symmetric vibration of N–H, and to νNH_2, respectively [25]. The ν(N–H) band of free ligand disappeared completely in the spectrum of the Pd^{II} complex indicating the deprotanation of the NH group and coordination *via* the thiolate S-atom. On the other hand, bands attributed to asymmetric and symmetric vibrations of NH_2 group underwent very small changes, indicating no interaction between Pd^{II} ion and terimal NH_2 group [26][27]. The bands assigned to ν(Pd–S) and ν(Pd–Cl) appeared at 400 and 340 cm^{-1}, respectively [28]. The medium intensity band observed at 850 cm^{-1} in the spectrum of the free ligand

assigned to ν(C–S–C) stretching vibration of thiophene moiety was shifted to *ca.* 825 cm^{-1} in the spectrum of Pd^{II} complexes, further evidencing the involvement of the S-atom in bonding with Pd^{II} ion [29]. The bands at 1595 and 1380 cm^{-1} observed in complex **2**, attributed to antisymmetric and symmetric stretching vibrations of the COO group, indicated the monodentate nature of the COO moiety. This was further confirmed by frequency separation between these two modes ($\nu_{as}(CO_2) - \nu_s(CO_2)$). In general, the difference between asymmetric ($\nu_{as}(CO_2)$) and symmetric ($\nu_s(CO_2)$) absorption frequency below 200 cm^{-1} evidences a bidentate COO moiety, while that greater than 200 cm^{-1} implies the unidentate COO moiety [30].

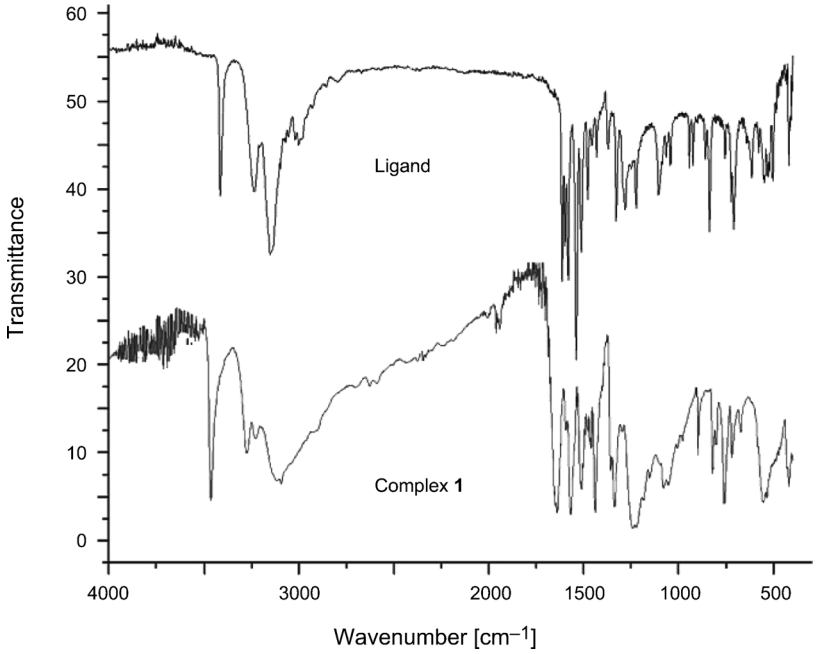


Fig. 1. *IR Spectra of ligand and its complex* **1**

NMR Studies. The ^{1}H- and ^{13}C-NMR spectra of ligand and its Pd^{II} complexes have been recorded in (D_6)DMSO and $CDCl_3$, respectively. The ^{1}H-NMR spectrum of the ligand showed a broad *singlet* at 11.47 ppm attributed to hydrazine H-atom which disappeared in the spectra Pd^{II} complexes, indicating the deprotonation of ligand and subsequently the replacement of the H-atom by Pd^{II} ion, inducing the shifts of NH_2 H-atoms to lower field in the spectra of Pd^{II} complexes. The signal for azomethine H-atom of the free ligand appeared at 8.24 ppm, while the *multiplet*s for thiophene H-atoms were detected in the region of 7.10–7.12 ppm. It is interesting to note the presence of two *singlet*s for NH_2 H-atoms at 7.65 and 7.7 ppm, respectively, in the spectrum of the free ligand, indicating that the free rotation around C=N bond was hindered because of its partial C=C bond character [31][32]. The coordinating mode of ligand was confirmed by comparing ^{1}H-NMR data of the ligand with those of Pd^{II} complex (*Fig. 2*). A significant downfield shift of the azomethine H-atom signal in the spectra of

