Synthesis, spectral characterization and antibacterial studies of palladium(II) complexes of heterocyclic thiones

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Abstract. Reactions of $K_2[PdCl_4]$ with heterocyclic thiones in molar ratios of 1:2 and 1:4 in water-methanol medium yielded the palladium(II) complexes with the general formula of either $[Pd(L)Cl_2]$, $[Pd(L)_2Cl_2]$ or $[Pd(L)_4]Cl_2$ where L = Imidazolidine-2-thione (Imt), 2-Mercaptopurine (Mpy), 2-Mercaptopurine (Mpm), 6-Mercaptopurine (6-Mp) and Thionicotinamide (Tna). The complexes were characterized by elemental analysis and spectroscopic (IR, 1H and ^{13}C NMR) methods. An upfield shift in the $>C=S$ resonance of thiones in ^{13}C NMR and downfield shift in N–H or aromatic proton resonances in 1H NMR are consistent with the sulfur coordination to palladium(II). The complexes were screened for antibacterial activity, and the results showed that the complexes exhibited moderate activities as compared to that of a standard drug.

Keywords: Palladium(II), thiones, NMR spectroscopy, antibacterial activity

1. Introduction

Heterocyclic thiones are among the ligand systems used to mimic bio-relevant metal–sulfur interactions and therefore, the complexes of heterocyclic thiones such as imidazolidine-2-thione (Imt), diazinane-2-thione (Diaz) and their derivatives with transition metals are of significant interest from bioinorganic chemistry point of view [1–10]. 6-Mercaptopurine and its riboside are anticancer metabolites and their complexes of Pd(II) and Pt(II) are known to exhibit antitumor activity [11–13]. In view of this importance, several complexes of thiones with Cu(I) [14–17], Ag(I) [18–24], Au(I) [25–27], Mo(II) [28], Pd(II) [29–34], Zn(II) [35–39], Cd(II) [39–45] and Hg(II) [46–50] have been widely studied. We have been interested in the spectral and structural chemistry of several metal ions with thiones in order to study their binding modes and to provide useful models for metalloproteins [16–20,26,27,33,34,41]. As

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Scheme 1. Structures of the ligands used in the study.

a part of our continuous interest in the structural chemistry of metal–sulfur interactions, we report here the synthesis of palladium(II) complexes with a number of heterocyclic thiones and their characterization by IR, ^1H and ^{13}C NMR spectroscopy. We have also investigated the antibacterial activities of these complexes, which in some cases are significant compared to that of a standard drug. The knowledge of coordination behavior of heterocyclic thiones towards palladium(II) would be useful to understand the interactions of heavy metals to nucleotides and related compounds, which may have antitumor activity. The structures of the ligands used in this study are shown in Scheme 1.

2. Experimental procedure

2.1. Materials

Palladium(II) chloride was purchased from Degussa AG 40474, Düsseldorf, Germany. 2-Mercaptopyridine (Mpy), 2-Mercaptopyrimidine (Mpm), 6-Mercaptopurine monohydrate (6-Mp) and Thionicotinamide (Tna) were purchased from ACROS Organics, USA. Nutrient agar was purchased from OXOID, England. Imidazolidine-2-thione (Imt) was prepared according to the published procedure [26].

2.2. Synthesis of the complexes

The potassium tetrachloropalladate(II) was prepared as described in the literature; by the reaction palladium chloride with an excess of potassium chloride [34]. The complexes were prepared by adding 2 and 4 equivalents of heterocyclic thiones in 15 ml methanol to a solution of $\text{K}_2[\text{PdCl}_4]$ (0.326 g) in 15 ml of water and stirring the solutions for one hour. For Imt complexes, mixing resulted in yellow (with 1:2 ratio) or dark brown color (with 1:4 ratio of Pd to Imt) solutions. In case of Mpy, reddish color, for Tna pale yellow color solutions, and for Mpm and 6-Mp, red color solutions were obtained. After filtration the solutions were kept at room temperature for three to five days. Solid products were obtained from water–methanol mixture on slow evaporation. The elemental analysis and melting points (m.p.) of the complexes are given in Table 1.

