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Nickel (II) complexes with symmetrical tridentate ligand: Synthesis, Spectral Characterization and Biological Evaluation

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ABSTRACT

Six heterocyclic base adducts of Nickel (II) complexes have been synthesized by the reaction of Nickel (II) chloride with 5-chloro-2-hydroxy acetophenone thiosemicarbazone in presence of heterocyclic base like pyridine (py), 2,2'-bipyridine (bipy), 1,10-phenanthroline (Phen), α/β-picoline. Thiosemcarbazone has been characterized by ^{13}C, ^{1}H *NMR as well as IR, electronic spectra. The synthesized adducts have been fully characterized by elemental analysis, IR, UV-visible spectra, magnetic measurement, electrical conductivity, TGA, The magnetic and spectroscopic data indicate a square planner geometry for the four coordinate and a distorted square pyramidal for five coordinate complexes. The thiosemicarbazone and its Nickel (II) complexes show growth inhibitory activity against Pseudomonas Putida, Escherichia Coli, Aspergillus Niger and Candida Albicans. Thiosemicarbazone and its Nickel (II) complexes have been found antioxidant.*

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Keywords: Thiosemicarbazone, Bioactive Ni (II) complexes, antimicrobial, antioxidant activity.

INTRODUCTION

Thiosemicarbazide contains hydrazine group which combines with aldehydes or ketones to generate the thiosemicarbazone derivatives, which have a wide range of biological activities, such as antitumour [1], antimalarial [2], antileukemic properties [3], antiviral activity [4], antibacterial [5] and antifertility property [6] because of its reduction capability. The thiosemicarbazone moiety is planar and this planar conformation is due to the extensive electron delocalization throught the moiety. Schiff bases form stable complexes with most transition metals [7-11]. The ligand 1,3-[bis(pyridine-2-imino)] propane possesses a remarkable capacity for coordination with transition metals, this ligand is good chelating ligand with extensive chemical properties. Therefore it can coordinate to transition metals as a bidentate, tridentate, quadridentate or pentadentate with variable structural properties [12]. In recent years, the coordination complexes of transition metals have been subject of investigation [13-16]. In past years,considerable attention has been paid to metal complexes of Schiff bases containing nitrogen and other donor atoms [17,18]. Bioorganometallic chemistry is dedicated to the study of metallic complexes and their biological applications [19]. Bioinorganic chemistry has increased the interest in shiff base complexes because it has been recognized that many of these complexes may serve as models for biologically important species [20-

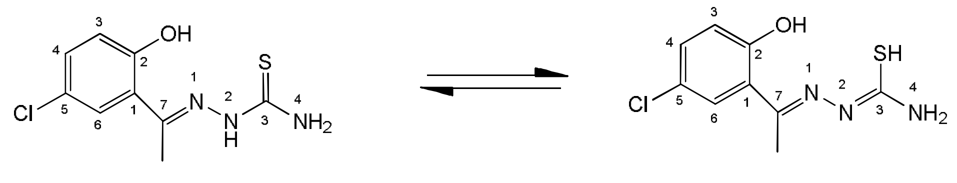
23]. Antioxidants are studied for their capacity to protect organisms and cells from damage induced by oxidative stress.Scientists have become interested in synthesizing new compounds that could provide active components to prevent or reduce the impact of oxidative stress on cells [24]. Thiosemicarbazone ligands form complexes with transition metal ions which have remarkable biological activity and hence thiosemicarbazone ligands are important in medicinal and pharmaceutical fields [25].

We now report here synthesis, spectral characterization and biological studies of four and five coordinate complexes of Ni(II) with 5-chloro 2-hydroxy acetophenone thiosemicarbazone.

MATERIALS AND METHODS

Magnetic measurements were carried out in the polycrystalline state by Faraday method. High purity [Co(SCN)$_4$] was used as standard. Diamagnetic corrections were made by Pascal's constants. IR spectra were recorded in the range 4000-200 cm^{-1} range using KBr discs. NMR spectra were recorded in the mixture of $CDCl_3$ and DMSO-d$_6$ (1:1 v/v) with a Bruker AC-300F 300 MHz spectrometer. Conductivity measurements were carried out on Conductivity Bridge, Systonics conductivity meter-304. Refluctance spectra were measured on Systonics UV-visible double beam spectrophotometer-2201.