Pd^{II} complexes [33] with respect to the corresponding free ligand confirmed the coordination of azomethine N-atom to Pd^{II} ion, while slight deshielding in the H-atoms of thiophene moiety further confirmed the coordination of ligand to Pd^{II} ion (*Figs. 2* and *3*). [34]. An additional signal at 2.08 ppm assigned to AcO (acetate) H-atom was observed in the spectrum of complex **2** (*Fig. 3*). The ^{13}C-NMR spectrum of ligand showed a sharp signal at 177.99 ppm corresponding to C=S group which underwent deshielding in Pd^{II} complexes, indicating the thiolate-like coordination rather than thione [35]. Various signals attributed to azomethine and thiophene C-atom appeared at 165.96, 153.50, 148.61, 139.70, and 127.98, respectively, which were deshielded in Pd^{II} complexes, confirming the coordination of Pd^{II} ion with ligand (*Figs. 4* and *5*) [34]. Two additional signals appearing at 178.78 and 25.50 ppm corresponding to C=O and Me C-atom, respectively, were observed in the spectrum of complex **2** (*Fig. 5*).

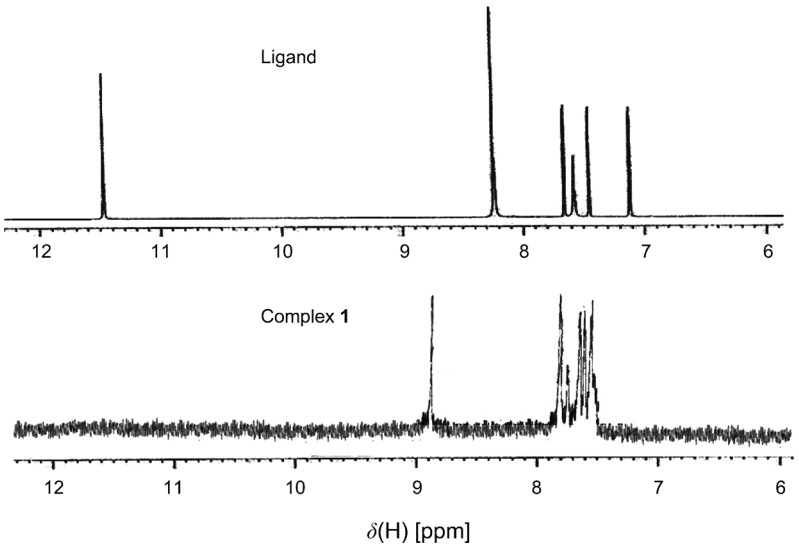


Fig. 2. *^{1}H-NMR Spectra of ligand and complex* **1**

Electronic Spectra. The electronic spectra in the ultraviolet and visible ranges (UV/VIS) of the Pd^{II} complexes were recorded in 0.25×10^{-3} M solution of CH_2Cl_2 (*Figs. 6* and *7*), and all spectra indicated square-planar geometry. The spectra exhibited prominent bands at *ca.* λ_{max} 260 (ε 10.80 M^{-1} cm^{-1}) and *ca.* λ_{max} 350 nm (ε 8.0 M^{-1} cm^{-1}), accompanied by a weak shoulder attributed to n-π^* transitions, and they were associated with azomethine functions of the TSC moiety [36–38].

Thermal Studies. Thermal stabilities of complexes **1** and **2** were examined by thermogravimetry (TG) in N_2 atmosphere at a heating rate of 20° min^{-1} in the temperature range of 20–800°. The TG curve showed three steps of weight loss. The first stage of the complexes **1** and **2** at 125° involved the loss of hydrated H_2O molecules, followed by the second step which included loss of chloride and acetate ions, and coordinated H_2O up to 295°. This step was followed by a third step at which the whole

