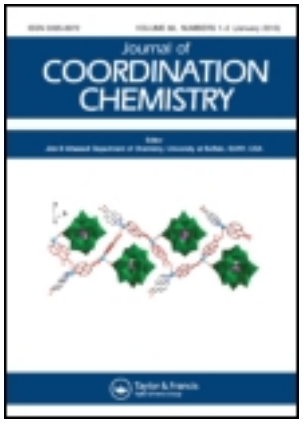

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Synthesis, spectroscopic studies, and preliminary antibacterial assays of a palladium(II) complex with 2-mercaptothiazoline

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Synthesis, spectroscopic studies, and preliminary antibacterial assays of a palladium(II) complex with 2-mercaptothiazoline

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In this article, synthesis of a palladium(II) complex with 2-mercaptothiazoline in aqueous solution is presented. Composition of the complex was defined as 1 : 2 (metal : ligand). Infrared and solid-state nuclear magnetic resonance indicate ligand coordination to Pd(II) through nitrogen of thiazole ring and sulfur of thiol. ESI–QTOF–mass spectrometric analysis shows primarily the dimeric form in solution. An antibiogram assay of the complex was performed by the disc diffusion method. The compound did not show antibacterial activity against the considered bacterial cells in the tested concentrations.

Keywords: Palladium(II); 2-Mercaptothiazoline; Infrared Spectroscopy; Solid-state NMR spectroscopy; ESI–QTOF–mass spectrometry

1. Introduction

Metal ions and their compounds have been used in medicine for centuries in the treatment of different human disorders, for reviews, see Farrell [1], Jakupec *et al*. [2], van Rijt and Sadler [3], and El-Gamel [4]. The rational development of drugs based on inorganic compounds started to increase only in the early 1900s with the use of potassium dicyanoaurate(I), $K[Au(CN)_2]$, in the treatment of tuberculosis, as well as the use of silver and gold salts as antibacterial agents [5]. In spite of their efficacy, metal-based compounds were shown to be highly toxic and progress in the synthesis and medicinal applications of these compounds was modest. However, the serendipitous discovery of the antineoplasic activity of *cis*-diamminedichloroplatinum(II) by Rosenberg *et al*. [6] and its clinical introduction in the 1970s, and description of synthesis and use of silver complexes as silver-sulfadiazine in the treatment of burns and wounds [7] led to the resurgence of the application of metals and their compounds in the treatment of human diseases.

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The similarities of platinum and palladium ions led researchers to consider the possibility of application of palladium(II) compounds as an alternative for the development of new antineoplastic drugs similar to cisplatin, as well as other platinum compounds used in the anticancer therapy, such as carboplatin and oxaliplatin [8]. As observed for platinum(II) compounds, analogs of palladium(II) exhibit square-planar geometries and form stable bonds with sulfur and nitrogen donors. Nevertheless, Pt(II) complexes are thermodynamically and kinetically more stable than analogous complexes of Pd(II), an important aspect when dealing with palladium(II) complexes [9].

Heterocyclic ligands containing sulfur and nitrogen are able to coordinate soft acids such as platinum(II) and palladium(II) forming stable N, S-chelated rings and also due to their capacity to mimic coordination of cysteine to metal ions in metalloenzymes [10–12]. Several Pd(II) complexes with nitrogen and sulfur, which exhibit antitumor and antibacterial activities *in vitro*, were recently reported. Mantesanz and Souza [13] reported Pd(II) complexes with alpha-diphenylethanedione bis(thiosemicarbazone) and alpha-diphenylethanedione bis(4-ethylthiosemicarbazone) with antitumor activity against cisplatin resistant cells. Also, synthesis, characterization and biological assays of Pd(II) and Pt(II) complexes with S-allyl-L-cysteine were described in the literature [14–16]. In both cases, coordination of the ligand to metal was shown to be through N and S, forming five-membered chelate rings. The palladium(II) complex was shown to be the most effective, able to inhibit proliferation of HeLa cells derived from human adenocarcinoma. Indeed, the Pd(II) complex was also shown to possess antibacterial activities against *Staphylococcus aureus* (Gram-positive) and *Escherichia coli* (Gram-negative) bacterial strains. More recently, a dimeric platinum(II) complex with methionine sulfoxide which exhibits S, N coordination was also described [17]. Preliminary antibacterial studies have shown the activity of this complex against *Pseudomonas aeruginosa*, a Gram-negative pathogenic microorganism.

