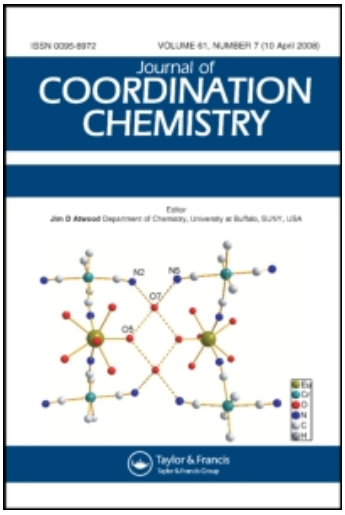

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Palladium(II) thiohydrazone complexes: synthesis, spectral characterization and antifungal study

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Palladium(II) thiohydrazone complexes: synthesis, spectral characterization and antifungal study

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Palladium(II) complexes of type $[Pd(L)Cl_2]$ [where, L = benzaldehyde-1,1-diphenyl-2-thiohydrazone (L^1), salicylaldehyde-1,1-diphenyl-2-thiohydrazone (L^2), acetaphenone-1,1-diphenyl-2-thiohydrazone (L^3) and cyclohexanone-1,1-diphenyl-2-thiohydrazone (L^4)] have been synthesized. The thiohydrazones can exist as thione-thiol tautomers and coordinate as a bidentate N–S ligand. The ligands are found to be monobasic bidentate. The complexes have been characterized by elemental analysis, IR, mass, electronic, ^1H NMR spectroscopic studies. *In vitro* antifungal studies against fungi *Aspergillus fumigatus, Aspergillus flavus* and *Aspergillus niger* for some complexes have also been carried out.

Keywords: Synthesis; Characterization; Spectral; Antifungal; Palladium

1. Introduction

Thiohydrazones and their metal complexes have been intensively studied due to their range of potential biological uses such as antibacterial, antimalarial, antineoplastic and antiviral activities [1–4]. Schiff bases of thiohydrazone moieties have an additional interest, because they also contain the –N=C– structural unit, which forms a strong chelate ring giving possible electron delocalization. The thiohydrazones are significantly affected by substitution at the moiety's N(4) position [5, 6]. A few papers have been published on palladium complexes of substituted thiohydrazides and thiohydrazones [4, 7–9]. The ligands with sulphur or nitrogen donor atoms in their structures are good chelating agents for transition and non-transition metal ions [10–11]. In view of the applications of thiohydrazones, we synthesize and characterize Palladium(II) thiohydrazone complexes. *In vitro* antifungal studies against fungi *Aspergillus fumigatus, Aspergillus flavus* and *Aspergillus niger* for some complexes have also been carried out.

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2. Experimental

2.1. *Materials and methods*

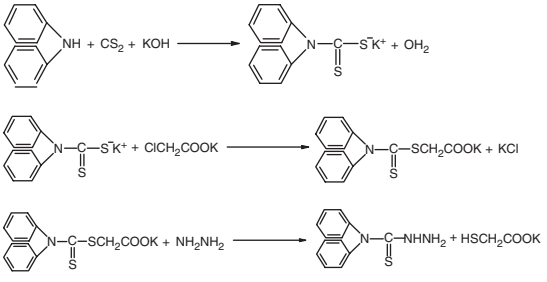
All the reagents used were AR grade. The analysis of CHNS content of ligands and metal complexes were done on Elementar Analysensysteme Gmbh Vario El-III. IR spectra were recorded using KBr pellets on Perkin–Elmer spectrum 2000 FTIR spectrometer. Electronic spectra of the ligands in methanol solution and the complexes in DMSO solution were recorded on Shimadzu UV-visible spectrophotometer Model 1601. Conductance measurements of the complexes in DMSO solution were carried out on Digital Conductometer Model PT-827, India. Model JEOL SX102/DA-600 (KV 10MA) was used for recording mass spectra of the ligands in methanol solution.

^{1}H NMR spectra of all the complexes were recorded in d_6-DMSO on Bruker Spectrospin 300 Spectrometer.

2.1.1. Preparation of 1,1-diphenyl-2-thiohydrazide (L^0). 1,1-diphenyl-2-thiohydrazide was prepared by modification of the literature method [3–7, 12].

