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THERMAL AND SPECTRAL STUDIES OF PALLADIUM(II) COMPLEXES

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Palladium(II) complexes of type $[Pd(L)Cl_2]$ [where *L*=2-aminopyridine-N-thiohydrazide (L^1), (2-aminopyridine-N-thio)-1,3-propanediamine (L^2), benzaldehyde 2-aminopyridine-N-thiohydrazone (L^3) and salicylaldehyde-2-aminopyridine-N-thiohydrazone (L^4)] have been synthesized. The thiohydrazide, thiodiamine and thiohydrazones can exist as thione-thiol tautomer and coordinate as a bidentate N–S ligand. The ligands found to act in bidentate fashion.

The complexes have been characterized by elemental analysis, IR, mass, electronic, ^{1}H NMR spectroscopic studies, and TG/DTA study. Antifungal studies of some complexes were also carried out. Various kinetic and thermodynamic parameters like order of reaction (n), activation energy (E_a), apparent activation entropy ($S^{\#}$) and heat of reaction (ΔH) have also been carried out for one complex.

Keywords: *characterization, palladium, synthesis*

Introduction

The thiohydrazides, thiodiamines and thiohydrazones have aroused considerable interest in chemistry and biology due to their significant antibacterial, antimalarial, antineoplastic and antiviral activities [1–4]. They are significantly affected by substitution at the moiety's N(4) position [5, 6]. The chemistry of transition metal complexes of thiohydrazides and thiohydrazones has been receiving considerable attention largely because of their pharmacological properties [7]. The combination of thiohydrazides and thiohydrazones with agents like platinum(II) or palladium(II) that damage DNA produces synergistic inhibition of tumor growth and may lead to improvements in the effectiveness of cancer chemotherapy [8–10].

The ligands with sulphur, nitrogen and oxygen donor atoms in their structures can act as good chelating agents for the transition and non-transition metal ions [11–18]. The biological active compounds and the thermochemical data in literature, concerning the thiohydrazides and thiohydrazones, are essentially originated from techniques such as thermogravimetry, differential thermal analysis and differential scanning calorimetry [19–21]. The main aim of the present work is to synthesize complexes of Pd(II) and to study the thermal decomposition. We have also studied the antifungal activity of some complexes. Thermodynamic parameters such as activation energy (E_a), apparent activation entropy ($S^{\#}$) and enthalpy change (ΔH) for the dehydration and decomposition reactions of the complexes have been evaluated.

Experimental

Materials and methods

All the reagents used were AR grade.

The analysis of CHNS/O contents of ligands and metal complexes were done on Elementar Analysensysteme GmbH Vario El-III. IR spectra were recorded on Perkin-Elmer spectrum 2000 FTIR spectrometer using KBr disc. Electronic spectra were recorded using DMSO as solvent on Shimadzu UV-Visible spectrophotometer Model 1601. Conductance measurements were carried out on Digital Conductometer Model PT-827, India in DMSO solvent. Model Jeol SX102/DA-600 (KV 10MA) was used for recording mass spectra of the ligands using methanol as solvent. ^{1}H NMR was recorded in d_6-DMSO on Brucker spectrospin 300 spectrometer.

TG/DTA curves for the complexes were recorded on Shimadzu, model 60 WS thermal analyzer, in static air at a heating rate of 10°C min^{-1}. The platinum crucible was used with alumina as the reference material.

Preparation of thiohydrazides

Preparation of 2-aminopyridine-N-thiohydrazides, (2-aminopyridine-N-thio)-1,3-propanediamine, benzaldehyde-2-aminopyridine-N-thiohydrazone and salicylaldehyde-2-aminopyridine-N-thiohydrazone were prepared by modified [3–6], literature method [22].