Table 1
Elemental analysis, melting points and % yield of palladium(II) complexes

Complexes	Found (calculated) (%)				m.p. (°C)	Yield (%)
	C	H	N	S		
[Pd(Imt) ₂ Cl ₂]*	22.21 (18.88)	3.81 (3.17)	17.06 (14.68)	19.25 (16.83)	190	75
[Pd(Imt) ₄]Cl ₂	24.38 (24.60)	4.34 (4.13)	18.73 (19.12)	22.27 (21.80)	207	70
[Pd(Mpy) ₂ Cl ₂]	30.96 (30.05)	2.79 (2.52)	7.45 (7.01)	17.14 (16.05)	284	70
[Pd(Mpy) ₄]Cl ₂ *	32.17 (38.62)	2.09 (3.24)	11.35 (9.01)	22.39 (20.62)	260	75
[Pd(Mpm) ₄]Cl ₂	29.98 (30.70)	2.56 (2.58)	15.99 (17.90)	18.37 (20.49)	225	70
[Pd(6-Mp) ₂ Cl ₂]	26.71 (24.93)	2.43 (1.67)	24.36 (23.26)	13.88 (13.31)	350	65
[Pd(Tna)Cl ₂]**	23.00 (22.82)	2.62 (1.91)	8.02 (8.87)	13.25 (10.16)	243	60
[Pd(Tna) ₂ Cl ₂]	28.17 (31.77)	2.78 (2.67)	11.10 (12.35)	12.58 (14.14)	247	70

*The analysis percentages of these complexes do not correspond to either composition, [PdL₂Cl₂] or [PdL₄]Cl₂ and are in between the two calculated values. However, in case of [Pd(Mpy)₄]Cl₂ it is close to [Pd(Mpy)₂Cl₂].

**The complex [Pd(Tna)Cl₂] was prepared in the reaction with the ratio of 1:4.

2.3. Measurements

Elemental analysis was carried out on a Leco CHNS-932, Leco Corporation, USA. Melting point was recorded on an Electrothermal IA 9000 Series, Essex SS2 5PH, UK. FT-IR spectra were recorded on a Thermo Nicolet Nexus 6700, USA. The ¹H and ¹³C NMR spectra of the ligands and their complexes in DMSO-d₆ were obtained on Bruker Avance 300 MHz NMR spectrometer operating at frequencies of 300.00 and 75.47 MHz respectively at 300 K. The spectral conditions were: 32 K data points, 1.822 s acquisition time, 2.00 s pulse delay and 6.00 μs pulse width. The ¹³C chemical shifts were measured relative to TMS.

2.4. Antibacterial activities of the complexes

The antibacterial activity of all synthesized metal complexes has been investigated against four bacteria, two G(+) i.e. *Staphylococcus aureus* ATCC 25923, *Bacillus subtilis* DSM 3256 (Germany), and two G(−) bacterial strains i.e. *Escherichia coli* ATCC 25922 and *Pseudomonas aeruginosa* ATCC 10197 by the agar well diffusion method [51–53]. Imipenem was used as standard antibiotic, which is β-Lactam antibiotic effective against G(+) as well as G(−) bacteria. 3 mg of the test samples (ligands and complexes) were dissolved in 1 ml of DMSO. 2–3 ml nutrient broth (0.8 g/100 ml) was prepared in distilled water with pH 7 and was autoclaved at 121°C, 15 psi pressure and for 20 min. Fresh culture grown in 24 h on nutrient broth at pH 7 were used for sensitivity testing. To compare the turbidity of bacterial cultures McFarland BaSO₄ solution was used as turbidity standard. To perform antibacterial assay, nutrient agar medium was prepared by dissolving 2 g/100 ml in distilled water with pH 7 and the medium