Mercaptothiazoline ($C_3H_5NS_2$, MTZ) is a N,S-heterocyclic ligand which has been described as a precursor for the synthesis of biologically active molecules [18]. The structure of MTZ can be represented by two tautomeric forms (figure 1) [19]. The first studies dealing with a palladium(II) complexes with 2-mercaptothiazoline were published by Dehand and Jordanov [20]. In that case, the complex was synthesized in a non-aqueous medium and characterized solely by elemental analysis and infrared (IR) spectroscopic measurements. Elemental analysis led to the proposition of a 1 : 2 metal/ligand composition while the IR data indicated coordination through N and S. The authors proposed a polymeric structure in a configuration (μ-N-C-S) between the two Pd centers.

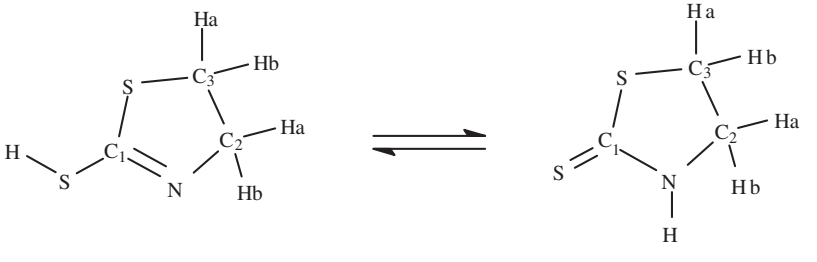

Figure 1. Structural formula of MTZ showing carbon and hydrogen numbering.

More recently, the crystal structures of palladium(II) complexes with MTZ synthesized in acidic medium were reported by Kubiak *et al.* [21] and Raper *et al.* [22]. The complexes were synthesized with an excess of MTZ and presented the respective general formulae: $[Pd(MTZ)_4]Cl_2 \cdot 2MTZ$ and $[Pd(MTZ)_4]Cl_2 \cdot MTZ$. Both compounds are consistent with the presence of $[Pd(MTZ)_4]^{2+}$ cations, Cl^- anions and uncoordinated MTZ molecules linked by a network of $NH \cdots Cl$ interactions. In addition, thermal studies for dimeric complexes of platinum(II) and palladium(II) with benzothiazoline-2-thione (mercaptobenzothiazoline, BTZ) and also with thiazoline-2-thione (2-mercaptothiazoline, MTZ) were reported [23]. The compounds were synthesized in neutral water/ethanol medium from K_2MCl_4 (M = Pd or Pt) and the corresponding ligand. The thermogravimetric data confirm the molar composition of the Pt-BTZ and Pd–MTZ complexes of 1 : 2 metal/ligand. Afterward, Raper [24] published a review describing the metal complexes of platinum(II), palladium(II), rhodium, iridium, molybdenum(II), and nickel(II) containing heterocyclic thionates acting as bridging ligands.

Lizarraga *et al.* [25] also reported the synthesis and characterization of $[Pd(L)BTZ]_2$ (L = 8-methylquinolyl-C,N), $[Pd(BTZ)_2]_2$, and [Pd(L)MTZ] complexes in non-aqueous medium. Spectroscopic data for $[Pd(BTZ)_2]_2$ suggest a dinuclear structure in which the two Pd(II) centers are bridged by N, S atoms (μ-N-C-S) in a S-trans-to-N disposition of the ligands. Here we describe a simple method of synthesis of a dimeric Pd(II) complex with 2-mercaptothiazoline in aqueous solution and its full characterization by elemental and ESI–QTOF–mass spectrometry analysis, IR studies, and also by ^{13}C and ^{15}N nuclear magnetic resonance measurements in the solid-state nuclear magnetic resonance (SSNMR). Preliminary antibacterial studies of the complex and the free ligand were also performed in order to evaluate their possible antibacterial activities against Gram-positive and Gram-negative bacterial cells.