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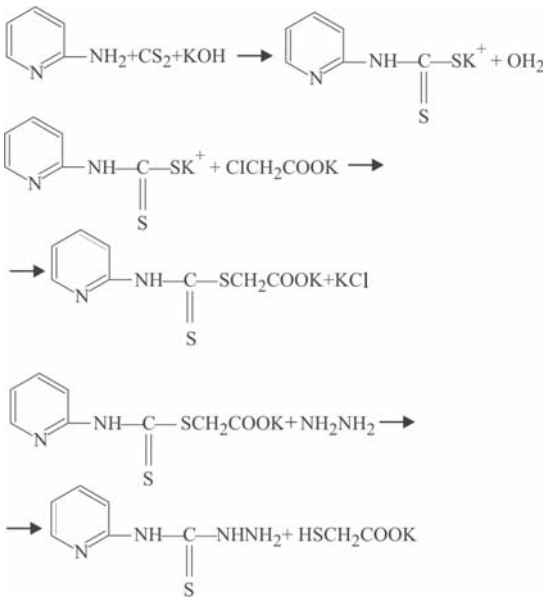
Preparation of 2-aminopyridine-N-thiohydrazide (L^1)

In a three-necked round bottle flask 4.71 g (0.05 mol) of 2-aminopyridine dissolved in 20 mL methanol taken and chilled it. 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 g cm^{-3}) in 3 mL methanol. The temperature of the reaction mixture was maintained below 10°C by keeping flask in a freezing mixture of common salt and ice. During the process, a yellowish-white crystalline precipitate of 2-aminopyridine 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 [{4.73 g chloroacetic acid (0.05 mol) 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 at about 40°C for an hour and the contents were left overnight at room temperature. After 24 h methanolic solution of 2.44 mL (0.05 mol) hydrazine hydrate (density 1.026 g cm^{-3}) was added to the reaction mixture. The content was then heated on a water bath for about 45 min when the desired product began to separate out. It was cooled in ice for 24 h and filtered. 2-aminopyridine-N-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

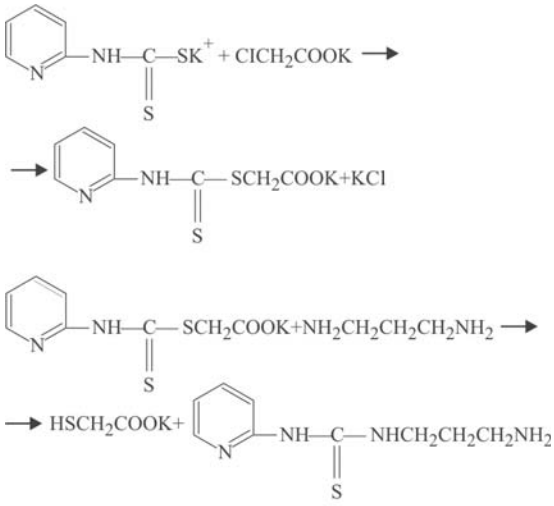


Scheme 1 CHNS – analysis; found (calculated) %; C: 43.46 (42.86), H: 4.28 (4.77), N: 34.23 (33.33), S: (18.67) 19.0. Mass spectra (CH_3OH); *m*/*z*: 94.76 (M^+), 168.76

Preparation of (2-aminopyridine-N-thio)-1,3-propanediamine (L^2)

10.4 g (0.05 mol) 2-aminopyridine dithiocarbamate prepared as earlier was suspended in 15 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 at about 40°C for an hour and the contents were left overnight at room temperature. After 24 h methanolic solution of 4.36 mL (0.05 mol) 1,3-propanediamine (density 0.85 g cm^{-3}) was added to the reaction mixture. The content was then heated on a water bath for about 45 min when the desired product began to separate out. It was cooled in ice for 24 h and filtered. (2-aminopyridine-N-thio)-1,3-propanediamine 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



Scheme 2 CHNS – analysis; found (calculated) %; C: 52.68 (51.40), H: 6.63 (6.67), N: 25.59 (26.67), S: (14.93) 15.20. Mass spectra (CH_3OH); *m*/*z*: 94.52 (M^+), 210.89

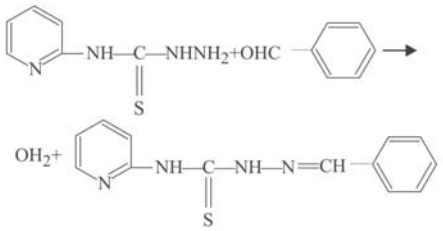
Preparation of thiohydrazones

The thiohydrazones were prepared by refluxing the thiohydrazides with corresponding aldehydes or ketones in methanol.

