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Nickel(II) thiohydrazide and thiodiamine complexes: Synthesis, characterization, antibacterial, antifungal and thermal studies

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Abstract

Nickel(II) complexes of type $[Ni(L)_2Cl_2]$ and $[Ni(L)_2(OCOCH_3)_2]$, where L = *N*,*N*-diphenyl-*N*-thiohydrazide (L^1) and (*N*,*N*-diphenyl-*N*-thio)-1,3-propanediamine (L^2), have been synthesized. The thiodiamines coordinate as a bidentate N–S ligand. The synthesized nickel(II) complexes of the thiodiamines were characterized by elemental analysis, IR, mass, electronic and ^{1}H NMR spectroscopic and TG/DTA studies. 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. These complexes were also screened for in vitro antifungal and in vitro antibacterial activities and significant activity have been found.

Keywords: Synthesis; Characterization; Thermal; Antifungal; Antibacterial; Spectral

1. Introduction

There is a considerable interest in the pharmacology of heterocyclic ligands and their metal chelates [1–3]. In general, nitrogen and sulphur containing organic compounds and their metal complexes display a wide range of biological activity such as antibacterial, antifungal, antiviral and antitumour [4–7].

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 [8–14]. Coordination of such compounds with metal ions, such as copper, nickel and iron, often enhance their activity [15,16], as has been reported for pathogenic fungi [17]. A few papers have been published on the transition metal complexes of substituted thiosemicarbazides and thiodiamines [14,18]. In view of number of applications of thiosemicarbazides, thiodiamines and their complexes we have synthesized nickel(II) thiodiamine complexes and characterized by elemental analysis, IR, mass, electronic and ^{1}H NMR spectroscopic studies. The synthesized complexes were also screened for antibacterial and antifungal activities.

2. Experimental

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 was recorded on Perkin-Elmer spectrum 2000 FTIR spectrometer using KBr dics. Electronic spectra were recorded on Shimadzu UV–vis spectrophotometer Model 1601 using acetone as solvent. Conductance measurements were carried out on Digital Conductometer Model PT-827, India using acetone as solvent. Model Jeol SX102/DA-600 (KV 10MA) was used for recording Mass spectra of the ligands in acetone solvent. ^{1}H NMR was recorded using deuterated acetone on Brucker spectrospin 300 spectrometer.

TG/DTA curves for one complex was 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.

2.1. Preparation of thiohydrazides and thiodiamines

Kazakova et al. has described the preparation of *N*,*N*-diphenyl-*N*-thiohydrazide and *N*,*N*-thiodiamines. In the present work, it has been synthesized with some modification from the method described earlier [10–12,14,19].

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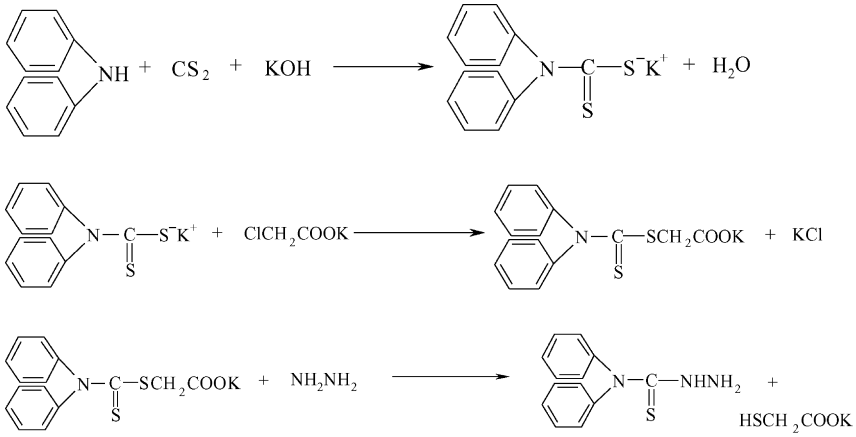
2.1.1. Preparation of N,N-diphenyl-N-thiohydrazide (L^1)

In a three necked round bottle flask 8.46 g (0.05 mol) of diphenylamine was dissolved in 40 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) 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 white crystalline precipitate of *N*,*N*-diphenyl 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 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) 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. *N*,*N*-Diphenyl-*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:

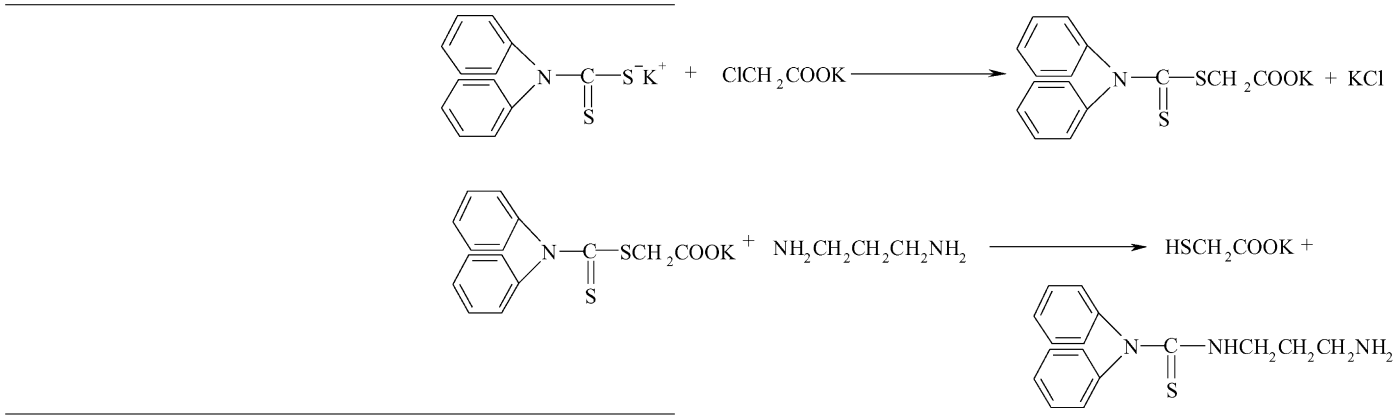


CHNS-analysis; found (calculated)%: C 63.89 (64.19), H 5.33 (5.35), N 18.68 (17.28), S (12.67) 13.16; mass spectra (CH_3OH); *m*/*z* 243.59.

2.1.2. Preparation of (N,N-diphenyl-N-thio)-1,3-propanediamine (L^2)

14.15 g (0.05 mol) *N*,*N*-diphenyl dithiocarbamate prepared as earlier was suspended in 25 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) 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. (*N*,*N*-Diphenyl-*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:



CHNS-analysis; found (calculated)%: C 68.23 (67.36), H 6.53 (6.67), N 16.23 (14.70), S (10.61) 11.20; mass spectra (CH_3OH); *m*/*z* 285.71.

2.2. Preparation of complexes

2.2.1. Preparation of thiohydrazide and thiodiamine $[Ni(L)_2Cl_2]$ & $[Ni(L)_2(OCOCH_3)_2]$ complexes where $L = L^1$ and L^2

The corresponding ligand L [where L^1 (0.122 g, 0.5 mmol), L^2 (0.143 g, 0.5 mmol)] in methanol and added with constant stirring to few drops of 1N HCl solutions of corresponding metal salt [Nickel chloride (0.059 g, 0.25 mmol) and Nickel acetate (0.062 g, 0.25 mmol)]. The solution was stirred for 4–5 h. The light green colour of nickel complex appeared immediately, which separated, washed with ether and dried in desiccator over $CaCl_2$ under vacuum.

2.3. In vitro antifungal activity

Most of the compounds have been screened in vitro against *Aspergillus fumigatus*, *Aspergillus flavus* and *Aspergillus niger*. Among several methods [20] available, the one method [21,22] that is common in use in recent times has been adopted.

2.3.1. 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 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*.

2.3.2. 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 was adjusted to 1×10^4 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 percent spore germination inhibition (PSGI) was calculated using following formula:

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

2.4. In vitro antibacterial activity

Most of the compounds have been screened in vitro against *Escherichia coli* (*E. coli*) and *Pseudomonas aeruginosa* (*P. aeruginosa*). Various methods [23–26] are available for the evaluation of the antibacterial activity of different types of drugs. However, the most widely used method [26] consists in determining the antibacterial activity of the drug is to add it in known concentrations to the cultures of the test organisms.