Preparation of 5-chloro 2-hydroxy acetophenone thiosemcarbazone (L): The thiosemicarbazone was synthesized by refluxing 5-chloro 2-hydroxy acetophenone and thiosemicarbazide in the mole ratio 1:1 for 4 hours, 2-3 drops of Conc. H_2SO_4 was added as a dehydrating agent. The product obtained was filtered and washed with cold ethanol and then diethyl ether. It was recrystalised by hot ethanol and dried over P_2O_5 in vacuum [26].



L = 5-Chloro-2-hydroxy acetophenone thiosemicarbazone and its thiol form

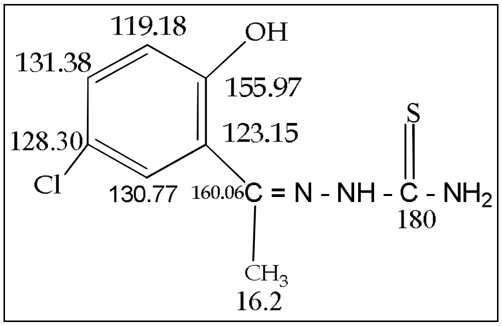
Preparation of complex: The complex Ni.L.H_2O (Where, L is 5-Chloro 2-hydroxy acetophenone thiosemicarbazone) was synthesized by refluxing hot ethanolic solutions of $NiCl_2.6H_2O$ and ligand (L) in the mole ratio 1:1 for 7-8 hours. The complex obtained was filtered and washed with hot water, cold ethanol and diethyl ether and dried over P_2O_5 in vacuum.

Preparation of adducts: The complex Ni.L.B (Where B is heterocyclic base like pyridine, 2-2'-bipyridine, 1, 10 phenanthroline, α-picoline, β-picoline) was synthesized by refluxing hot ethanolic solutions of $NiCl_2.4H_2O$ and ligand and heterocyclic base in the mole ratio 1:1:1 for 7-8 hours. The adduct obtained was filtered and washed with hot water, cold ethanol and diethyl ether and dried over P_2O_5 in vacuum [27].

RESULTS AND DISCUSSION

The colours, elemental analysis, stoichiometries of ligand and its complexes are presented in Table 1. Elemental analysis data are consistent with 1:1 ratio of metal ion, thiosemicarbazone for complex and 1:1:1 ratio for metal thiosemicarbazone and heterocyclic base for all adducts. The complex and all adducts are insoluble in most of the common polar and non polar solvents. They are soluble in DMF in which conductivity measurements were made (27^{0}C), showing all complexes to be non electrolyte [28]. The room temperature magnetic susceptibility of all complexes in polycrystalline state showed four coordinate complexes Ni.L.H_2O,Ni.L.B (B-Pyridine,α-Pico,β-Pico) are diamagnetic. Five coordinate high spin complexes have magnetic moments in the range 3.05-3.10 B.M. [29]. The observed values of magnetic moment for five coordinate complexes are slightly lower than those calculated for five coordinate trigonal bipyramidal configuration [30]. Lower μ_{eff} values for Ni (II) complexes [31] arise from quenching of the orbital contribution to the magnetic moment due to distortion of D_3h symmetry or due to strong in plane π-bonding [32,33]. The ^{1}HNMR signals at 13.00 and 3.39 ppm are assigned to –OH and –CH_3 protons respectively. L does not show any peak corresponds to S-H proton, indicating it exists in thioketo form. Absence of ^{2}NH proton signal suggests enolisation of ^{2}NH – C = S group to ^{2}N=C-SH. Little low field position of ^{4}NH (7.8 ppm) could be attributable to the deshielding caused by – N = C〈 of the system N=CSH = NH. Aromatic protons show multiples at 6.9, 7.25 and 7.50 ppm range.

^{13}C-NMR (DMSO-D_6): 119.18 (C = C stretching), 131.38 (C = C stretching), 128.30 (C = C – Cl), 130.77 (C = C stretching), 123.15 (C = C stretching), 155.97 (C = C – OH), 160.06 (C = N),180.0 (C=S),16.2 (C-CH_3).