2. Experimental

2.1. *Reagents and equipments*

2-Mercaptothiazoline (98%), potassium hydroxide and lithium tetrachloropalladate(II) (98%) were purchased from Sigma-Aldrich Laboratories. Elemental analyses for carbon, hydrogen, and nitrogen were performed using a Perkin Elmer 2400 CHN Analyzer. IR spectra from 4000–400 cm^{-1} of MTZ and the palladium(II) complex (Pd–MTZ) were measured using an FT-IR spectrophotometer ABB Bomen MB Series; samples were prepared as KBr pellets. The ^{13}C-{^1H} SSNMR spectra of MTZ and of the Pd–MTZ complex were recorded on a Bruker AVANCE 400 MHz (9.395 T) spectrometer operating at 100 MHz, using the combination of cross-polarization, proton decoupling, and magic angle spinning (CP/MAS) at 10 kHz. The ^1H radio-frequency field strength was set to give a 90° pulse. Contact time and recycle delay were 4 ms and 1 s, respectively. Samples were analyzed at room temperature and the chemical shifts were referenced to TMS.

The ^{15}N NMR chemical shift of pure MTZ was indirectly detected in the solution state by a heteronuclear [^1H–^{15}N] multiple bond coherence (HMBC) experiment. The ^1H–^{15}N NMR data were acquired on a Bruker AVANCE 400 MHz spectrometer using

a 5-mm probe at 303 K. The compound was analyzed in deuterated dimethylsulfoxide solution. Due to the insolubility of the Pd–MTZ complex, the ^{15}N NMR data were obtained in the solid state on a Bruker AVANCE 400 MHz spectrometer using CP/MAS. Contact time and recycle delay time were 4 ms and 1 s, respectively.

Electrospray ionization quadrupole time-of-flight mass spectrometric (ESI–QTOF–MS) measurements were carried out in a Waters Synapt HDMS instrument. Sample was prepared as follows: 1.0 mL of dimethylsulfoxide was added to 0.6 mg of the solid sample and the resulting suspension was homogenized and then centrifuged. Subsequently, 15.0 μL of the supernatant was diluted in 1.0 mL of a 50 : 50 H_2O/MeCN (0.1% formic acid, v/v) solution and infused into the instrument's ESI source. Typical acquisition conditions were capillary voltage 3 kV, sampling cone voltage 30 V, source temperature 100°C, desolvation temperature 200°C, cone gas flow 30 L h^{-1}, desolvation gas flow 900 L h^{-1}, and Trap and Transfer collision energies at 6 and 4 eV, respectively. The ESI(+) mass spectra were acquired in reflectron W-mode, while fragment ion spectra for quadrupole-isolated ions (QTOF–MS/MS) were acquired in reflectron V-mode. The instrument was calibrated in both V- and W-modes with phosphoric acid oligomers (H_3PO_4 0.05% in H_2O/MeCN 50 : 50) ranging from m/z 99 to 1960.

2.2. *Synthesis*

The palladium(II) complex with MTZ was synthesized by reaction of 5.0 mL of an aqueous solution of lithium tetrachloropalladate(II) (Li_2PdCl_4) (5.0×10^{-4} mol) with 10.0 mL of a freshly prepared aqueous solution of the potassium salt of 2-mercaptothiazoline containing 1.0×10^{-3} mol of the ligand. The $Li_2[PdCl_4]$ aqueous solution was added to a stirred solution of alkaline MTZ at room temperature. After 2 h of constant stirring the yellowish solid obtained was vacuum-filtered, washed with copious cold water and dried in a desiccator over P_4O_{10}. Elemental analysis led to the following composition for the complex: $PdC_6H_8N_2S_4$. Anal. Calcd for $PdC_6H_8N_2S_4$ (%): C, 21.0; H, 2.35; N, 8.18. Found (%): C, 21.8; H, 2.25; N, 8.06. The Pd–MTZ complex is insoluble in water, ethanol, methanol, acetonitrile, chloroform, acetone, and hexane. It is very slightly soluble in a mixture of water and acetonitrile (50 : 50 v/v) and in dimethylsulfoxide. The composition of the complex matches with the molar ratio of 1 : 2 metal/ligand. The potassium salt of MTZ was prepared by the reaction of equimolar quantities of 2-mercaptothiazoline and potassium hydroxide at room temperature.