Preparation of benzaldehyde-2-aminopyridine-N-thiohydrazone (L^3)

5.04 g (0.03 mol) of 2-aminopyridine-N-thiohydrazide and 3.05 mL (0.03 mol) of benzaldehyde (density 1.044 g cm^{-3}) were refluxed in methanol for 3 h. On cooling yellowish mass obtained was filtered

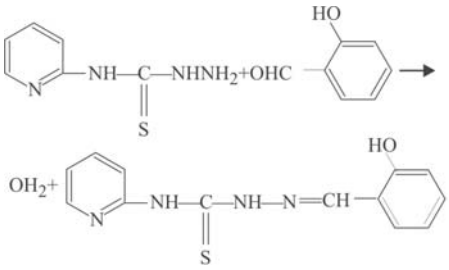
and washed with cold methanol. It was recrystallized from hot methanol.



Scheme 3 CHNS – analysis; found (calculated) %; C: 61.17 (60.93), H: 4.73 (4.70), N: 20.99 (21.87), S: (11.86) 12.50. Mass spectra (CH_3OH); *m*/*z* : 94.25 (M^+), 256.73

Preparation of salicylaldehyde-2-aminopyridine-N-thiohydrazone (L^4)

5.04 g (0.03 mol) of 2-aminopyridine-N-thiohydrazide and 3.15 mL (0.03 mol) of salicylaldehyde (density 1.164 g cm^{-3}) were refluxed in methanol for 3 h. On cooling yellowish mass obtained was filtered and washed with cold methanol. It was recrystallized from hot methanol.



Scheme 4 CHNS – analysis; found (calculated) %; C: 56.96 (57.35), H: 4.26 (4.41), N: 19.47 (20.59), S: (11.98) 11.76. Mass spectra (CH_3OH); *m*/*z*: 94.16 (M^+), 272.43

Preparation of complexes

Preparation of thiohydrazide[$Pt(L)_2Cl_2$] complexes where *L*=L^1, L^2, L^3 and L^4

The corresponding ligand L [where *L*=L^1 (0.084 g, 0.5 mmol), L^2 (0.105 g, 0.5 mmol), L^3 (0.128 g, 0.5 mmol) and L^4 (0.141 g, 0.5 mmol) in methanol and added with constant stirring to 1 N HCl solution of palladium chloride (0.089 g, 0.5 mmol). The solution was stirred for 4–5 h. The colour of solution changed yellow to yellowish orange. It was washed with double distilled water several times and dried in desiccator over $CaCl_2$ under vacuum.

Analysis

Estimation of chloride

Chloride was determined gravimetrically as silver chloride [23]. 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.

Estimation of metal [23]

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

In vitro antifungal activity

Most of the compounds have been screened in vitro against *Aspergillus fumigatus*, *Aspergillus flavus* and *Aspergillus niger*. Among several methods [24] available, the one method [25, 26] that is common in use in recent times has been adopted.

Microbroth dilution assay

The susceptibility of the fungi to various fractions of compounds was assayed by microbroth dilution method. 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 1000–15 μg mL^{-1} of various fractions were prepared in duplicate wells and then the wells were incubated with 10 μL of conidial suspension containing $1 \cdot 10^4$ 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 *Aspergillus fumigatus*, *Aspergillus flavus* and *Aspergillus niger*.