2.4.1. Disc diffusion assay

The disc diffusion assay was used to determine antibacterial activity of the drug using Gram positive and gram negative strains of bacteria namely *Escherichia coli* (*E. coli*) and *Pseudomonas aeruginosa* (*P. aeruginosa*). Base plates were prepared by pouring 10 mL of autoclaved Muller–Hinton agar (Biolab) into sterile Petri dishes (9 cm) and allowing them to settle. Molten autoclaved Muller–Hinton that had been kept at 48 °C was inoculated with a broth culture (10^6 to 10^8 mL^{-1}) of the test organism and then poured over the base plate. The discs were air dried and placed on the top of the agar layer. Four replicants of each drug tested (four disc per plate) with a gentamycin disc (0.5 μg/disc) as a reference. The plated were then incubated for 18 h at room temperature. Antibacterial activity is expressed as a ratio of the inhibition zone produced by the drug to the inhibition zone produced by the gentamycin standard.

2.4.2. Micro-dilution antibacterial assay

The serial dilution technique, using 96-well micro-plates to determine the minimum inhibitory concentration (MIC) of the drugs for antibacterial activity was used. Two milliliters cultures of four bacterial strains of *Escherichia coli* (*E. coli*) and *Pseudomonas aeruginosa* (*P. aeruginosa*) were prepared and placed in a water bath overnight at 37 °C. The overnight cultures were diluted with sterile Muller–Hinton broth. The drugs were resuspended to a concentration of 60 μg/disc (in dmso) with sterile distilled water in a 96-well micro-plate. A similar twofold serial dilution of gentamycin (Sigma) was used as positive control against each bacterium. One hundred microliters of each bacterial culture was added to each well. The plates were covered and incubated overnight at 37 °C. To indicate bacterial growth *p*-iodonitrotetrazolium violet was added to each well and the plates incubated at 37 °C for 30 min. Bacterial growth in the wells was indicated by a red colour, whereas clear wells indicated inhibition.

3. Result and discussion

3.1. Elemental analysis

Elemental analysis (Table 1) reveals the purity of the complexes. All complexes are soluble in acetone, DMF, etc. The

Table 1
Elemental analysis of the complexes

Complexes	Found (calculated) (%)					
	C	H	N	S	Cl	Metal
$Ni(L^1)_2Cl_2$	50.45 (50.65)	4.23 (4.22)	13.89 (13.64)	10.96 (10.39)	11.12 (11.53)	9.85 (9.58)
$Ni(L^1)_2(OCOCH_3)_2$	54.18 (54.29)	4.77 (4.83)	12.74 (12.67)	9.55 (9.65)	–	8.95 (8.89)
$Ni(L^2)_2Cl_2$	55.10 (54.86)	5.36 (5.43)	11.79 (12.00)	9.29 (9.14)	10.86 (10.14)	8.50 (8.43)
$Ni(L^2)_2(OCOCH_3)_2$	57.47 (57.83)	5.80 (5.89)	11.56 (11.24)	8.86 (8.57)	–	8.06 (7.89)

molar conductance values of the isolated complexes measured in DMSO are found to be less than 12 $ohm^{-1}\,cm^2\,mol^{-1}$ suggesting their non-electrolytic nature.

3.2. Electronic spectra

The electronic spectra (Table 2) of the ligands exhibits bands at ~280 nm is observed which is assigned to a π–π^* electronic transition. The electronic spectrum of the nickel(II) complex show d–d bands at ~640 nm. These bands can safely be assigned to the $^3A_{2g} \rightarrow {}^3T_{2g}$ and $^3A_{2g} \rightarrow {}^3T_{1g}(F)$ transition, respectively, of six coordinate nickel(II). In addition to showing the intra-ligand and d–d bands, the complex also exhibits a strong band at ~480 nm, which can safely be assigned to ligand to metal charge-transfer transition [27,28].

3.3. IR spectra

In the IR spectra (Table 3), Strong bands at 2920–3250 cm^{-1} in thiodiamines are assigned due to –NH stretching vibrations of NH_2 and NH groups. The NH stretching of ligand has been found to shift to higher frequencies, the change being associated with coordination of terminal NH_2 nitrogen to the metal ion. Band located at ~1600 cm^{-1} is assigned to NH_2 deformation vibration. A sharp and strong band at ~890 cm^{-1} in IR spectra of free ligands which is shifted in complexes is attributed due to ν(C=S) [14,29]. In the far of the Ni(II) complexes, the metal nitrogen vibration, ν(M–N) are assigned to the new bands [30] in the far IR between 470 and 490 cm^{-1}, while in the region between 370 and 390 cm^{-1} gives metal–sulphur, ν(M–S) band stretching [31]. The band at ~280–300 cm^{-1} is assigned due to $\nu_{(Ni–Cl)}$ stretching vibrations.