was autoclaved. A 25 ml of the nutrient agar medium was poured in Petri plates of 9 cm diameter and allowed to solidify. Using sterile cotton swabs lawns of test cultures were prepared on labeled plates. Four wells per plate were prepared with the help of sterile cork borer (2 mm). Using micropipette, 30 μ l of test solution were poured in respective labeled wells. Now, these Experimental plates were incubated for 24 h and average of zones of inhibition (%) of three replicates were measured and compared with the zone of standard antibiotic imipenem with zone inhibition of 21, 18, 16 and 18 mm respectively, which were taken as 100% (Table 4).

3. Results and discussion

3.1. IR studies

The palladium(II) complexes of the types, $[\text{Pd}(\text{thione})_2\text{Cl}_2]$ and $[\text{Pd}(\text{thione})_4]\text{Cl}_2$ were obtained from reaction of $\text{K}_2[\text{PdCl}_2]$ with thiones in 1:1 and 1:2 molar in methanol–water media. However, the elemental analysis suggests that only in case of Imt and Mpy, both types of products were formed. For Mpm only $[\text{Pd}(\text{thione})_4]\text{Cl}_2$ type, while for 6-Mp, only $[\text{Pd}(\text{thione})_2\text{Cl}_2]$ type complexes were obtained. In the reactions of Tna, the analysis shows that the complex of the type $[\text{Pd}(\text{thione})\text{Cl}_2]$ was also formed. Selected IR spectroscopic vibrational bands for the free ligands and their palladium(II) complexes are given in Table 2. In the IR spectrum of thiones, the characteristic bands are observed in three frequency regions; $\nu(\text{C}=\text{S})$ appears around 600 cm^{-1} , $\nu(\text{C}-\text{N})$ at about 1500 cm^{-1} and $\nu(\text{N}-\text{H})$ is observed near 3200 cm^{-1} . The presence of N–H vibrations in the complexes confirms the thione forms of the ligands in the solid state. The $\delta(\text{N}-\text{H})$ bands were observed at $1675\text{--}1515\text{ cm}^{-1}$. The absorptions at $366\text{--}320\text{ cm}^{-1}$ and at $302\text{--}270\text{ cm}^{-1}$ were attributed to $\nu(\text{Pd}-\text{S})$ and $\nu(\text{Pd}-\text{Cl})$ vibrations respectively [54].

3.2. NMR studies

In ^1H NMR spectra of the complexes the N–H signal of thiones become less intense upon coordination and shifted slightly downfield with respect to their positions in free ligands. However, it could not be

Table 2
Selected IR absorption (cm^{-1}) for free ligands and their palladium(II) complexes

Species	$\nu(\text{C}=\text{S})$	$\nu(\text{N}-\text{H})$	$\delta(\text{N}-\text{H})$	$\nu(\text{C}-\text{N})$	$\nu(\text{Pd}-\text{S})$	$\nu(\text{Pd}-\text{Cl})$
Imt	510	3237	1515	1454	–	–
$[\text{Pd}(\text{Imt})_2\text{Cl}_2]$	497	3362	–	1476	326	280
$[\text{Pd}(\text{Imt})_4]\text{Cl}_2$	526	3419, 3318	1617	1435	329	282
Mpy	613	3176	1578	1487	–	–
$[\text{Pd}(\text{Mpy})_2\text{Cl}_2]$	590	3179	1567	1485	343	291
$[\text{Pd}(\text{Mpy})_4]\text{Cl}_2$	546	3180	1571	1490	345	292, 268
Mpm	624	3053	1602	1491	–	–
$[\text{Pd}(\text{Mpm})_4]\text{Cl}_2$	630	3070	1548	1466	354	291
6-Mp	588	3431	1614	1576	–	–
$[\text{Pd}(6\text{-Mp})_2\text{Cl}_2]$	626	3398	1626	–	366	302
Tna	698	3180	1675	1468	–	–
$[\text{Pd}(\text{Tna})\text{Cl}_2]$	695	3230	1674	1405	302	273
$[\text{Pd}(\text{Tna})_2\text{Cl}_2]$	669	–	1674	1406	325	273