ESI-MS m/z ion ligand (L) 243.80 (243.70) M$^+$, ESI-MS m/z ion Ni.L.H_2O 319.79 (318.39) M$^+$, ESI-MS m/z Ni.L.py 366.96 (365.46) M$^+$, ESI-MS m/z ion Ni.L.bipy 457.00 (456.55) M$^+$, ESI-MS m/z ion Ni.L.phen 481.80 (481.51) M$^+$, ESI-MS m/z ion Ni.L.α-pico 394.99 (394.47) M$^+$, ESI-MS m/z ion Ni.L.β-pico 394.64(394.47) M$^+$. Mass spectra data confirm the structure of ligand as indicated by molecular ion peak (M+1) corresponding to their molecular weight.

Table 1. Physicochemical analysis of synthesized compounds

Compounds	Colour	Empirical Formula	Molar conductance Ohm^{-1}cm^{2}mole^{-1}	Magnetic Moment B.M.	Elemental Analysis Found (Calculated) %				
					Metal%	%C	%H	%N	%S
L	Faint yellow	$C_9H_{10}N_3SClO$	-	-	-	44.03 (44.35)	4.36 (4.14)	17.62 17.24)	13.33 (13.16)
Ni-L.H_2O	Brown	$C_9H_{10}N_3SClO_2Ni$	41.6	Diamagnetic	18.01 (18.43)	34.02 (33.95)	3.44 (3.17)	13.25 (13.20)	10.33 (10.07)
Ni-L.Py	Brown	$C_{14}H_{13}N_4SClONi$	83.6	Diamagnetic	15.69 (16.06)	46.76 (46.00)	3.31 (3.59)	11.02 (11.50)	8.33 (8.77)
Ni-L.Bipy	Brown	$C_{19}H_{16}N_5SClONi$	52.6	3.08	12.78 (12.85)	49.08 (49.98)	3.10 (3.53)	15.05 (15.34)	7.64 (7.02)
Ni-L.Phen	Brown	$C_{21}H_{16}N_5SClONi$	41.6	3.09	12.20 (12.21)	52.11 (52.48)	3.12 (3.36)	14.74 (14.57)	6.34 (6.67)
Ni.L.α-Pico	Brown	$C_{15}H_{15}N_4SClONi$	93.6	Diamagnetic	15.10 (14.91)	45.52 (45.78)	3.37 (3.84)	14.54 (14.24)	8.71 (8.15)

Ni-L.β-Pico	Brown	$C_{15}H_{15}N_4SClONi$	83.6	Diamag netic	15.11 (14.92)	45.52 (45.78)	3.62 (3.84)	14.54 (14.24)	8.37 (8.15)

UV Studies: UV-visible spectra of metal complexes in DMF solution and solid state indicate that all complexes have same structure both in solid state and solution state (table 2). Typical planer Ni(II) spectra show a strong visible band in the 15000-25000 cm^{-1} range and in many cases a second strong band between 23000 and30000 cm^{-1}.they are referred as to as v_2 and v_3 bands. Lower energy v_1 band has been observed in planer complexes containing S-ligands [34]. The planer complexes of Ni(II) are readily distinguished from octahedral and tetrahedral complexes by absence of transitions below 10000 cm^{-1}. The presence of intense π- π*and n- π* transitions cause the lower energy d-d bands and LMCT bands to appear as weak shoulders. The electronic spectra show shoulder band at 40000-41000 cm^{-1} range (π- π*) and 28000-31500 cm^{-1} range (n-π*). This can be assigned to aromatic ring and thiosemicarbazone moiety respectively. The broad bands at 28000-31500 range are assigned for n-π* transitions [35]. The shift of π- π* bands to the longer wavelength region is the result of the C=S bond being weakened and conjugation system being enhanced after the formation of the complex [36]. Ni.L.H_2O, Ni.L.py, Ni.L.α-Pico, Ni.L.β-Pico show shoulder bands at 16000-17000 cm^{-1} range. These d-d spectral transitions are assigned to $A_1g \rightarrow A_2g$ [37]. The d-d bands appearing as weak shoulders centred around 17000 cm^{-1} region are typically of square planer Ni(II) complexes [38]. The presence of intense π- π* and n-π* transitions cause the lower energy d-d bands and LMCT bands to appear as weak shoulders. The bands at 23000-27000 cm^{-1} range correspond to L→M. It is associated with $^1A_1g \rightarrow {}^1Eg$ transition, no band below 10000 confirms the planer structure of these complexes. This is because of large crystal field splitting in a square planer complex, the energy separation between dx^2-y^2 and lower orbital is greater than 10000 cm^{-1} [39]. Ni.L.α-Pico, Ni.L. β-Pico show broad band at around 23000 and 26600 cm^{-1} range. This band may be due to tetrahedral complex in addition to square planer complexes. This indicates the possibility of tetrahedral↔square planer equilibrium in these complexes. The electronic spectra of Ni.L.bipy and Ni.L.Phen do not resemble the spectra of five ccodinate [33,40], but resemble to pseudo-octahedral Ni(II) complexes [39,41].