2.3. *Antimicrobial assays*

Three referenced bacteria (*Escherichia coli* – ATCC 25922, *Pseudomonas aeruginosa* – ATCC 27853, and *Staphylococcus aureus* – ATCC 25923) were considered for the antibacterial experiments *in vitro*. The antibiogram assay was performed by the disc diffusion method as described [26–28].

Sterile filter paper discs (10 mm diameter) were aseptically impregnated with 800 μg of Pd–MTZ according to the following procedure: 20.0 mg of Pd–MTZ were suspended in 500 μL of water, homogenized, and 20 μL of the suspension were collected with a micropipette and transferred to the paper discs. Sterile discs impregnated with 800 μg of

pure MTZ were used as a negative control. Discs impregnated with 800 μg of lithium tetrachloropalladate (Li_2PdCl_4) were also prepared in order to provide a possible antibacterial activity of the Pd(II) ions in the same experimental conditions.

Discs impregnated with the Pd–MTZ, Li_2PdCl_4 or with MTZ were dried and sterilized in a vertical laminar flow under UV radiation for 45 min before the experiment. All impregnated discs were placed on the surface of the solid agar. The plates were incubated for 18 h at 35–37°C and examined thereafter. Clear zones of inhibition around the discs were measured and the complex sensitivity was assayed from the diameter of the inhibition zones (in millimeters). The obtained results were compared to the standard antibiotic gentamicin (GEN). Experiments were performed in duplicate.

3. Results and discussion

3.1. *^{13}C and ^{15}N NMR spectroscopic measurements*

The structural formula of MTZ with hydrogen and carbon numbering is shown in figure 1. Due to the low solubility of the Pd–MTZ complex in both polar and non-polar solvents the SSNMR technique was applied to provide a structural characterization of the complex. The ^{13}C-{^1H} SSNMR spectrum of the Pd–MTZ complex was obtained and analyzed in comparison to that of pure MTZ. The ^{13}C NMR spectra in the solid state with the respective carbon assignment are provided in figure 2.

According to the experimental data the chemical shifts, C_1 in the free ligand spectrum and in the complex spectrum are observed at 200 ppm and at 181 ppm, respectively, with a $\Delta\delta$ (δ complex $-$ δ ligand) of -19 ppm. C_2 NMR signals are observed at 54.7 ppm in the spectrum of the free ligand and at 65.4 ppm in the spectrum of the complex, with a $\Delta\delta = 10.7$ ppm. No chemical shift difference is observed for C_3 ($\Delta\delta = 1.5$ ppm). The observed chemical shifts for C_1 and C_2 when the ligand and complex spectra are compared suggest coordination through nitrogen of the heterocyclic ring and sulfur of the thiol. The NMR results suggest that no coordination occurs through sulfur of the heterocyclic ring (C–S–C) since no significant chemical shift is observed for C_3.

Solution-state ^{15}N NMR data for MTZ was indirectly obtained from 2D spectra *via* the HMBC technique, as described for other palladium(II) and platinum(II) complexes with N-donor ligands [15, 16]. The assignment of the nitrogen resonance was performed by its correlation with protons $H^{(3a)}$ and $H^{(3b)}$ in figure 1. Analysis of the HMBC spectrum of MTZ identified the ^{15}N signal at 154.4 ppm. The ^{15}N NMR data of the Pd–MTZ complex was obtained in the solid state due to its low solubility. The ^{15}N NMR spectrum of the complex showed the ^{15}N signal at 191.1 ppm. The observed ^{15}N $\Delta\delta$ of 36.7 ppm further supports nitrogen coordination of MTZ to Pd(II) as proposed by the ^{13}C NMR spectroscopic analysis.