In a three-necked round bottom flask 8.46 g (0.05 mol) of diphenyl amine was dissolved in 40 mL methanol and chilled in an ice bath. To this, a chilled solution of 2.8 g (0.05 mol) potassium hydroxide in 1 mL water and 10 mL methanol was mixed with constant stirring. The mixed solution was treated with an ice-cold solution of 3.02 mL (0.05 mol) carbon disulphide (density 1.26) in 3 mL methanol. The temperature of the reaction mixture was maintained below 10°C by keeping the flask in a freezing mixture of common salt and ice. During the process, a white crystalline precipitate of 1,1-diphenyl-2-dithiocarbamate separated. It was filtered, washed with ice-cold aqueous methanol. The product was then suspended in 10 mL methanol and treated with freshly prepared potassium chloroacetate [(0.05 mol){potassium chloroacetate was obtained by dissolving 4.73 g chloroacetic acid in 3 mL ice cold water and mixing it in 5 mL aqueous solution of 2.8 g potassium hydroxide}]. The temperature of the reaction mixture was kept ~40°C on a water bath for an hour and the contents were left overnight at room temperature (25°C). After 24 h methanolic solution of 2.44 mL (0.05 mol) hydrazine hydrate (density 1.026) was added to the reaction mixture. The content was then heated on a water bath at 40°C for about 45 min till the desired product began to separate out. It was then cooled in ice for 24 h and filtered. 1,1-diphenyl-2-thiohydrazide thus obtained was recrystallized from methanol and dried under vacuum over $CaCl_2$ at room temperature.

The reactions taking place in the preparation are shown below:

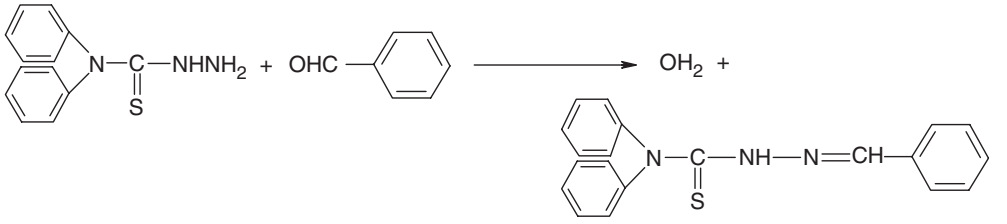


CHNS-Analysis; found (Calcd)%: C; 63.89 (64.19), H; 5.33 (5.35), N; 18.68 (17.28), S; (12.67) 13.16.

Mass spectra; *m*/*z*: 243.59; 169.15.

2.1.2. Preparation of thiohydrazones. The thiohydrazones were prepared by refluxing the 1,1-diphenyl-2-thiohydrazide with corresponding aldehydes or ketones in methanol.

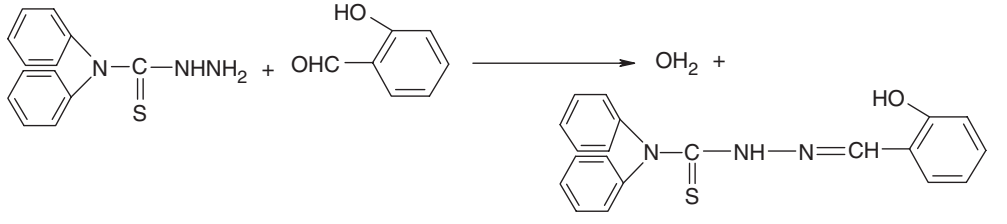
Preparation of benzaldehyde-1,1-diphenyl-2-thiohydrazone (L^1). 7.29 g (0.03 mol) of 1,1-diphenyl-2-thiohydrazide and 3.05 mL (0.03 mol) of benzaldehyde (density 1.044) were refluxed in methanol for three hours. On cooling the yellowish mass obtained was filtered and washed with cold methanol. It was recrystallized from hot methanol.



CHNS-Analysis; found (Calcd)%: C; 73.49 (72.50), H; 5.07 (5.10), N; 12.66 (12.70), S; (8.93) 9.70.

Mass spectra; *m*/*z* 331.34; 243.45; 169.23.

Preparation of salicylaldehyde-1,1-diphenyl-2-thiohydrazone (L^2). 7.29 g (0.03 mol) of 1,1-diphenyl-2-thiohydrazide and 3.15 mL (0.03 mol) of salicylaldehyde (density 1.164) were refluxed in methanol for three hours. On cooling the yellowish mass obtained was filtered, washed with cold methanol and recrystallized from hot methanol.