Table 2. Electronic spectral assignments (cm^{-1})

Complex	State	d–d	L → M	n → π*	π → π*
Ni LH_2O	DMF	16722	23,474, 26,882	30,960	40,816
Ni L H_2O	Solid	17575	22,124, 25,773	28,409	40,000
Ni L Py	DMF	16667	23,148, 26,316	30,303	40,816
Ni L Py	Solid	16000	22,222, 28,409	28,986	38,662
Ni L bipy	DMF	17094	23,810 27,778	28,169	40,983
Ni L bipy	Solid	18018	22,124, 26,455	30,120	37,879
Ni L phen	DMF	17241	23697, 23316	31,250 (sh)	40,650

Ni L phen	Solid	19048	22222, 27,397	28,571, 30,303	42,553
Ni L α–pico	DMF	16,949	23,697, 26,316	31,056	40,486
Ni L α–pico	Solid	17,482	21,459, 30,488	28,409	43,478
Ni L β–pico	DMF	16,892	23,364, 26,525	30,769 (sh)	40,323
Ni L β–pico	Solid	17,857	22,124, 29,586	28,409	36,765

IR Studies: The absence of any band in 2600-2800 cm^{-1} region of the IR spectrum of L shows the absence of thiol tautomer in the solid state [42]. Coordination of the azomethine nitrogen ^{7}C=N^1 shift the frequency to the lower side by 15-25 cm^{-1}. The band is shifting from 1624 cm^{-1} in uncomplexed thiosemicarbazone spectra to ca 1589 cm^{-1} in the spectra of complexes. The ν(NN) shifting to higher wavenumber in spectra of complexes than that of thiosemicarbazones confirm the coordination of azomethine nitrogen [43]. The presence of new band at 400-470 cm^{-1} assignable to ν (Ni-N) in the complexes,confirms the coordination of azomethine nitrogen. There is a loss of -^{2}NH proton on coordination via thiolate sulphur [44]. Decrease in frequency (10-90 cm^{-1}) of the ν (C=S) bands found at 758,1311. The coordination through sulphur is confirmed by the presence of new band in the 300-325 cm^{-1} range assinable to ν (NiS). The phenolic oxygen occupies the third coordination on the loss of OH proton. This causes shifting of ν (CO) to low wavenumbers by 50-60 cm^{-1} from 1281 cm^{-1} in the spectra of L. The band at 500-520 cm^{-1} is assignable to ν (NiO). The coordination of heterocyclic nitrogen atom(s) is confirmed by the presence of ν (NiN) band at 260-285 cm^{-1} range. The characteristic bands of coordinated heterocyclic bases are also observed in IR spectra of all complexes (table 3).