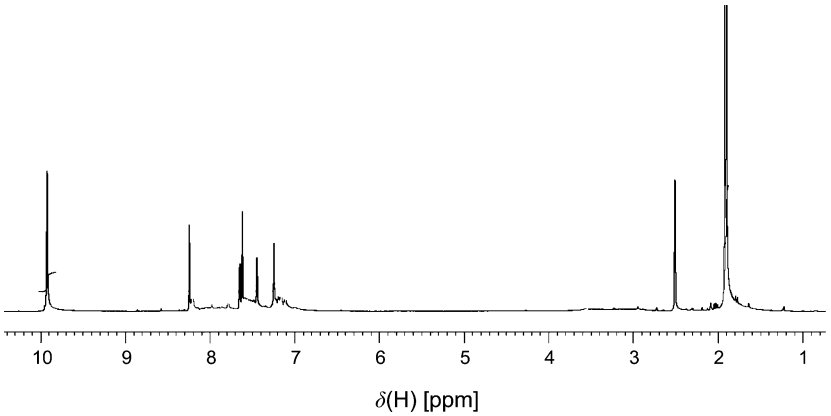


Fig. 3. *^{1}H-NMR Spectrum of complex* **2**

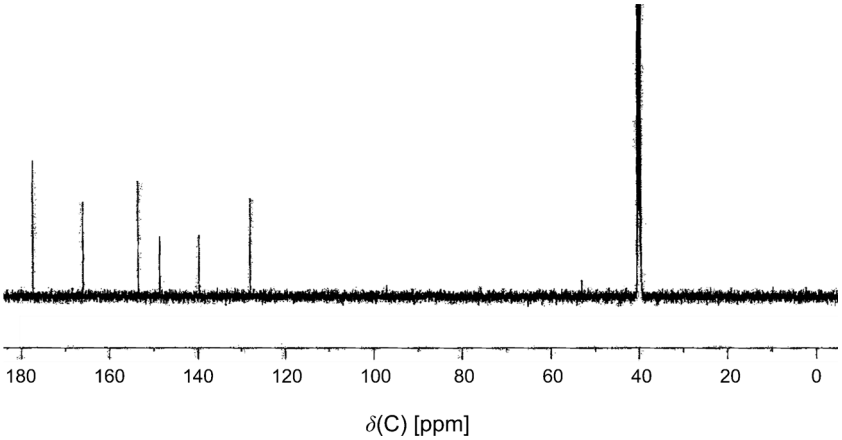


Fig. 4. *^{13}C-NMR Spectrum of ligand*

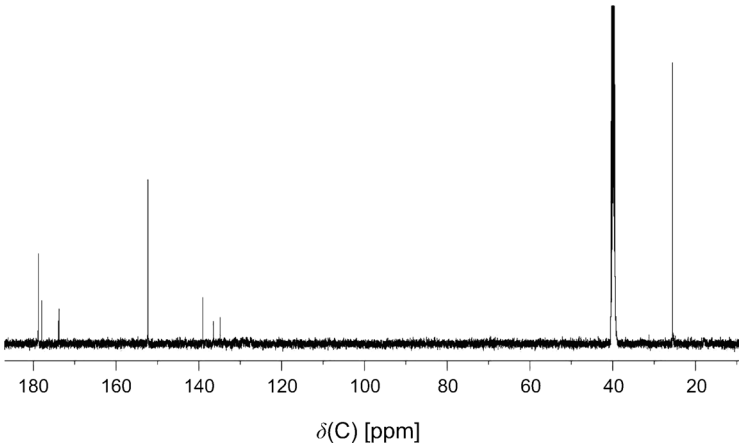


Fig. 5. *^{13}C-NMR Spectrum of complex* **2**

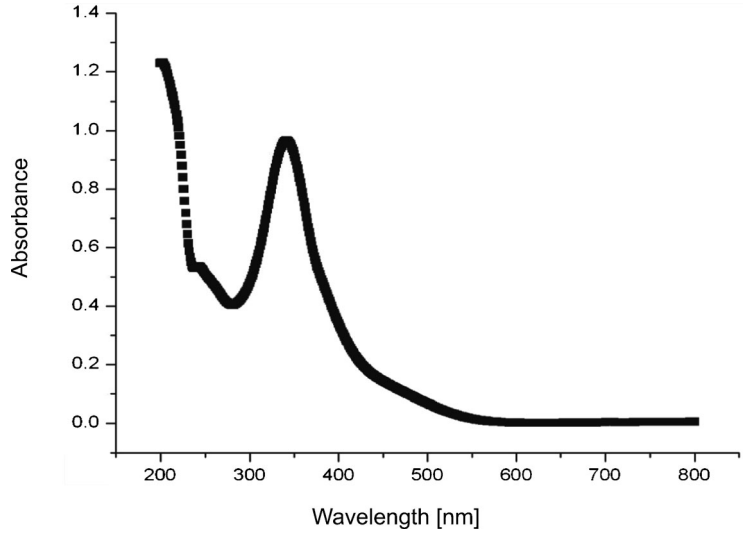


Fig. 6. *Electronic spectrum of complex* **1** *in* 0.25×10^{-3} M *solution of* CH_2Cl_2