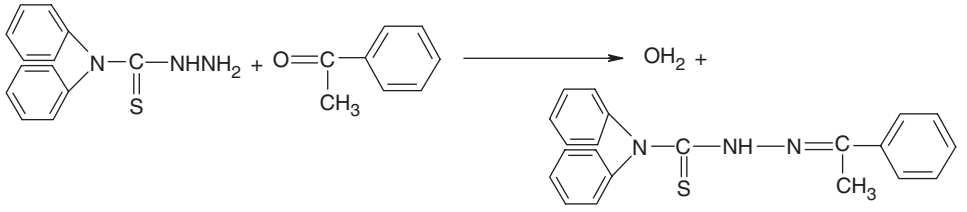


CHNS-Analysis; found (Calcd)%: C; 68.99 (69.16), H; 4.93 (4.90), N; 12.43 (12.10), S; (8.17) 9.20.

Mass spectra; *m*/*z*: 347.69; 243.55; 169.47.

Preparation of acetaphenone-1,1-diphenyl-2-thiohydrazone (L^3). 7.29 g (0.03 mol) of 1,1-diphenyl-2-thiohydrazide and 3.52 mL (0.03 mol) of acetaphenone (density 1.025) were refluxed in methanol for three hours. On cooling the yellowish mass obtained

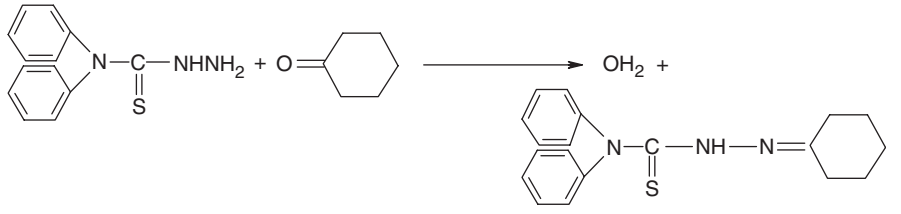
was filtered, washed with cold methanol and recrystallized from hot methanol.



CHNS-Analysis; found (Calcd)%: C; 74.11 (73.04), H; 5.49 (5.51), N; 11.86 (12.17), S; (9.07) 9.28.

Mass spectra; *m*/*z*: 345.53; 243.61; 169.85.

Preparation of cyclohexanone-1,1-diphenyl-2-thiohydrazone (L^4). 7.29 g (0.03 mol) of 1,1-diphenyl-2-thiohydrazide and 3.12 mL (0.03 mol) of cyclohexanone (density 0.945) were refluxed in methanol for three hours. On cooling the yellowish mass obtained was filtered, washed with cold methanol and recrystallized from hot methanol.



CHNS-Analysis; found (Calcd)%: C; 68.86 (69.45), H; 6.73 (6.75), N; 12.98 (13.50), S; (11.19) 10.28.

Mass spectra; *m*/*z*: 311.18; 243.78; 169.92.

2.2. *Preparation of complexes*

2.2.1. Preparation of $[Pd(L)Cl_2]$ complexes where $L = L^1$, L^2, L^3 & L^4. The corresponding ligand L [where $L = L^1$ (0.166 g, 0.5 mmol), L^2 (0.174 g, 0.5 mmol), L^3 (0.173 g, 0.5 mmol), L^4 (0.156 g, 0.5 mmol) in methanol was added with constant stirring to 1N HCl solution of palladium chloride (0.089 g, 0.5 mmol). The solution was stirred for 2–3 h. The brownish colour precipitate appeared immediately, was separated, washed with double distilled water several times and dried in desiccator over $CaCl_2$ under vacuum.

2.3. *Estimation of chloride*

Chloride was determined [13] gravimetrically as silver chloride. The sample was acidified with 5N HNO_3 and 1% silver nitrate solution was added, till the precipitation was complete. The precipitate was filtered through a G-4 sintered glass crucible, dried at 110°C and weighed as silver chloride.

2.4. *Estimation of metal*

The synthesized palladium complexes were determined gravimetrically [13]. The palladium complexes were decomposed by nitric acid and precipitated as palladium dimethylglyoxime complex by adding 1% solution of dimethylglyoxime in 95% ethanol till palladium completely precipitated. The orange yellow precipitates of palladium dimethylglyoxime were washed with water and dried at 100°C to constant weight and weighed as $Pd(C_4H_7O_2N_2)_2$.