Table 3. Infrared Spectroscopic Assignment (cm^{-1})

Compounds	νOH	ν^2NH	νCO	νCN	νCS	ν(C=N-N=C)	νNN	νMO	νMN.H.B	νMS	νM^{1}N	Bands due to heterocyclic bases
L	3147	2943	1281	1624	758,1374	-	1049	-		-	-	-
Ni.LH_2O	-	-	1226	1603	750,1304	1555	1136	518	-	312	423	-
Ni.L.Py	-	-	1229	1598	687,1297	1555	1072	516	282	311	425	1297,425,619
Ni.L.Bipy	-	-	1226	1597	682,1301	1545	1110	514	269	324	425	1404,1013
Ni.L.Phen	-	-	1227	1618	685,1301	1545	1135	511	284	316	425	1400,470,613
Ni.L.α-Pico	-	-	1238	1609	686,1312	1528	1103	500	278	300	419	1405,762,469
Ni.L.β-Pico	-	-	1228	1589	674,1304	1545	1128	507	278	309	420	1304,674,420

TGA Analysis: The TGA curve of the Ni.L.H_2O complex was carried out within a temperature range from room temperature up to 800^{0}C. The data from gravimetric analysis clearly indicated that the decomposition of complex proceed in several steps. Hydrations of water molecules were lost in between 30-100^{0}C. One coordinated water molecule was lost between the temperature 100-125^{0}C. There are two breaks in curves at 225^{0}C and 357.14^{0}C due to evaporation of organic ligand. NiO was formed and decomposition completed at 732.14^{0}C. The complexes prepared with different metals decompose in two steps. It is evaluated that the coordination of metal ion to ligand is responsible for the thermal stabilities of metal complexes [45].

Differencial scaning colorimetry (DSC): Two sharp peaks were observed in DSC thermogram of Ni.L.H_2O. One peak corresponds to endothermic and another for exothermic. The sharp endothermic peak at 171.81^{0}C corresponds to melting point of the complex. The exothermic peak at 295^{0}C corresponds to the decomposition of the complex. The glass transition temperature is 248.75^{0}C and ΔH is -71.57 Jg^{-1}

Biological activity (Agar well diffusion method): The antibacterial activity was determined using the agar well diffusion method. The prepared culture plates were inoculated with different bacteria and fungus by using plate method. Wells were made on the agar surface with 6 mm cork borer, the solutions of complexes were poured into the well using sterile syringe. The plates were incubated at 37±2^{o}C for 24 hours for bacterial activity and 48 h for fungal activity. The plates were observed for the zone formation around the wells. The zone of inhibition was calculated by measuring inhibition zone around the well (in mm) including the well diameter. The activity was determined using two different concentrations 10^{-3} M and 10^{-4} M. In order to compare activity of the synthesized complexes,followed the same procedure with metal chlorides. The activity index was calculated to express the activity in comparison to the antibiotics [46]. The diameters of the inhibition zones for all tested compounds are presented in table 4. The results showed that the complexes showed better activity than free ligand. The adducts with bipyridine and 1,10 phenanthroline showed better activity. The most probable reason for this difference might be due to chelation, which reduces the polarity of the central metal atom because of the partial sharing of its partial positive charge with donor groups and possible Π-electron delocalization within the whole chelating ring. As a result of this,the lipophilic nature of the central metal atom increases, which favours the permeation of the complexes through the lipid layer of the cell membrane[47]. Out of these seven compounds tested, Ni.L.phen was found more active against four cultures. The 5-chloro 2-hydroxy acetophenone thiosemicarbazone was found less active than its Ni(II) complex and adducts. Thus increase in coordination number from four to five in copper complexes increases microbial activity [48]. In gram negative bacteria (*Pseudomonas Putida*, *Escherichia Coli*) the outer membrane, so it might not be ease for the complexes to diffuse inside the bacterial cell. The metal ion chloride salts were more effective than complexes. This shows free metal ions are more effective than binded in complexes.