3.2. *IR spectroscopic data*

The Pd–MTZ IR spectrum was analyzed in comparison to that of free MTZ (Supplementary material). A medium intensity band at 3145 cm^{-1} in the spectrum of free ligand can be assigned to ν(N–H) [29]. The absence of this band in the IR spectrum of the complex shows coordination through nitrogen [20]. Sharp and strong bands at

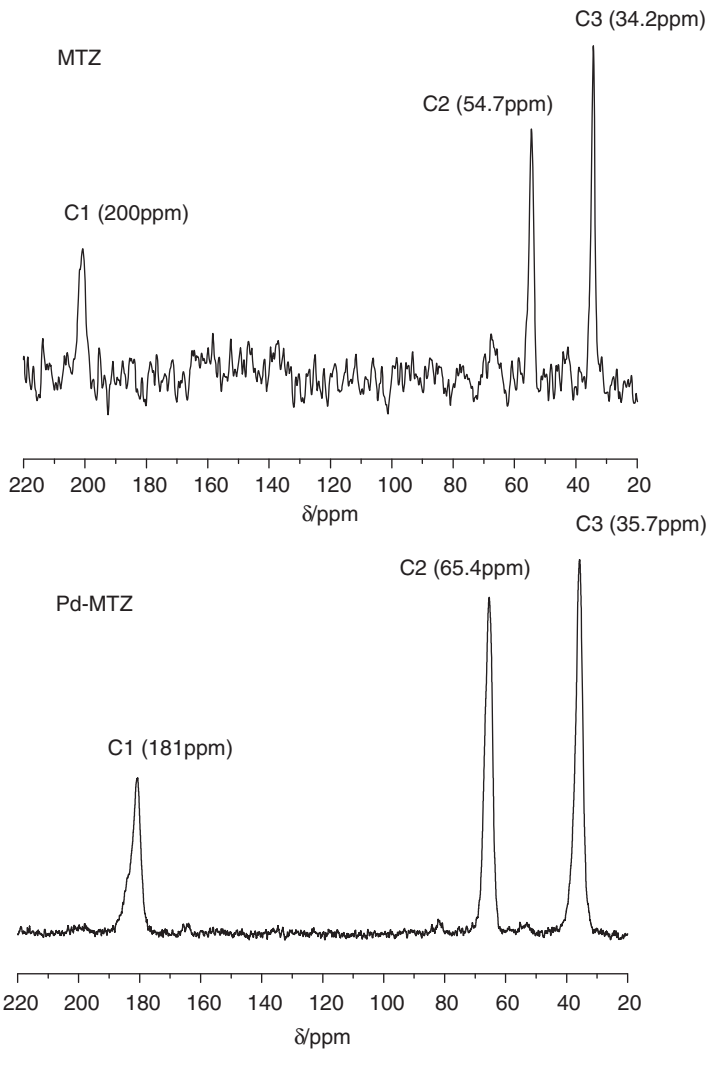

Figure 2. Solid-state ^{13}C NMR spectra of MTZ and Pd–MTZ.

1517 cm^{-1} in the IR spectrum of the ligand and at 1533 cm^{-1} in the spectrum of the Pd–MTZ complex were observed. According to previous work these bands are assigned to a ν(–C=N–) of the heterocyclic ring [20]. As a final point, coordination of MTZ to Pd(II) through sulfur of thiol was proposed by considering the C–S vibration band. In the spectrum of the complex, this band is at 670 cm^{-1}. The absence of this band in the same region of the IR spectrum of the Pd–MTZ complex can be considered as an indicative of coordination of the ligand through sulfur [20].

3.3. *Mass spectrometric measurements*

The ESI–QTOF–MS analyses of the Pd(II)–MTZ complex clearly demonstrate the dimeric structure as the major species in solution in the form of a single charged

monoprotonated ion ($[Pd_2MTZ_4 + H]^+$, m/z 684.73). Also, the $[Pd_2MTZ_3]^+$ species (m/z 565.74) was detected (figure 3a), being attributed to the dimeric form less one ligand. Although low abundance, the trimeric ($[Pd_3MTZ_6 + H]^+$, m/z 1026.59) and the tetrameric ($[Pd_4MTZ_8 + H]^+$, m/z 1368.45) forms (figure 3a) were also detected in solution.