2.5. In vitro *antifungal activity*

Most of the compounds have been screened *in vitro* against *A. fumigatus, A. flavus* and *A. niger*. Among several methods [14] available, the one method [15, 16] that is common in use in recent times has been adopted.

2.5.1. Microbroth dilution assay. The susceptibility of the fungi to various fractions of compounds was assayed by microbroth dilution method [17]. Sabouraud dextrose medium was dissolved in glass double distilled water and autoclaved at 10 psi for 15 min. A volume of 90 μL of medium was added to the wells of cell culture plates (Nunc Nunclon). The different concentrations in the range of 1000–250 $\mu g\,mL^{-1}$ of various fractions were prepared in duplicate wells and then the wells were incubated with 10 μL of conidial suspension containing 1×10^4 conidia. The plates were incubated at 37°C and examined macroscopically after 48 h for the growth of *Aspergillus* mycelia. The activity was represented as −ve if growth was there and +ve if medium appeared clear without any visible growth of *A. fumigatus, A. flavus* and *A. niger*.

2.5.2. Spore germination inhibition assay. The basic method for spore germination inhibition was modified and used to evaluate the activity of various test fractions against fungi. The *A. fumigatus, A. flavus* and *A. niger* were grown on Sabouraud dextrose agar plates and their homogenous conidial suspension was prepared in the Sabouraud maltose broth. The conidia were counted and their number in the suspension adjusted to $1 \times 10^4\,mL^{-1}$. Various concentrations of the test samples in 90 μL of culture medium were prepared in 96-well flat bottom micro-culture plates (Nunc Nunclon) by double dilution method. The wells were prepared in duplicates for each concentration and were inoculated with 10 μL of conidial suspension containing 100 ± 5 conidia. The plates were incubated at 37°C for 10 h and then examined for spore germination under inverted microscope (Nikon Diphot). The number of germinated and non-germinated conidia was recorded. The precent spore germination inhibition (PSGI) was calculated using the following formula:

$$\text{PSGI} = 100 - \frac{\text{No. of conidia germinated in drug treated well}}{\text{No. of conidia germinated in control well}} \times 100.$$

Table 1. Elemental analysis of the complexes.

Complexes	Found (Calcd)%					
	C	H	N	S	Cl	Metal
$Pd(L^1)Cl_2$	47.17 (47.24)	3.41 (3.35)	8.50 (8.27)	6.25 (6.30)	14.09 (13.98)	20.55 (20.87)
$Pd(L^2)Cl_2$	45.61 (45.80)	3.22 (3.24)	7.89 (8.02)	6.25 (6.11)	14.08 (13.55)	20.15 (20.23)
$Pd(L^3)Cl_2$	47.79 (48.28)	3.59 (3.64)	8.15 (8.05)	6.45 (6.13)	12.89 (13.60)	20.60 (20.31)
$Pd(L^4)Cl_2$	44.45 (44.26)	4.26 (4.30)	8.79 (8.61)	6.23 (6.56)	14.51 (14.55)	21.55 (21.72)

3. Result and discussion

3.1. *Elemental analysis*

Elemental analysis (table 1) reveals the purity of the complexes. All complexes are soluble in DMSO. The molar conductance values of the isolated complexes measured in DMSO are found to be less than 15 $ohm^{-1}\,cm^2\,mol^{-1}$ suggesting their non-electrolytic nature.

3.2. *Electronic spectra*

In the present studies, all the complexes are diamagnetic. The Palladium(II) complexes are square planar and their geometries are supported by electronic spectra. Palladium(II) is a d^8 system and three spin allowed singlet-singlet d–d transitions are predicted [18, 19]. The ground state is $^1A_{1g}$ and the three transitions are $^1A_{1g} \rightarrow {}^1A_{2g}$ (16,800–12,000 cm^{-1}), $^1A_{1g} \rightarrow {}^1B_{1g}$ (17,500–23,100 cm^{-1}) and $^1A_{1g} \rightarrow {}^1E_g$ (21,000–26,500 cm^{-1}).

These transitions take place from the lower lying d-orbital to the empty d_{x2-y2} orbital. Strong charge transfer transitions may interfere and prevent the observation of all the expected bands [20–22]. Strong bands between 350 and 410 nm (24,500–28,500 cm^{-1}) are assignable to a combination of metal ligand charge transfer ($M \rightarrow LCT$) and d–d bands. The very intense band ~410 is assignable to combination of sulphur $\rightarrow$ metal charge transfer ($L\pi \rightarrow MCT$) and d–d bands.