Table 2
Electronic spectra of the complexes

Complexes	λ_{max} (nm)	log (ε)
$Ni(L^1)_2Cl_2$	300	3.93
	365	3.18
	420	2.74
	610	2.24
$Ni(L^1)_2(OCOCH_3)_2$	293	3.88
	387	3.41
	426	2.94
	614	2.49
$Ni(L^2)_2Cl_2$	278	4.12
	338	3.78
	410	3.44
	617	2.98
$Ni(L^2)_2(OCOCH_3)_2$	278	4.18
	358	3.78
	416	2.96
	623	2.89

3.4. NMR spectra

^{1}H NMR spectra of ligands and complexes were recorded in deuterated acetone taking TMS as internal standards:

- δ (ppm): 7.16–6.57 (m, 10H, Ar–H), 9.09 (br s, 1H^a, –NH), 3.26 (br s, 2H^b, –NH_2).
- $[Ni(L^1)_2Cl_2]$ δ (ppm): 8.21–7.29 (m, 20H, Ar–H), 9.16 (br s, 2H^a, –NH), 4.19 (br s, 4H^b, –NH_2).
- $[Ni(L^1)_2(OCOCH_3)_2]$ δ (ppm): 8.18–7.06 (m, 20H, Ar–H), 9.16 (br s, 2H^a, –NH), 4.02 (br s, 4H^b, –NH_2).
- δ (ppm): 7.19–6.46 (m, 10H, Ar–H), 8.92 (br s, 1H^a, –NH), 2.9 (t, 4H^b, –CH_2), 1.47 (m, 2H^c, –CH_2), 3.8 (br s, 2H^d, –NH_2).
- $[Ni(L^2)_2Cl_2]$ δ (ppm): 8.11–7.36 (m, 20H, Ar–H), 9.02 (br s, 2H^a, –NH), 2.97 (t, 8H^b, –CH_2), 1.79 (m, 4H^c, –CH_2), 4.21 (br s, 4H^d, –NH_2).
- $[Ni(L^2)_2(OCOCH_3)_2]$ δ (ppm): 8.49–7.42 (m, 20H, Ar–H), 8.96 (br s, 2H^a, –NH), 3.08 (t, 8H^b, –CH_2), 1.67 (m, 4H^c, –CH_2), 4.17 (br s, 4H^d, –NH_2).

The ^{1}H NMR spectrum of thiodiamines [32–34] shows signals at $\delta \sim 9.0$ and $\delta \sim 4.0$ 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. Two signals at $\delta \sim 2.5$ and $\delta \sim 1.5$ ppm, which show the presence of different –CH_2 group in the complex.

3.5. In vitro antifungal study

In the current study (Table 4) of some synthesized complexes were tested against pathogenic fungal strains such as *A. fumiga-*

Table 3
Electronic spectra of the complexes

Compounds	$\nu_{N–N}$	$\nu_{C=S}$	$\nu_{M–N}$	$\nu_{M–S}$	$\nu_{M–Cl}$
$Ni(L^1)_2Cl_2$	1022	805	484	365	310
$Ni(L^1)_2(OCOCH_3)_2$	1022	818	474	375	299
$Ni(L^2)_2Cl_2$	1033	865	466	390	295
$Ni(L^2)_2(OCOCH_3)_2$	1024	854	468	381	285

Table 4
In vitro antifungal studies of the complexes

S. No.	Complexes	*A. fumigatus*		*A. flavus*		*A. niger*	
		MDA (μg/mL)	PSGI (μg/mL)	MDA (μg/mL)	PSGI (μg/mL)	MDA (μg/mL)	PSGI (μg/mL)
1	$Ni(L^1)_2(OCOCH_3)_2$	62.5	62.5	62.5	62.5	125	125
2	$Ni(L^1)_2Cl_2$	125	125	125	125	250	250
3	$Ni(L^2)_2(OCOCH_3)_2$	250	250	250	250	500	500
4	$Ni(L^2)_2Cl_2$	500	500	500	500	1000	1000
	Amphotericin B	5	5	5	5	5	5

Where, MDA: Micro-dilution activity and PSGI: percent spore germination inhibition.

tus, *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) is 62.5–500 μg/mL. The complex $[Ni(L^2)_2(OCOCH_3)_2]$ and $[Ni(L^2)_2Cl_2]$ had highest in vitro antifungal activity against pathogenic fungal strains. The reason for the highest activity might be related to the presence of acetate group and 1,3-propanediamine group in the $[Ni(L^2)_2(OCOCH_3)_2]$ complex. The other complex show moderate activity may be due to the fact that *Aspergillii* have hard chitinous outer wall and therefore, higher concentration of fungicidal compounds may be often required to kill the fungi.