observed in all cases. The deshielding of the N–H proton is related to an increase of the π electron density in the C–N bond upon complexation [22]. A slight downfield shift was also observed in the C–N and aromatic protons. For example, in $[\text{Pd}(\text{Mpy})_2\text{Cl}_2]$ the aromatic protons at C-3, C-4, C-5 and C–N appear at 7.78, 7.20, 7.65, 7.94 ppm respectively (for the free ligand; 7.338, 6.808, 7.467 and 7.705 ppm). The protons at C-3 and C–N appear as doublets, while the other two appear as triplets. In 6-MP, the H-2 and H-8 protons appear at 8.20 and 8.40 ppm respectively [13]. Palladium complexation causes a downfield shift of about 0.3 ppm H-8 proton and the signal is also broadened, while the H-2 proton is only slightly shifted. The shift in H-8 suggests the involvement of N-7 in binding to metal ion (Pd^{2+}). In the ^1H NMR spectrum of Mpm, two signals were observed, a triplet at 6.90 ppm and a broad signal at 8.33 ppm. On coordination the signal at 6.90 ppm was shifted to 7.07 ppm, while the one at 8.33 ppm split into two resonances, 8.31 and 8.92 ppm. All three signals appeared as quartets.

The ^{13}C NMR chemical shifts of the ligands and their complexes are given in Table 3. Upfield shifts are observed in the $>\text{C}=\text{S}$ resonance of the ligands on their complexation with palladium(II). The upfield is attributed to the lowering of $>\text{C}=\text{S}$ bond of $\text{N} \rightarrow \text{C}$ electron density producing a partial double bond character in the C–N bond, as observed in the other palladium(II) complexes of thiones [34,55]. However, in case of 6-MP complexes instead of an upfield, a downfield shift was observed in the $>\text{C}=\text{S}$ resonance. This observation is consistent with the other reported studies [13,28]. Also in the 6-Mp complex, the C-5 and C-8 signals split into two resonances, showing that 6-Mp forms two geometrical isomers with palladium(II). A similar observation has been made for a gold complex [56]. Significantly large shifts in these two resonances indicate that N-7 nitrogen is involved in metal binding. As the shift difference may be related to the strength of metal–sulfur bond, Table 3 suggests that the Tnm complex with the most significant shift in the C=S resonance would be the most stable.

3.3. Antibacterial studies

The antibacterial activities of Pd(II) complexes have been determined against four strains of bacteria (*Staphylococcus aureus* (ATCC 25923), *Bacillus subtilis* (DSM 3256), *Escherichia coli* (ATCC 25922)

Table 3
 ^1H and ^{13}C chemical shifts of heterocyclic thiones and their palladium(II) complexes in DMSO-d_6

Species	N–H	C-2	C-3	C-4	C-5	C-6	C-7/C-8
Imt	7.99	183.86	–	44.40	44.40	–	–
$[\text{Pd}(\text{Imt})_2\text{Cl}_2]$	8.82	178.22	–	45.46	45.46	–	–
$[\text{Pd}(\text{Imt})_4]\text{Cl}_2$	8.26	177.22, 176.79	–	46.80, 46.33	46.80, 46.33	–	–
Mpy	–	177.69	133.22	113.94	137.49	137.91	–
$[\text{Pd}(\text{Mpy})_2\text{Cl}_2]$	–	157.79	122.29	120.03	138.64	150.19	–
$[\text{Pd}(\text{Mpy})_4]\text{Cl}_2$	–	167.02	132.11	118.93	140.00	141.06	–
Mpm	–	181.90	–	155.00	109.96	155.00	–
$[\text{Pd}(\text{Mpm})_4]\text{Cl}_2$	–	180.87	–	157.11	115.86	159.55	–
6-Mp	–	144.55	–	150.95	128.75	171.25	145.08
$[\text{Pd}(6\text{-Mp})_2\text{Cl}_2]$	9.23	148.40	–	156.36	119.95, 116.45	174.13	128.54, 131.09
Tna	9.77, 10.12	151.59	135.31	134.87	123.06	147.61	197.92
$[\text{Pd}(\text{Tna})_2\text{Cl}_2]$	–	154.56	138.00	136.16	126.50	149.35	178.08