Solutions of thiohydrazones in DMSO feature a strong band at ca 350 nm ($\log \varepsilon = 3.91$) because of the $n \rightarrow \pi^*$ transition for the azomethine fuction with shoulders at higher and lower energy. These values show very little shift in complexes but the intensity is enhanced. One absorption band observed at ca 285 nm, is assigned to the $\pi \rightarrow \pi^*$ intraligand electron transition, N=C=S. This band shifts on complexation, revealing involvement of the C=S group in complexation, in all the complexes. Additional bands appear in the complexes because d–d and charge transfer transition. The electronic spectra of the thiohydrazone complexes are shown in table 2.

3.3. *Infrared spectra*

The IR spectra (table 3) of the thiohydrazones show –NH–C=S groups as a potential bond forming site. The IR bands are shifted on complex formation due to increased double bond character of $\nu C=N$ group on complexation. The $\nu C=N$ bands at

Table 2. Electronic spectra of the complexes.

Complexes	λ_{max} (nm)	log (ε)
L^0	209	3.54
	283	2.65
L^1	209	3.55
	287	3.10
	302	2.28
$Pd(L^1)Cl_2$	293	4.01
	347	3.91
	418	2.75
L^2	208	4.21
	285	3.78
	308	2.95
$Pd(L^2)Cl_2$	281	3.62
	376	2.92
	406	2.39
L^3	210	4.02
	286	3.85
	300	2.78
$Pd(L^3)Cl_2$	293	4.38
	356	3.76
	426	2.32
L^4	207	4.52
	281	3.90
	299	3.36
$Pd(L^4)Cl_2$	295	3.95
	367	3.17
	416	2.69

Table 3. IR spectra of the complexes.

Compounds	$\nu_{C=N}$	ν_{N-N}	$\nu_{C=S}$	ν_{M-N}	ν_{M-S}	ν_{M-Cl}
L^0	–	1023	875	–	–	–
L^1	1607	1032	873	–	–	–
$Pd(L^1)Cl_2$	1619	1023	789	473	368	296
L^2	1608	1012	878	–	–	–
$Pd(L^2)Cl_2$	1601	1020	793	479	383	325
L^3	1585	1028	877	–	–	–
$Pd(L^3)Cl_2$	1612	1038	765	482	380	295
L^4	1610	1025	880	–	–	–
$Pd(L^4)Cl_2$	1590	1029	805	489	381	305

ca 1590 cm^{-1} are shifted by 10–40 cm^{-1} in the metal chelates, suggesting positive involvement of the azomethine nitrogen in bonding to the metal ion [23, 24]. Significant changes in ligand bands upon complexation include an increase in $\nu C=N$. These data indicate coordination through the azomethine nitrogen, but no interaction between terminal amine nitrogen and the metal ion. The bands at ca 870 cm^{-1}, assignable to a $\nu C=S$, shift to lower frequency, suggest coordination of thiocarbonyl sulphur to the metal ion [25]. L^2 has salicylaldehyde O–H group, which can also take part in coordination. However, $\nu_{(C-O)}$ does not shift from its position at ca 1260 cm^{-1} in the ligand i.e., the phenolic oxygen does not participate in coordination. Also, in the far IR region no band corresponding to M–O was observed in the 400–430 cm^{-1} range.

In all the Pd(II) complexes the metal nitrogen vibrations, ν(M–N) are assigned to the new bands [26] in the far IR between 460–490 cm^{-1}, while in the region between 350–390 cm^{-1} are metal-sulphur, ν(M–S) band stretching [27]. The band at ~330–270 cm^{-1} is assigned due to $\nu_{(Pd-Cl)}$ stretching vibrations.

3.4. *NMR spectra*

^{1}H NMR spectra of ligands and complexes were recorded in d_6-DMSO taking TMS as internal standard. The ^{1}H NMR spectrum of thiohydrazones shows the thioamide –NH resonance in the $\delta = \sim 9.0$–10.5 range, consistent with hydrogen bonding to DMSO [28]. This is observable in the complexes, suggesting that hydrogen bonding to the solvent occurs in the complexes as well as in the free ligands. The resonances assigned to the aldehyde –CH are generally shifted upfield, indicating coordination of azomethine nitrogen. In the palladium complexes the signal due to –NH acetothioamide is present, which indicates that the ligands are not deprotonated.