A comparison of the isotope patterns for the monoprotonated dimeric and tetrameric ions (figure 3b and c, respectively) are in good agreement with the theoretical predictions. Considering the monoisotopic ion of each composition, mass errors were +2.2 ppm for the monoprotonated dimer ($C_{12}H_{17}N_4S_8Pd_2^+$, Calcd m/z 684.7288, exp. m/z 684.7303) and of −0.5 ppm for the monoprotonated tetramer ($C_{24}H_{33}N_8S_{16}Pd_4^+$, Calcd m/z 1368.4499, exp. m/z 1368.4492).

To further investigate the structure of the observed ions, fragment ion spectra were acquired for the monoprotonated dimeric and tetrameric ions. Both spectra are presented as Supplementary material. The spectrum of the dimer, $[Pd_2MTZ_4 + H]^+$, showed two consecutive losses of 119 Da, which can be attributed to the elimination of neutral MTZ ligands. Also, the tetrameric ion $[Pd_4MTZ_8 + H]^+$ showed the loss of a neutral dimeric subunit ($[Pd_2MTZ_4]$) of 683 Da, as well as the loss of MTZ (119 Da). The observed data confirm the previously proposed dimeric and tetrameric structures.

3.4. *Antibacterial studies*

Antibiotic sensitivity profiles of bacterial strains demonstrate non-activity of the Pd–MTZ complex against the Gram-negative (*E. coli* and *P. aeruginosa*) and Gram-positive (*S. aureus*) microorganisms in the tested concentrations, as observed by the disc diffusion method. Impregnated paper discs with gentamicin exhibited inhibition zones for *E. coli*, *P. aeruginosa,* and *S. aureus* of 24.0 ± 0.1 mm, 24.0 ± 0.1 mm, and 31.0 ± 0.1 mm, respectively. The Li_2PdCl_4 also presented antibacterial activities against the considered bacterial cells with inhibition zones for *E. coli*, *P. aeruginosa,* and *S. aureus* of 16.0 ± 0.1 mm, 16.0 ± 0.1 mm, and 18.0 ± 0.1 mm, respectively. Pure MTZ did not show antibacterial activities against the considered bacterial cells in the same experimental conditions.

4. Conclusions

The molar composition of the palladium(II) complex with MTZ was 1 : 2 (metal : ligand). The IR and ^{13}C NMR spectroscopic measurements in the solid state confirmed coordination of the ligand to Pd(II) through nitrogen of the heterocyclic ring and sulfur of the thiol. The ^{15}N NMR measurements reinforced nitrogen coordination of the ligand to Pd(II). Mass spectrometric measurements supported formation of a dimeric structure for the complex, which was further confirmed by fragment ion experiments. Based on chemical and spectroscopic data and considering the previous structural reports of a Pd(II) complex with mercaptobenzothiazole, a dimeric structure with the coordination formula $[Pd(C_3H_4NS_2)_2]_2$ is proposed for the Pd–MTZ complex (figure 4). In this case, each MTZ ligand bridges two metals in a −Pd-(μ-N-C-S)-Pd− arrangement.