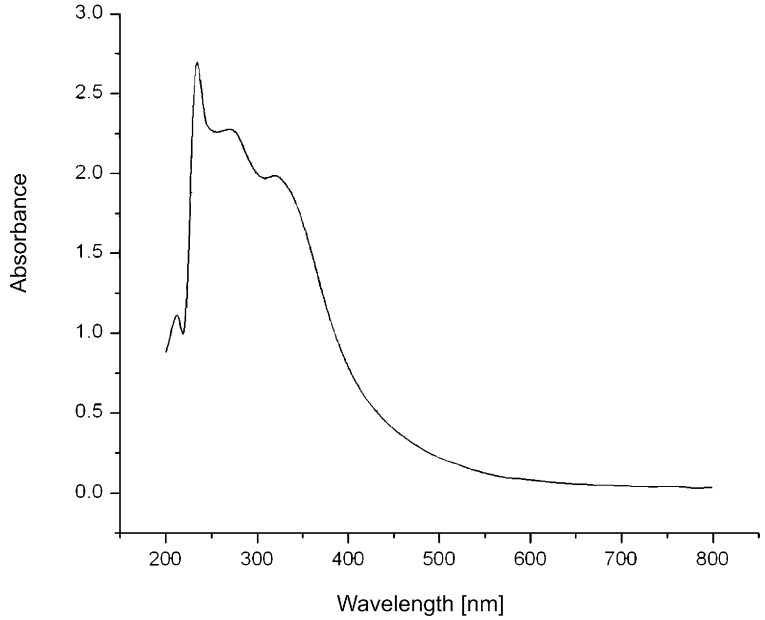


Fig. 7. *Electronic spectrum of complex* **2** *in* 0.25×10^{-3} M *solution of* CH_2Cl_2

organic moiety decomposed at temperature up to 670°, and, finally, metal oxide formed.

Crystallography of the Ligand. Molecular structure of ligand together with atom numbering is shown in an ORTEP diagram (*Fig. 8*). Selected bond lengths are listed in

Table 1. The ORTEP diagram shows two molecules which are independent of each other. There are two independent molecules and plenty of intermolecular H-bonds. In the crystal structure of ligand, only the (*E*)-isomer of imine bond is observed. It is known that the TSC group can present a thione⇌thiol tautomerism. The C(12)–S(3) and C(6)–S(4) bond distances are similar to those found in other TSCs which evidence the thione form in the solid state [39], indicating that the ligand is in that form. The C(11)–N(3) and C(5)–N(1) bond distances are in accordance with N=C bond character. The difference in the C(1)–C(2) compared to the C(3)–C(4) bond also reflects the double-bond character of the C(1)–C(5) bond.

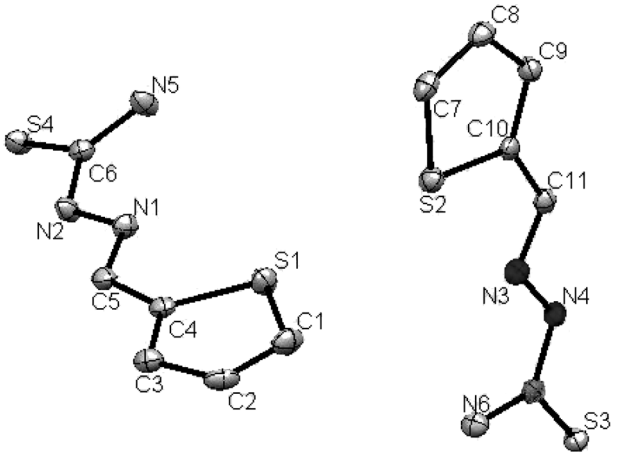


Fig. 8. *ORTEP Diagram showing the molecular structure of the ligand*

Table 1. *Selected Bond Distances and Angles of the Ligand* (L)