3.6. In vitro antibacterial study

In the antibacterial study (Table 5) of some synthesized complexes was tested against pathogenic bacterial strains such as *Escherichia coli* (*E. coli*) and *Pseudomonas aeruginosa* (*P. aeruginosa*) using the disc diffusion method. Gentamycin was used as reference drug for bacteria. In general, the compounds showed significant antibacterial activity and the bacterial strains with the zone of inhibition, 8 mm at minimum inhibitory concentration (MIC) of 60.0 μg/disc.

Table 5
In vitro antibacterial studies of the complexes

S. No.	Complexes	Zone of inhibition (mm)	
		E. coli	*P. aeruginosa*
1	$Ni(L^2)_2(OCOCH_3)_2$	8	8
2	$Ni(L^2)_2Cl_2$	–	8
	Gentamycin	16.0	16.0

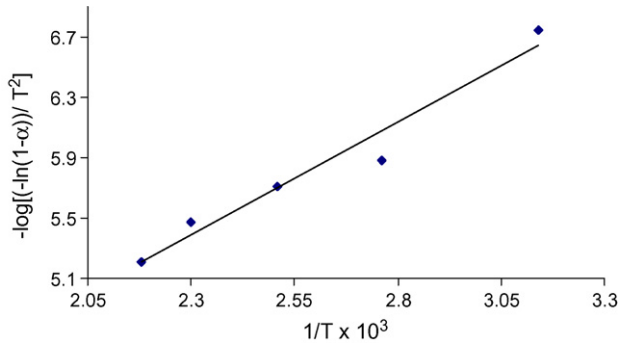


Fig. 1. The curve plotted by Coats-Redfern method for $[Ni(L^1)_2(OCOCH_3)_2]$ for step I.

3.7. Thermal studies of the complexes

The thermogravimetry (TG) and differential thermal analysis (DTA) study in air atmosphere has been carried out for one

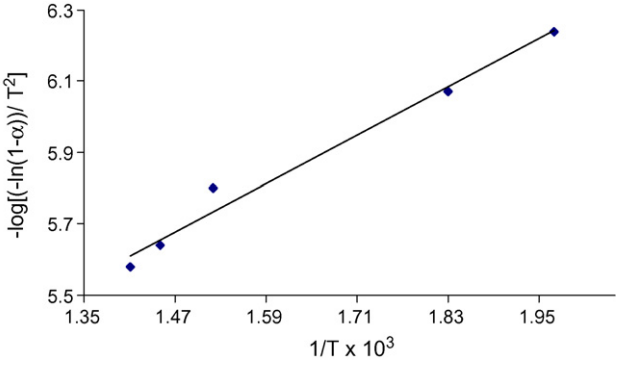


Fig. 2. The curve plotted by Coats-Redfern method for $[Ni(L^1)_2(OCOCH_3)_2]$ for step II.

Table 6
Kinetic parameters from TG for $[Ni(L^1)_2(OCOCH_3)_2]$ complex by Coats-Redfern method (step I)

α	$1-\alpha$	T (K)	T^2	$1/T \times 10^{-3}$	$-\log\left(\frac{-\ln(1-\alpha)}{T^2}\right)$
0.04	0.96	318	101,124	3.14	6.76
0.33	0.67	362	131,044	2.76	5.88
0.51	0.49	398	158,404	2.51	5.71
0.77	0.23	434	188,356	2.30	5.47
0.95	0.05	458	209,764	2.18	5.21

Table 7
Kinetic parameters from TG for $[Ni(L^1)_2(OCOCH_3)_2]$ complex by Coats-Redfern method (step II)

α	$1-\alpha$	T (K)	T^2	$1/T \times 10^{-3}$	$-\log\left(\frac{-\ln(1-\alpha)}{T^2}\right)$
0.29	0.71	508	258,064	1.97	6.24
0.44	0.56	546	298,116	1.83	6.07
0.79	0.21	658	432,964	1.52	5.8
0.92	0.08	691	477,481	1.45	5.64
0.95	0.05	708	501,264	1.41	5.58