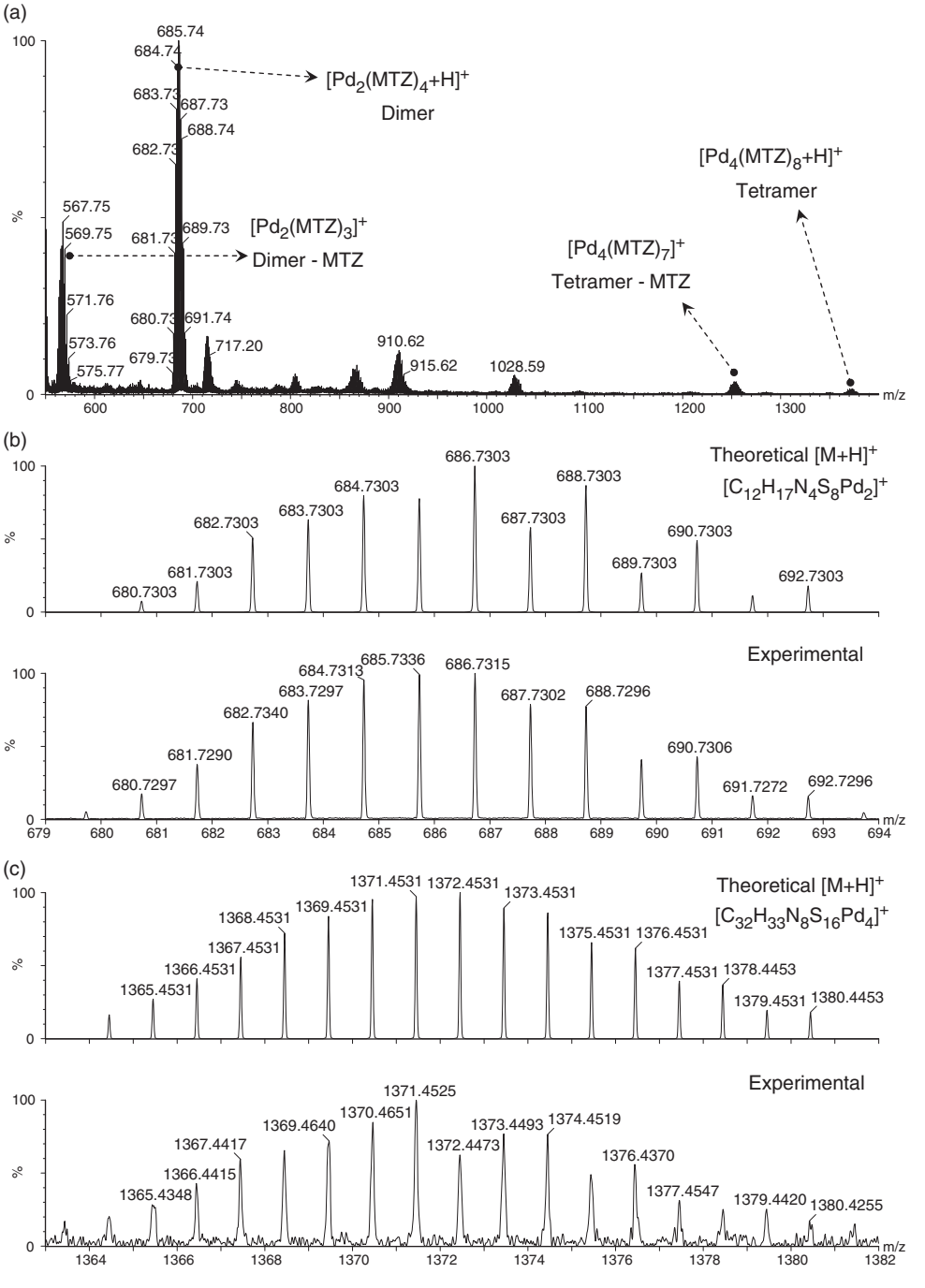

Figure 3. Mass spectra for the Pd–MTZ complex: (a) ESI(+)–QTOF–mass spectrum from m/z 550 to 1400; (b) isotope pattern comparison for the monoprotonated dimer, $[Pd_2MTZ_4+H]^+$ of m/z 684.72; (c) isotope pattern comparison for the monoprotonated tetramer, $[Pd_4MTZ_8+H]^+$ of m/z 1368.45.

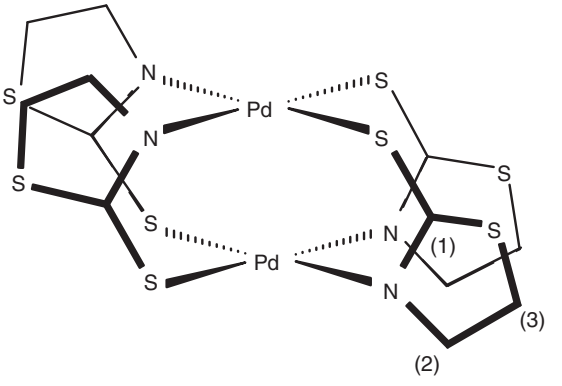

Figure 4. Proposed structure for the Pd–MTZ complex. Hydrogens were omitted for clarity.

The compound did not show antibacterial activity against *E. coli*, *P. aeruginosa*, and *S. aureus* microorganisms as observed by antibiogram assays. Further studies of the biological activity of the Pd–MTZ complex may be envisaged in order to provide additional information concerning a possible antibacterial activity of the compound in different concentrations and also against different bacterial species.

Acknowledgments

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