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 *Aspergillus fumigatus*, *Aspergillus flavus* and *Aspergillus niger* were grown on Sabouraud dextrose agar plates and their homogenous conidial suspension was prepared

Table 1 Elemental analysis of the complexes

Complexes	Found (calculated)/%					
	C	H	N	S	Cl	Metal
$Pd(L^1)Cl_2$	21.36 (20.87)	2.31 (2.32)	15.94 (16.23)	9.17 (9.28)	29.54 (29.58)	30.75 (30.72)
$Pd(L^2)Cl_2$	28.18 (27.91)	3.67 (3.62)	14.43 (14.47)	7.89 (8.27)	18.19 (18.35)	27.08 (27.39)
$Pd(L^3)Cl_2$	36.12 (36.03)	2.78 (2.77)	12.84 (12.93)	7.26 (7.39)	16.12 (16.39)	24.60 (24.48)
$Pd(L^4)Cl_2$	34.63 (34.74)	2.63 (2.67)	12.53 (12.47)	7.08 (7.13)	15.58 (15.81)	23.89 (23.61)

in the Sabouraud maltose broth. The conidia were counted and their number in the suspension was adjusted to $1 \cdot 10^4$ 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. The wells 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 present spore germination inhibition (PSGI) was calculated using following formula:

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

Results and discussion

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.

Electronic spectra

The electronic spectra (Table 2) of the thiohydrazides (L^1), thiodiamines (L^2), thiohydrazones (L^3 and L^4) show spectral bands because of $\pi \rightarrow \pi^*$ and $n \rightarrow \pi^*$ transition. On complexation these bands are shifted. Strong charge transfer transitions may interfere and prevent the observation of all the expected bands [27, 28]. Strong bands ~340 nm is assignable to a combination of metal ligand charge transfer (M→LCT) and *d–d* band. The very intense band ~390 is assignable to combination of sulphur→metal charge transfer (Lπ→MCT) and *d–d* bands.

Table 2 Electronic spectra of the complexes

Complexes	λ_{max} (nm)	log (ε)
$Pd(L^1)Cl_2$	270	3.44
	308	2.64
	389	2.07
$Pd(L^2)Cl_2$	284	3.79
	326	2.82
	394	2.16
$Pd(L^3)Cl_2$	281	3.85
	351	3.41
	403	2.38
$Pd(L^4)Cl_2$	293	4.36
	356	3.74
	410	2.91

Infrared spectra

In the present studies, the IR spectra (Table 3) of the thiohydrazide, thiodiamine and thiohydrazones contain groups –NH–C=S as a potential bond forming site. Complexes of the ligands containing thioamide group have been extensively studied. The thioamide group displays four prominent IR bands due to $\nu_{(C=N)}$, $\nu_{(N-H)}$, $\nu_{(C-N)}$ and $\nu_{(C=S)}$. The thioamide band I have been observed in the region of 1460–1630 cm^{-1} which is due to $\nu_{(C=N)}$ and $\nu_{(N-H)}$ stretching vibrations. The thioamide band II is observed in the range of 1300–1380 cm^{-1}. The band has major contribution from $\nu_{(N-H)}$ and minor contributions from $\nu_{(C=N)}$ stretching vibrations. The thioamide band III 1210–1290 cm^{-1} has major contributions from $\nu_{(C=S)}$ vibration. All these IR bands are shifted on complex formation due to increased double bond character of C–N group on complexation. Thioamide IV 750–900 cm^{-1} is due to $\nu_{(C=S)}$ as major contributor and $\nu_{(C-N)}$ as minor. This is shifted to lower frequency on complexation indicates the coordination to metal ion is through thioamide sulphur C=S. This shift is ~ 120–150 cm^{-1}, if coordination is through thiol sulphur [29] and 30–40 cm^{-1}, if coordination is through the thione sulphur [30].

Table 3 IR spectra of the complexes

Complexes	Wavenumber/cm^{-1}					
	$\nu_{C=N}$	$\nu_{N–N}$	$\nu_{C=S}$	$\nu_{M–N}$	$\nu_{M–S}$	$\nu_{M–Cl}$
L^1	–	1025	876	–	–	–
$Pd(L^1)Cl_2$	–	1026	856	461	379	262
L^2	–	1032	880	–	–	–
$Pd(L^2)Cl_2$	–	1022	808	470	380	273
L^3	1633	1026	890	–	–	–
$Pd(L^3)Cl_2$	1635	1020	761	475	390	298
L^4	1614	1036	888	–	–	–
$Pd(L^4)Cl_2$	1624	1032	789	462	389	297