Note: NMR spectra of $[\text{Pd}(\text{Tna})\text{Cl}_2]$ could not be recorded because it did not dissolve in any solvent. It was only partially dissolved in DMSO on boiling but we were failed to analyze it.

Table 4
Antibacterial activities of palladium(II) complexes of heterocyclic thiones

Name of complex/ligand/Std.	Microorganism (% zone of inhibition of Std. drugs, ligands and complexes)			
	<i>Staphylococcus aureus</i> ATCC 25923	<i>Bacillus subtilis</i> DSM 3256	<i>Escherichia coli</i> ATCC 25922	<i>Pseudomonas aeruginosa</i> ATCC10197
	% value			
Imipenem	100 (21 mm)*	100 (18 mm)*	100 (16 mm)*	100 (18 mm)*
Imt	0	22	38	28
[Pd(Imt) ₂ Cl ₂]	19	45	25	28
[Pd(Imt) ₄]Cl ₂	10	11	13	11
Mpy	52	95	100	83
[Pd(Mpy) ₂ Cl ₂]	48	28	69	39
[Pd(Mpy) ₄]Cl ₂	19	28	38	28
Mpm	19	45	63	45
[Pd(Mpm) ₄]Cl ₂	48	33	13	17
6-Mp	10	17	13	11
[Pd(6-Mp) ₂]Cl ₂	0	0	0	11
Tna	0	0	18.7	0
[Pd(Tna) ₂ Cl ₂]	10	11	0	17

*Percentage corresponding to zone of inhibition.

and *Pseudomonas aeruginosa* (ATCC 10197). The results (average of three measurements) shown in Table 4 suggest that the complexes exhibit a wide range of activities against these bacteria. The mercaptopyridine complex, [Pd(Mpy)₂Cl₂] exhibits the most significant activity among these complexes especially, its activity against *Escherichia coli* is remarkable. However, the activity of mercaptopyridine as a free ligand is even more pronounced. Similarly, uncomplexed mercaptopyrimidine also shows greater activity than the complexes. The complexes of mercaptopyrimidine, and imidazolidine-2-thione exhibited a moderate activity against all of these bacteria. The 6-mercaptopurine complex is only effective against *Pseudomonas aeruginosa* and inactive against all others. Thionicotinamide complex is effective against all three bacteria and inactive against *Escherichia coli*.

The antibacterial activities of the complexes are due to a direct interaction of metal ions with biological ligands such as proteins, enzymes and membranes [57–59]. The antibacterial activity of Pd(II) complexes may be attributed to their tendency to undergo further ligand replacement reactions with the biological ligands such as proteins and DNA. The greater activity of mercaptopyridine and mercaptopyrimidine complexes is possibly because of the formation of a strained 4-membered ring due to which Pd(II) becomes more labile in these complexes. In case of 6-mercaptopurine and thionicotinamide, a stable chelate is formed due to which the ligands could not be displaced easily by biological ligands and as a result the activities are poor.

The present study shows that thiones can form complexes with palladium(II) with different M:L ratios in which the ligands exist in the thione form. One of the complexes exhibits significant biological activity showing the potential for its use as antibacterial agent. It has been observed that antibacterial activity decreases on complexation, while some ligands are biologically inactive but upon coordination showed biological activity. The inactivity or decreased biological activity of some of the complexes may be related to the strongly coordinated ligands with the metal [59].

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