Bond	Distance [Å]	Bonds	Angle [°]
S(3)–C(12)	1.695(2)	N(4)–C(12)–S(3)	119.33(17)
S(4)–C(6)	1.703(2)	N(1)–C(5)–C(4)	120.1(2)
S(1)–C(1)	1.718(2)	C(11)–N(3)–N(4)	114.76(19)
S(1)–C(4)	1.729(2)	C(5)–N(1)–N(2)	115.37(19)
S(2)–C(7)	1.718(2)		
S(2)–C(10)	1.728(2)		
C(11)–N(3)	1.278(3)		
C(11)–C(10)	1.447(3)		

Antibacterial Activity. The antibacterial activities of all the compounds were determined against both *Gram*-positive (*Bacillus subtilis* and *Staphylococcus aureus*) and *Gram*-negative (*Escherichia coli* and *Pseudomonas aeroginosa*) bacteria (*Table 2*). Ligand (L), and its complexes **1** and **2** exhibited significant activities against *Gram*-positive strains compared to *Gram*-negative strains. *Gram*-positive bacterial stain showed highest sensitivity against L, with observed maximum zones of inhibition of 25 and 18 mm on overnight-incubated plates of *B. subtilis* and *S. aureus*, respectively. Maximum growth inhibitions of *Gram*-negative bacterial stains *E. coli* and *P.*

aeruginosa were detected at 22 and 14 mm on nutrient agar palates after overnight incubation under optimum conditions. Antibacterial activities of synthesized compounds (L > **1** > **2**) were significant compared to the positive control antibiotics tetracycline.

Table 2. *Antibacterial Activities of Synthesized Compounds at 100 μg/ml Concentration*

Compound	Zone of inhibition [mm][a])			
	B. subtilis	*S. aureus*	*E. coli*	*P. aeroginosa*
L	25 ± 1.05	18 ± 1.23	22 ± 1.10	14 ± 1.84
1	16 ± 0.95	14 ± 1.48	19 ± 0.90	15 ± 1.36
2	18 ± 1.25	25 ± 1.54	15 ± 0.75	11 ± 1.02
Tetracycline	18 ± 1.10	22 ± 1.33	20 ± 1.50	15 ± 0.75

[a]) Mean zone of inhibition (millimeter ± standard deviation).

Conclusions. – The synthesis and spectral characterization of Pd^{II} complexes derived from thiosemicarbazone were described. The *in vitro* antibacterial studies were performed on ligand and its Pd^{II} complexes, revealing significant activities.

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Experimental Part

General. All the reagents used were of AR (anal. reagent) grade and were purchased from *Merck* and used as received. Thermal analyses were carried out with a *SDT-Q 600* instrument in a He atm. Electronic spectra of Pd^{II} complexes in CH_2Cl_2 were recorded on *Pharmacia-LKB Biochem 4060* UV/VIS spectrophotometer at r.t. FT-IR (4000–400 cm^{-1}) Spectra were recorded as KBr discs on a *Perkin-Elmer 621* spectrophotometer; $\tilde{\nu}$ in cm^{-1}. ^{1}H- and ^{13}C-NMR spectra for ligand and its Pd^{II} complexes were recorded in (D_6)DMSO and $CDCl_3$, resp., using *Bruker Avance II 400 MHz* and *JEOL 400 MHz* NMR spectrometer, resp.; δ in ppm, J in Hz. Elemental analyses were conducted on a *Elementar Vario EL* analyzer.

Synthesis of Thiosemicarbazone Ligand, L. A MeOH soln. of thiophene-2-carboxaldehyde (1 ml) was added dropwise to the MeOH soln. of thiosemicarbazide (1 ml). The mixture was refluxed for 2 h resulting in a clear yellow-colored soln. The soln. was kept for evaporation at r.t. After 4 d, yellow crystals suitable for X-ray diffraction were obtained.

*(2*E*)-2-(Thiophen-2-ylmethylidene)hydrazinecarbothioamide* (L). Yield: 85%. M.p. 137°. IR (KBr): 3395, 3310, 3190, 1585, 785. ^{1}H-NMR ((D_6)DMSO): 11.47 (*s*, NH); 8.24 (*s*, CH=N); 7.65, 7.7 (2*s*, NH_2). ^{13}C-NMR ((D_6)DMSO): 177.99 (C=S); 165.96 (CH=N). Anal. calc. for $C_6H_7N_3S_2$ (185.27): C 38.89, H 3.80, N 22.68, S 34.61; found: C 38.65, H 3.72, N 22.50, S 34.56.