^{1}H NMR spectrum (CD_3OD) [L^0]; 7.16–6.57 m, 10 H, (Ar–H); 9.09 s, 1 H, (NH); 3.26 s, 2 H, (NH_2).

^{1}H NMR spectrum (CD_3OD) [L^1]; 7.3–6.44 m, 15 H, (Ar–H); 10.45 s, 1 H, (NH); 8.6 s, 1 H, (CH).

^{1}H NMR spectrum (d_6 DMSO) [Pd(L^1)Cl_2]; 8.27–7.05 m, 15 H, (Ar–H); 10.21 s, 1 H, (NH); 8.15 s, 1 H, (CH).

^{1}H NMR spectrum (CD_3OD) [L^2]; 7.21–6.96 m, 15 H, (Ar–H); 10.5 s, 1 H, (NH); 8.47 s, 1 H, (CH); 11.15 s, 1 H, (OH).

^{1}H NMR spectrum (d_6 DMSO) [Pd(L^2)Cl_2]; 7.96–7.21 m, 15 H, (Ar–H); 10.29 s, 1 H, (NH); 8.31 s, 1 H, (CH); 11.15 s, 1 H, (OH).

^{1}H NMR spectrum (CD_3OD) [L^3]; 7.36–6.32 m, 15 H, (Ar–H); 9.89 s, 1 H, (NH); 2.51 s, 3 H, (CH).

^{1}H NMR spectrum (d_6 DMSO) [Pd(L^3)Cl_2]; 8.07–7.26 m, 15 H, (Ar–H); 10.19 s, 1 H, (NH); 2.33 s, 3 H, (CH).

^{1}H NMR spectrum (CD_3OD) [L^4]; 7.73–6.71 m, 10 H, (Ar–H); 10.79 s, 1 H, (NH); 1.2–2.23 m, 11 H, (cyclohexyl).

^{1}H NMR spectrum (d_6 DMSO) [Pd(L^4)Cl_2]; 8.28–7.17 m, 10 H, (Ar–H); 10.57 s, 1 H, (NH); 1.37–2.51 m, 11 H, (cyclohexyl).

3.5. In vitro *antifungal study*

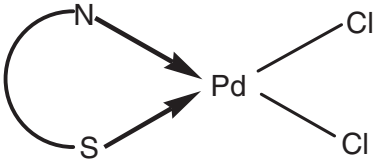
Some synthesized complexes were tested against pathogenic fungal strains such as *A. fumigatus, A. flavus* and *A. niger*. Amphotericin B was used as reference drug for fungi. The minimum inhibitory concentrations (MICs) by microbroth dilution assays (MDA) and percent spore germination inhibition assays (PSGIA) being 250–1000 $\mu g\,mL^{-1}$ (table 4). Complexes show significant activity may be due to the fact that *Aspergillii* has hard chitinous outer wall and therefore, higher concentration of fungicidal compounds may be required to kill the fungi.

Table 4. Antibacterial study of the complexes.

S. No.	Complexes	*A. fumigatus*		*A. flavus*		*A. niger*	
		MDA MIC ($\mu g\,mL^{-1}$)	PSGI MIC ($\mu g\,mL^{-1}$)	MDA MIC ($\mu g\,mL^{-1}$)	PSGI MIC ($\mu g\,mL^{-1}$)	MDA MIC ($\mu g\,mL^{-1}$)	PSGI MIC ($\mu g\,mL^{-1}$)
1	$Pd(L^1)Cl_2$	500	500	500	500	1000	1000
2	$Pd(L^2)Cl_2$	250	250	250	250	500	500
Amphotericin B		5	5	5	5	5	5

4. Conclusion

All the complexes are diamagnetic. The $\nu(C=S)$ shift towards lower frequency on complexation, indicates the coordination to metal ion is through thioamide sulphur. The *in vitro* antifungal activity of complexes as compared with standard drug Amphotericin B shows siginificant activity. The minimum inhibitory concentrations (MICs) by microbroth dilution assays (MDA) and percent spore germination inhibition assays (PSGIA) being 250–1000 $\mu g\,mL^{-1}$. On the basis of these spectroscopic studies the probable structure of the complexes is:



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