Table 4 Antifungal study of the complexes

S. no.	Complexes	*A. fumigatus*/μg mL^{-1}		*A. flavus*/μg mL^{-1}		*A. niger*/μg mL^{-1}	
		MDA	PSGI	MDA	PSGI	MDA	PSGI
1	$Pd(L^1)Cl_2$	250	250	250	250	500	500
2	$Pd(L^2)Cl_2$	–	–	–	–	–	–
3	$Pd(L^3)Cl_2$	500	500	250	250	500	500
4	$Pd(L^4)Cl_2$	250	250	500	500	500	500

where MDA = micro dilution activity and PSGI = percent spore germination inhibition

In all the Pd(II) complexes the metal nitrogen vibration, $\nu_{(M–N)}$ are assigned to the new bands [31] in the far IR between 460–490 cm^{-1}, while in the region between 350–390 cm^{-1} gives metal–sulphur, $\nu_{(M–S)}$ band stretching [32]. The band at ~330–270 cm^{-1} is assigned due to $\nu_{(Pd–Cl)}$ stretching vibrations.

NMR spectra

^{1}H NMR spectra of ligands and complexes were recorded in d_6–DMSO taking TMS as internal standards.

L^1 $\delta_{(ppm)}$ 7.73–6.4 (m, 4H, Py–H), 9.16 (br s, $1H^a$, –NH), 3.43 (br s, $2H^b$, $–NH_2$)

$[Pd(L1)Cl_2]$ $\delta_{(ppm)}$ 8.2–7.78 (m, 4H, Py–H), 9.19 (br s, $1H^a$, –NH), 3.73 (br s, 2Hb, $–NH_2$)

L^2 $\delta_{(ppm)}$ 7.7–6.6 (m, 4H, Py–H), 9.12 (br s, $1H^a$, –NH), 3.3 (t, $4H^b$, $–CH_2$), 1.8 (m, $2H^c$, $–CH_2$), 3.67 (br s, $2H^d$, $–NH_2$)

$[Pd(L^2)Cl_2]$ $\delta_{(ppm)}$ 8.37–7.5 (m, 4H, Py–H), 9.27 (br s, $1H^a$, –NH), 3.45 (t, $4H^b$, $–CH_2$), 1.83 (m, $2H^c$, $–CH_2$), 3.8 (br s, $2H^d$, $–NH_2$)

L^3 $\delta_{(ppm)}$ 7.7–6.51 (m, 4H, Py–H), 9.6 (br s, $1H^a$, –NH), 9.16 (br s, $1H^b$, –NH), 8.23 (s, $1H^c$, –CH), 7.3–6.4 (m, 5H, –Ar–H)

$[Pd(L^3)Cl_2]$ $\delta_{(ppm)}$ 7.7–6.51 (m, 4H, Py–H), 9.6 (br s, $1H^a$, –NH), 9.21 (br s, $1H^b$, –NH), 8.1 (s, $1H^c$, –CH), 7.7–6.8 (m, 5H, –Ar–H)

L^4 $\delta_{(ppm)}$ 7.21–6.42 (m, 4H, Py–H), 10.42 (br s, $1H^a$, –NH), 9.1 (br s, 1Hb, –NH), 8.3 (s, $1H^c$, –CH), 7.4–6.26 (m, 5H, –Ar–H), 11.3 (br s, $1H^d$, –OH)

$[Pd(L^4)Cl_2]$ $\delta_{(ppm)}$ 8.5–7.41 (m, 4H, Py–H), 10.2 (br s, $1H^a$, –NH), 9.11 (br s, $1H^b$, –NH), 8.2 (s, $1H^c$, –CH), 7.8-6.9 (m, 5H, –Ar–H), 11.23 (br s, $1H^d$, –OH)

The ^{1}H NMR spectrum of thiohydrazides, thiodiamines and thiohydrazones [33, 34] shows two signals at δ ~ 9.0–10.3 and δ ~ 4.0 ppm, due to the presence of NH protons which are lost on D_2O exchange. This is observable in the complexes also suggesting that hydrogen bonding to the solvent occurs in the complexes as well as free ligands. The resonance assigned to aldehyde –CH is generally shifted upfield, indicating coordination of azomethine nitrogen [35].