Synthesis of Complexes, [PdLCl] and [PdL(OAc)], **1** *and* **2***, Resp.* A soln. of Pd^{II} salt (1 ml) dissolved in 15 ml of CH_2Cl_2 was added in 10 ml of CH_2Cl_2 soln. of L (1 ml). The resulting mixture was stirred for 0.5 h resulting in a colored soln. The soln. was concentrated to 1 ml, followed by addition of 10 ml of hexane to cause precipitatation. The resulting colored precipitate was collected and recrystallized in CH_2Cl_2/hexane to give the complex in anal. pure form.

*Chloro{2-[(thiophen-2-yl-κ*S*)methylidene]hydrazinecarbothioamide-κ²*N²*,*S*}palladium(1+) Chloride* (**1**). Yield: 65%. M.p. 245°. IR (KBr): 3397, 3314, 1475. ^{1}H-NMR ($CDCl_3$): 8.90 (*s*, CH=N); 7.82, 7.9 (2*s*, NH_2); 7.5–7.77 (*m*, thiophene). ^{13}C-NMR ($CDCl_3$): 177.97 (Pd–S–C); 170.58 (Pd–N=CH). Anal.

calc. for $C_6H_7Cl_2N_3PdS_2$ (362.59): C 19.87, H 1.95, Cl 19.55, N 11.59, S 17.68, Pd 29.35; found: C 19.79, H 1.83, Cl 19.49, N 11.52, S 17.60, Pd 29.23.

(Acetato-κO){2-[(thiophen-2-yl-κS)methylidene]hydrazinecarbothioamide-κ²N²,S}palladium(1+) Acetate (**2**). Yield: 70%. M.p. 237°. IR (KBr): 3392, 3320, 1470. ^{1}H-NMR ((D$_6$)DMSO): 9.92 (*s*, CH=N); 8.00, 7.61 (2*s*, NH_2); 7.24–7.65 (*m*, thiophene); 2.08 (*s*, AcO). ^{13}C-NMR ((D$_6$)DMSO): 178.78 (Pd–OCO); 177.94 (Pd–S–C); 173.81 (Pd–N=CH). Anal. calc. for $C_{10}H_{13}N_3O_4PdS_2$ (409.78): C 29.31, H 3.19, N 10.25, O 15.61, S 15.65, Pd 25.97; found: C 29.25, H 3.15, N 10.18, O 15.52, S 15.58, Pd 25.85.

Crystallographic Data Collection and Refinement for the Ligand[1]). A yellow crystal suitable for X-ray diffraction was obtained by slow evaporation of MeOH. Single-crystal data were collected using graphite-monochromated MoK_α radiation (λ 0.71073 Å) on a *Bruker SMART APEX CCD* diffractometer at 293 K. The data integration and reduction were processed with SAINT program. The structure was solved by direct methods using SIR 97 and refined on F^2 by the full-matrix least-square technique by using the program contained in SHELXL-97 packages [40][41]. Parameters associated with unit cell dimensions, intensity data collection, and refinement for the crystal are compiled in *Table 3*.

Table 3. *Crystallographic Data of 2-(thiophen-2-ylmethylidene)hydrazine-1-carbothioamide* (L)

Empirical formula	$C_{24}H_{28}N_{12}S_8$
Formula weight	741.06
Temp. [K]	293(2)
Wavelength [Å]	0.71073
Crystal system	Monoclinic
Space group	*P*2(1)/*n*
Unit cell dimensions:	
a [Å]	13.411(4)
b [Å]	5.7754(16)
c [Å]	21.300(6)
α [°]	90
β [°]	96.311(4)
γ [°]	90
V [Å^3]	1639.7(8)
Z	2
D_x(calc.) [Mg/m^3]	1.501
Absorption coefficient [mm^{-1}]	0.584
F(000)	768
Crystal size [mm]	0.24 × 0.22 × 0.18
θ Range for data collection [°]	1.89–26.50
Index ranges	$-16 \le h \le 16$, $-2 \le k \le 7$, $-26 \le l \le 26$
Reflections collected	8775
Independent reflections [R(int.) = 0.0319]	3364
Completeness to $\theta = 25.00°$	99.2%
Absorption correction	None
Max. and min. transmission	0.9022; 0.8726
Refinement method	Full-matrix least-squares on F^2
Data/restraints/parameters	3364/1/231
Goodness-of-fit on F^2	1.040
Final R indices [$I > 2\sigma(I)$]	$R_1 = 0.0375$, $wR_2 = 0.0874$
R Indices (all data)	$R_1 = 0.0446$, $wR_2 = 0.0944$
Largest diff. peak and hole [e Å^{-3}]	0.340; −0.368

[1]) CCDC-779194 contains the supplementary crystallographic data for this article. These data can be obtained free of charge from the *Cambridge Crystallographic Data Centre via* www.ccdc.cam.ac.uk/data_request/cif.