Table 4 .% Activity Index of Ni(II) complexes

Compound	*Pseudomonas Putida*		*Escherichia Coli*		*Aspergillus Niger*		*Candida Albicans*	
	10^{-3}M	10^{-4}M	10^{-3}M	10^{-4}M	10^{-3}M	10^{-4}M	10^{-3}M	10^{-4}M
L	35.29	27.78	34.62	25.81	66.67	52.63	58.82	45
Ni.L.H2O	35.29	30.56	42.31	32.26	66.67	57.89	76.47	60
Ni.L.Py	35.29	36.11	57.69	38.71	72.22	63.16	88.24	70
Ni.L.Bipy	44.12	38.89	53.85	41.94	77.78	68.42	64.12	75
Ni.L.Phen	47.06	41.67	61.54	45.16	94.44	78.95	94.12	75
Ni.L. α-Pico	35.29	30.56	46.15	35.38	61.11	42.11	70.59	55
Ni.L. β-Pico	35.29	27.76	50.00	35.38	61.11	52.63	76.47	40
Std	100	100	100	100	100	100	100	100
$NiCl_2.6H_2O$	91.18	77.78	100	100	122.22	136.84	123.53	115

(Std-Amphicilin,Bicip)

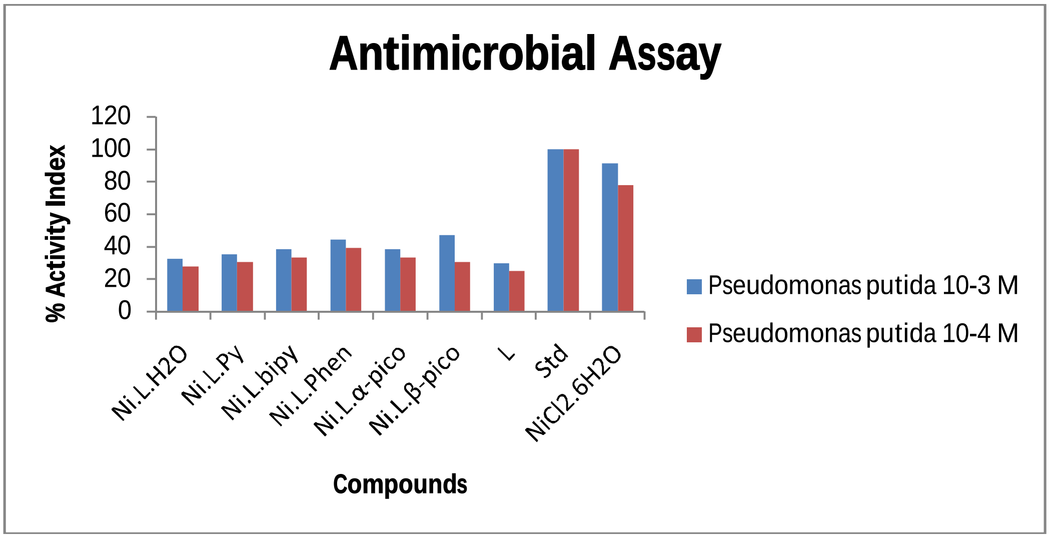


Fig 1

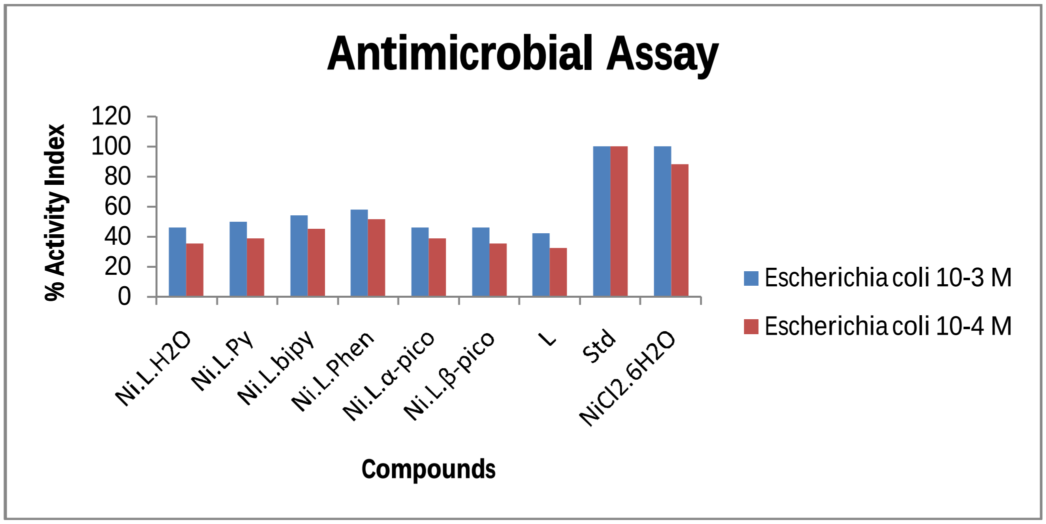


Fig 2

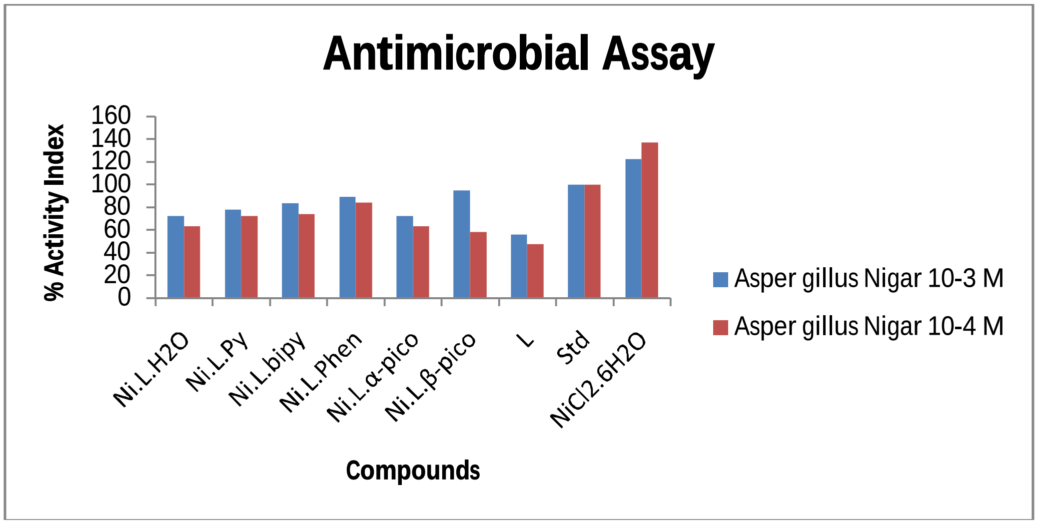


Fig 3

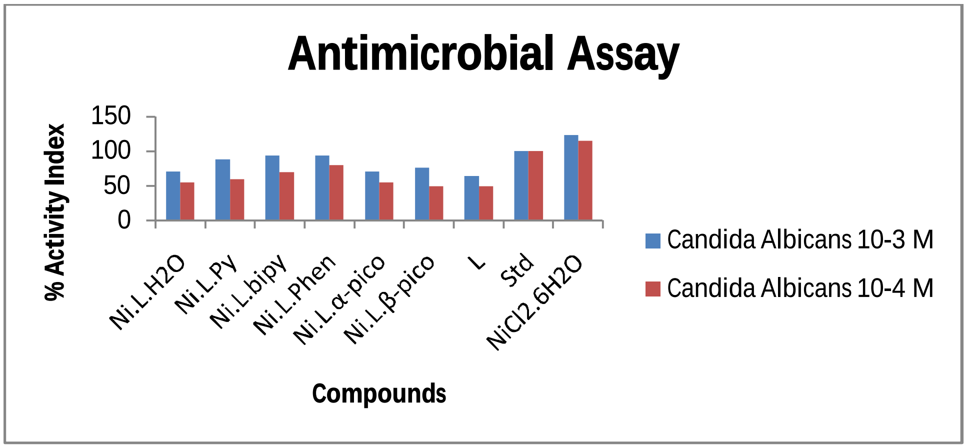
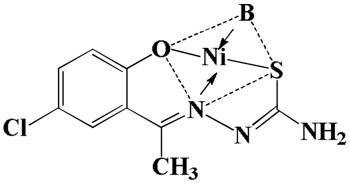
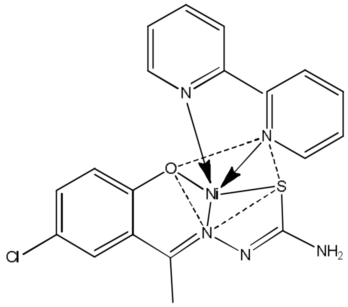
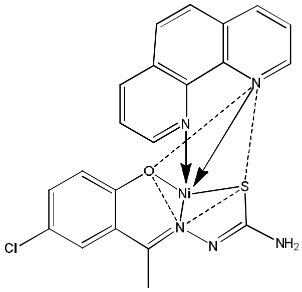


Fig 4

Expected Structures:







Where B = H_2O and Heterocyclic base, i.e. Pyridine, α-Picoline and β-Picoline.