Table 8
Thermal data of the thiohydrazide

Complexes	Step No.	TG (Coats-Redfern method)				ΔH (kJ g^{-1})
		Temperature range (K)	n	E_a (kJ mol^{-1})	$S^{\#}$ (J K^{-1} mol^{-1})	
$[Ni(L^1)_2(OCOCH_3)_2]$	I	301–469	1	28.62	8.55	42.45
	II	469–714	1	21.49	6.18	106.12

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 [35]. From the DTA curves, the heat of reaction was calculated. Kinetic parameters of each step from Coats-Redfern method were shown in Figs. 1 and 2 and the thermal data were tabulated in Tables 6–8.

3.7.1. $[Ni(L^1)_2(OCOCH_3)_2]$ complex

TG curve (Fig. 3) shows two-step decomposition. The first decomposition step (301 K–469 K) corresponds to the loss of all organic moieties for which observed and calculated weight losses are 73.42% and 73.30%, respectively. The second step starts at (469–714 K) corresponds to the formation of nickel sulphide for which the observed and calculated weight losses are 85.0% and 86.27%.

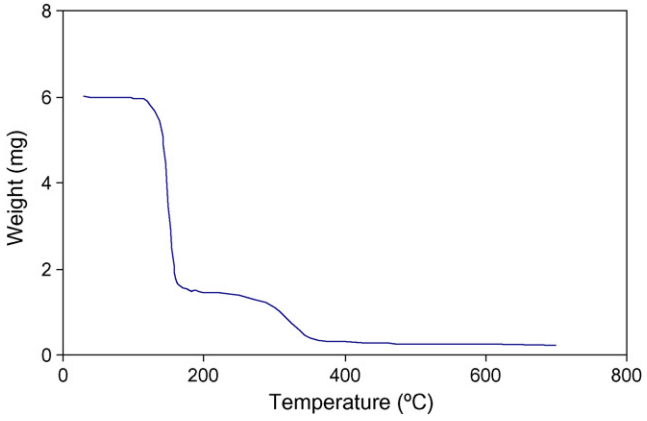


Fig. 3. TG curve of $[Ni(L^1)_2(OCOCH_3)_2]$ complex.

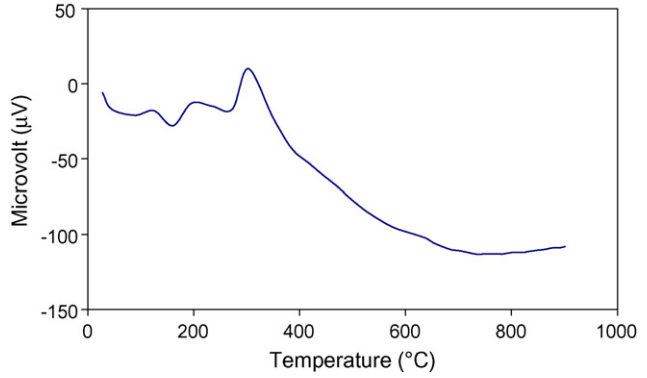


Fig. 4. DTA curve of $[Ni(L^1)_2(OCOCH_3)_2]$ complex.

The DTA profile (Fig. 4) shows one endotherm at 338 K and one endotherm at 445 K correspond to the fusion of the compounds and one exotherm at 578 K corresponding to the oxidation of organic moieties.

4. Conclusion

The electronic spectra of the complexes suggest that all the complexes are found to be diamagnetic. The spectral studies indicate that, the complexation takes place to the metal ion is through azomethine nitrogen and thioamide sulphur. The in vitro antifungal activity of complexes as compared with standard drug Amphotericin B shows significant activity. The minimum inhibitory concentrations (MICs) by microbroth dilution assays (MDA) and percent spore germination inhibition assays (PSGIA) is found to be 62.5–500.0 μg/mL. The in vitro antibacterial study of the complexes as compared with standard drug Gentamycin shows significant activity. The bacterial strains with the zone of inhibition were observed, 8 mm. The thermal data (TG/DTA) of the complex indicates the reaction orders are found to be one and activation energy, apparent activation entropy and heat of reaction are found to be significant. It is worth to mention that trials to get crystal suitable for X-ray structure determination went in vain due to amorphous character of the complexes.

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