Antimicrobial Assay of Pd^{II} Complexes. The antimicrobial-activity assays for the ligand (L) and its Pd^{II} complexes were performed by modified *Kirby–Bauer* (1957) agar well diffusion method [42]. Fresh overnight-grown cultures of test organisms (10^6 CFU/ml) were used to evaluate the antibacterial activities. Test bacterial culture (100 µl) was spread over the nutrient agar palates by sterilized glass spreader in sterilized condition. Plates were left standing for 5 min to let the culture get absorbed. The 8-mm-size wells were prepared in nutrient agar plates with help of sterile micropipette tip back point. Wells were sealed with one drop of molten agar (0.8% agar) to prevent leakage from the bottom of the plate. The wells were loaded with 100 µl of test compounds (30 µg/100 µl). Solvent blank (DMSO) was used as negative control. Antibiotic tetracycline (30 µg/disc) was used as a positive control. Plates were incubated at $35 \pm 2^\circ$ for 36 h. The antibacterial activity was determined by measuring the zone of bacterial growth inhibition.

REFERENCES

[1] J. P. Scovill, D. L. Klayman, C. Lambros, G. E. Childs, J. D. Notsch, *J. Med. Chem.* **1984**, *27*, 87.
[2] S. G. Teon, S. H. Ang, H. K. Fun, C. W. Ong, *J. Organomet. Chem.* **1999**, *580*, 17.
[3] R. W. Brockman, J. R. Thomson, M. J. Bell, *Cancer Res.* **1956**, *16*, 167.
[4] F. A. French, E. Blanz Jr., *J. Med. Chem.* **1970**, *13*, 1117.
[5] L. M. Fostiak, I. Gracia, J. K. Swearinger, E. Bermejo, A. Castineivas, D. X. West, *Polyhedron* **2003**, *22*, 83.
[6] R. Prabhakaran, R. Karvembu, T. Hashimoto, K. Shimizu, K. Natrajan, *Inorg. Chim. Acta* **2005**, *358*, 6093.
[7] F. Basuli, S.-M. Peng, S. Bhattacharya, *Inorg. Chem.* **2000**, *39*, 1120.
[8] T. S. Lobana, Rekha, A. P. S. Pannu, G. Hundal, R. J. Butcher, A. Castineiras, *Polyhedron* **2007**, *26*, 2621.
[9] A. C. Sartorelli, K. C. Agarwal, A. S. Tsiftsoglou, A. C. Moore, *Adv. Enzyme Regul.* **1977**, *15*, 117.
[10] I. G. Santos, U. Abraham, R. Alberto, E. V. Lopez, A. Sanchez, *Inorg. Chem.* **2004**, *43*, 1834.
[11] J. S. Casas, M. S. Garcia-Tasende, J. Sordo, *Coord. Chem. Rev.* **2000**, *209*, 157.
[12] D. T. Minkel, D. H. Petering, *Cancer Res.* **1978**, *38*, 117.
[13] D. H. Petering, *Bioinorg. Chem.* **1972**, *1*, 255.
[14] E. Wong, C. M. Giandomenico, *Chem. Rev.* **1999**, *99*, 2451.
[15] M. A. Jakupec, M. Galanski, B. K. Keppler, *Rev. Physiol. Biochem. Pharmacol.* **2003**, *146*, 1.
[16] L. Giovagnini, L. Ronconi, D. Aldinucci, D. Lorenzon, S. Sitran, D. Fregona, *J. Med. Chem.* **2005**, *48*, 1588.
[17] M. Das, S. E. Livingstone, *Br. J. Cancer* **1978**, *37*, 466.
[18] E. Bermejo, R. Carballa, A. Castineiras, R. Dominguez, A. E. Liberta, C. M. Mössmer, M. M. Salberg, D. X.West, *Eur. J. Inorg. Chem.* **1999**, 965.
[19] A. G. Quiroga, J. M. Perez, I. L. Solera, J. R. Masaguer, A. Luque, P. Roman, A. Edwaeds, C. Alonso, C. Navarro-Ranninger, *J. Med. Chem.* **1998**, *41*, 1399.
[20] Z.-H. Liu, C.-Y. Duan, J.-H. Li, Y.-J. Liu, Y.-H. Mei, X.-Z. You, *New J. Chem.* **2000**, *24*, 1057.
[21] M. B. Ferrari, S. Capacchi, F. Bisceglie, G. Pelosi, P. Tarasconi, *Inorg. Chim. Acta* **2001**, *312*, 81.
[22] J. B. Wang, W. F. Shi, 'Spectral Methods in Organic Chemistry', Peking University Press, Beijing, 2001, p. 42.
[23] Y. Tian, C. Duan, C. Zhao, X. You, *Inorg. Chem.* **1997**, *36*, 1247.
[24] M. B. Ferrari, S. Capacchi, G. Reffo, G. Pelosi, P. Tarasconi, R. Albertini, S. Pinelli, P. Lunghi, *J. Inorg. Biochem.* **2009**, *81*, 89.
[25] P. Bindu, M. R. P. Kurup, T. R. Satyakeerty, *Polyhedron* **1991**, *18*, 321.
[26] D. Kovala-Demertzi, J. R. Miller, N. Kourkoumelis, S. K. Hadjikakou, M. A. Demertzis, *Polyhedron* **1999**, *18*, 1005.
[27] D. Kovala-Demertzi, P. N. Yadav, M. A. Demertzis, M. Coluccia, *J. Inorg. Biochem.* **2000**, *78*, 347.
[28] M. B. Ferrari, A. Bonardi, G. G. Fava, C. Pelizzi, P. Tarasconi, *Inorg. Chim. Acta* **1994**, *223*, 77.