APPLICATIONS

Antioxidant activity: The antioxidant activity of ligand and complexes was assessed on the basis of the radical scavenging effect of the stable DPPH free radical (table 6). About 100 _l of each concentrations or standard (from 21 mg ml^{-1} to 21_g ml^{-1}) was added to 2 ml of DPPH in methanol solution (100_M) in a test tube. After incubation at 37 ^{0}C for 30 min, the absorbance of each solution was determined at 517 nm using spectrophotometer. The corresponding blank readings were also taken and the remaining DPPH was calculated. IC_{50} value is the concentration of the sample required to scavenge 50% DPPH free radical. Lower the absorbance of the reaction mixture indicated higher free radical scavenging activity [49].

Table 6. Antioxidant activity data (%Radial scavenging)

µg/ml	Ni-L.H_2O	Ni-L-Py	Ni-L-Bipy	Ni-L. Phen	NiL.α-Pico	Ni-L. β-Pico	Vit C Std
20	4.44	58.14	2.20	-	53.48	2.20	39.53
40	13.33	79.06	3.33	-	67.44	3.33	46.51
60	27.77	81.39	6.66	4.34	72.09	6.66	58.13
80	30.00	83.72	25.55	20.28	74.41	25.55	60.46
100	65.55	93.02	26.66	31.88	74.41	26.66	65.11
IC_{50}	76.27	17.19	187.59	158.83	18.69	187.59	51.00

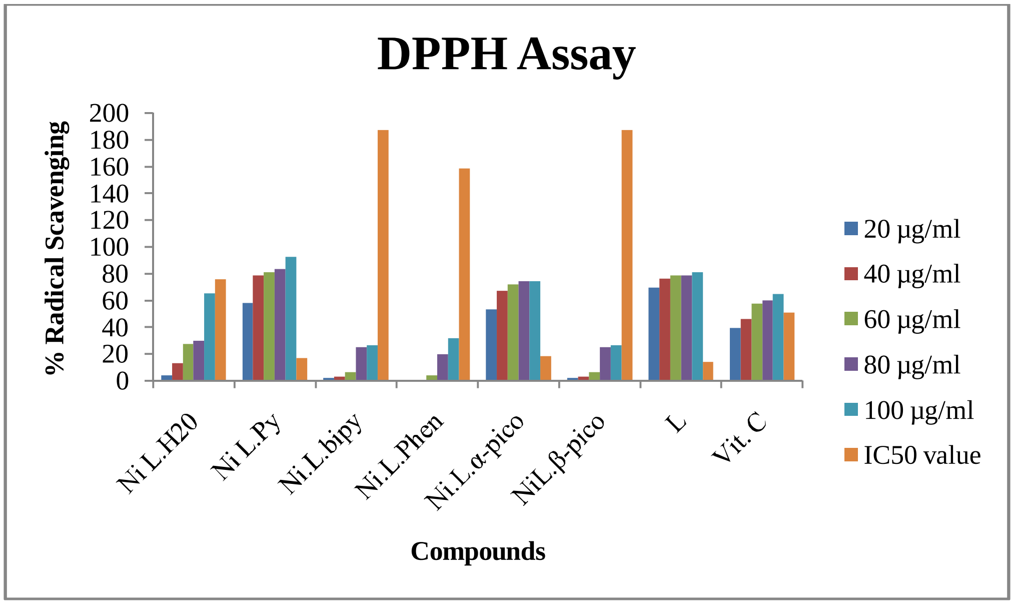


Figure 5. Effect of synthesized compounds on DPPH assay

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