In vitro antifungal study

In the current study (Table 4) of some synthesized was tested against pathogenic *Aspergillus fumigatus*, *Aspergillus flavus* and *Aspergillus niger*. The minimum inhibitory concentrations (MICs) by microbroth dilution assays (MDA) and percent spore germination inhibition assays (PSGIA) being 250–500 μg mL^{-1} (Table 4). Amphotericin B was used as reference drug for fungi. The activity of compounds did not appear to be very high. But it is known fact that *Aspergillii* have hard chitinous outer wall and therefore, higher concentration of fungicidal compounds may be often required to kill the fungi.

Table 5 Thermal data of the complexes

Complexes	Step No.	TG (Coats–Redfern method)				ΔH/kJ g^{-1}
		Temperature range/°C	n	E_a/kJ mol^{-1}	$S^{\#}$/J K^{-1} mol^{-1}	
$Pd(L^1)Cl_2$	I	29–450	1	17.35	3.96	55.58
	II	450–842	1	8.15	0.32	85.12

Thermal study

The TG and DTA study in air atmosphere have been carried out for one complex. Thermal studies were utilized to elucidate the number of kinetic and thermodynamic parameters. From TG curve, order of reaction (n), activation energy (E_a), apparent activation entropy ($S^{\#}$) were enumerated by the Coats–Redfern method [36]. From the DTA curves, the heat of reaction was calculated. Thermal data were tabulated in Table 5.

$[Pd(L^1)Cl_2)]$ complex

TG curve (Fig. 1) shows two-step decomposition. The first decomposition step (29–450°C) corresponds to the loss of all organic moieties for which observed and calculated mass losses are 48.19 and 48.69% respectively. The final step starts at 450°C and the final observed mass loss at 842°C is 68.05%, which corresponds to the palladium metal residue, calculated mass loss for which is 68.8%.

The DTA profile (Fig. 2) shows the only one exotherm at 348°C corresponds to the oxidation of organic moieties.

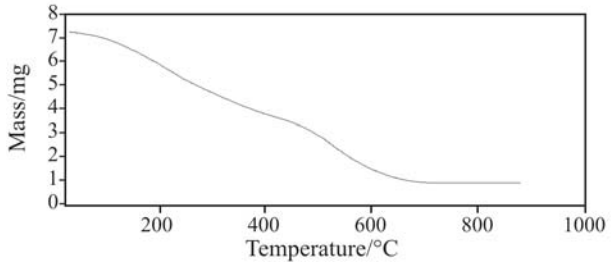


Fig. 1 TG curve of $[Pd(L^1)Cl_2]$ complex

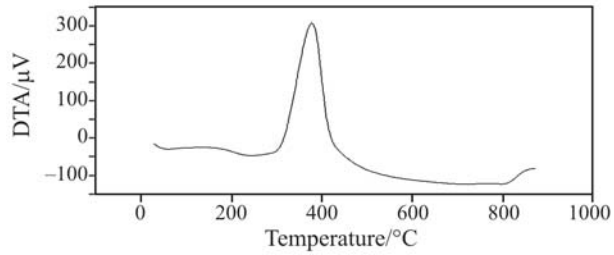
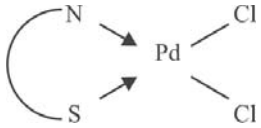


Fig. 2 DTA curve of $[Pd(L^1)Cl_2]$ complex

Conclusions

The shifts observed from IR, electronic and NMR spectra on complexation, indicates the coordination to metal ion is through nitrogen and sulphur. In the antifungal activity against *Aspergillus fumigatus*, *Aspergillus flavus* and *Aspergillus niger*, the minimum inhibitory concentrations (MICs) by microbroth dilution assays (MDA) and percent spore germination inhibition assays (PSGIA) was found to be 250–500 μg mL^{-1}. The thermal data (TG/DTA) of the complex indicates that for all the two steps, the reaction order is found to be one and heat of reaction for the first step are found to be higher. On the basis of these spectroscopic studies the probable structure of the complexes is:



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