[29] K. Nakamoto (3rd Ed.), 'Infrared and Raman Spectra of Inorganic and Coordination Compounds', John Wiley & Sons, New York, 1978, p. 305.
[30] G. B. Deacon, R. J. Phillips, *Coord. Chem. Rev.* **1980**, *33*, 227.
[31] C. M. Sharaby, *Spectrochim. Acta, Part A* **2007**, *66*, 1271.
[32] N. C. Saha, R. J. Butcher, S. Chaudhuri, N. Saha, *Polyhedron* **2003**, *22*, 383.
[33] W. S. Hong, C.-Y. Wu, C.-S. Lee, W.-S. Hwang, M. Y. Chiang, *J. Organomet. Chem*. **2004**, *869*, 277.
[34] A. R. Cowley, J. R. Dilworth, P. S. Donnelly, J. W. Shore, *Dalton Trans.* **2003**, 748.
[35] V. M. Leovac, S. B. Novakovic, G. A. Bogdanovic, M. D. Joksovic, K. M. Szecsenyi, V. I. Cesljevic, *Polyhedron* **2007**, *26*, 3783.
[36] A. B. P. Lever, 'Inorganic Electronic Spectroscopy', 2nd edn., Elsevier, Amsterdam, 1984.
[37] L. Mao, T. Moriuchi, H. Sakurai, H. Fujii, T. Hirao, *Terahedron Lett.* **2005**, *46*, 8419.
[38] D. Kovala-Demertzi, A. Galani, J. R. Miller, C. S. Frampton, M. A. Demertzis, *Polyhedron* **2012**, in press.
[39] E. V. Zahinos, F. L. Giles, P. T. Garcia, M. C. F. Calderon, *Eur. J. Med. Chem.* **2001**, *46*, 150.
[40] G. M. Sheldrick, SHELXL-97, 'Programme for Crystal Structure Refinement', University of Gottenberg, Gottenberg, 1997.
[41] A. M. C. Burla, M. Camalli, G. L. Cascarano, C. Giacovazzo, A. Guagliardi, A. G. G. Moliterni, G. Polidori, R. Spagna, *J. Appl. Crystallogr*. **1999**, *32*, 115.
[42] W. M. M. Kirby, G. M. Yoshihara, K. S. Sundsted, J. H. Warren, *Antibiot. Annu.* **1957**, *892*, 1956.

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