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Synthesis, spectral and antioxidant assay of Nickel (II) adducts with heterocyclic bases derived from 5-chloro-2-hydroxy acetophenone *N*(4) methyl thiosemicarbazone

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ABSTRACT

We have synthesized heterocyclic base adducts [pyridine (py), 2,2'-bipyridine (bipy), 1,10-phenanthroline (Phen), α/β -picoline] of Nickel (II) complexes by the reaction of Nickel (II) chloride with 5-chloro-2-hydroxy acetophenone *N*(4) methyl thiosemicarbazone in presence of heterocyclic base. Ligand was characterized by ¹³C, ¹H NMR as well as IR, electronic spectra. The synthesized adducts were characterized by IR, ESI-MS, UV-visible, magnetic measurement, molar conductivity, TGA and DSC. The magnetic and spectroscopic data indicate a square planer geometry for the four coordinate and a distorted square pyramidal for five coordinate complexes. The Nickel (II) bipy and Nickel (II) β -pico adducts show higher antioxidant activity.

Keywords: Thiosemicarbazone, Bioactive metal complexes and antioxidant activity.

INTRODUCTION

Thiosemicarbazones are the compounds used in the treatment of many diseases, for ex: cancer and its development is in progress [1-3]. Aromatic o-hydroxyaldehydes and ketones have biological properties. These thiosemicarbazones co-ordinate as the dianion to form mononuclear as well as binuclear complexes with the metal ion on deprotonation of the ring hydroxyl group and the loss of the N(2) hydrogen of the thiosemicarbazone moiety. In recent years, such thiosemicarbazones and their transition metal complexes have been studied due to their pharmacological interest [4,7]. The most promising areas in which thiosemicarbazone compounds are developed is their use against cancer. The presence of metal ion in thiosemicarbazone complexes increases the activity or contributes to migrate the side effects of the organic parent compounds [8]. The main known effects related to their anticancer activity are reactive oxygen species (ROS) production [9], topoisomerase II inhibition [10], mitochondria disruption [11] and amultidrug resistance protein (MDRI) inhibition [12,13] 3-aminopyridine-2-carboxaldehyde thiosemicarbazone has been developed as an anticancer drug and has in clinical phase II on several cancer types [14,15]. In recent years coordination complexes of transition metals have been the subject of detailed investigation [16-19]. Among these transition metals Ni (II) is recognized as an essential trace element for bacteria, plants, animals and humans. It has wide applications in industrial homogeneous catalysis [20, 59]. There can be many attractive structures and frameworks with many ligands [21-23]. Backbones with desirable structures and properties can be created by controlling coordination environment. The first crystal of Ni (II) complex with phen-dione as a ligand was reported [18]. Thiosemicarbazones exist in two tautomeric forms, thione and thiol. The thione functions as bidentate neutral ligand and the thiol can deprotonate and act as an anionic ligand [24]. As a part of studies on

N(4) substituted thiosemicarbazones [25-32], the crystal structure of 2-hydroxyacetophenone N(4) cyclohexyl thiosemicarbazone was reported [33].

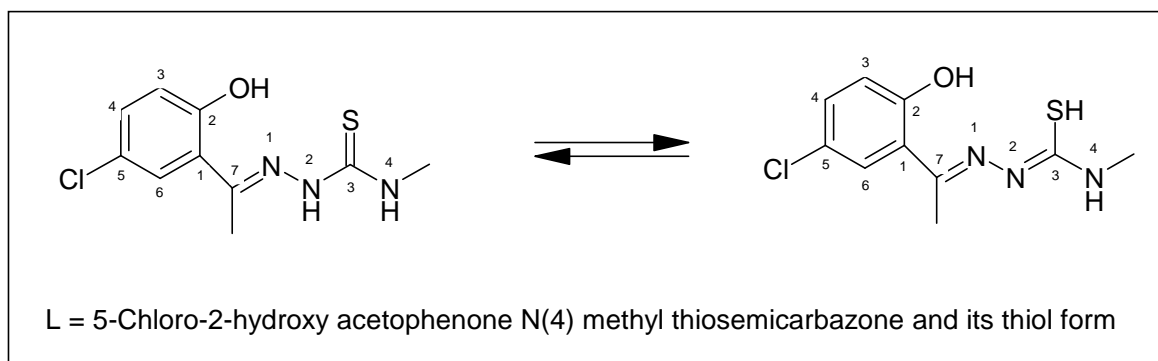
We know here report the synthesis, spectral characterization and biological studies of four and five coordinate complexes of Ni (II) with 5-chloro 2-hydroxy acetophenone N(4) methyl thiosemicarbazone and their antioxidant activity.

MATERIALS AND METHODS

Magnetic measurements were carried out in the polycrystalline state by Faraday method. High purity $[\text{Co}(\text{SCN})_4]$ was used as standard. Diamagnetic corrections were made by Pascal's constants. IR spectra were recorded in the range $4000\text{-}200\text{ cm}^{-1}$ 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 300MHz spectrometer. Conductivity measurements were carried out in 10^{-3} M DMF solutions on Conductivity Bridge, Systonics conductivity meter-304. UV-visible spectra were measured in DMF solutions and in solid state on Systonics UV-visible double beam spectrophotometer-2201.

Synthesis of ligand

The N(4) thiosemicarbazone was synthesized by refluxing 5-chloro 2-hydroxy acetophenone and N(4) methyl thiosemicarbazide in the mole ratio 1:1 for 3-4 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 recrystallised by hot ethanol and dried over P_2O_5 in vacuum [34].



Synthesis of complexes

The complex $\text{Ni.L.H}_2\text{O}$ (Where, L is 5-Chloro 2-hydroxy acetophenone N(4) methyl thiosemicarbazone) was synthesized by refluxing hot ethanolic solutions of $\text{NiCl}_2.6\text{H}_2\text{O}$ 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.

Synthesis 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 $\text{CuCl}_2.4\text{H}_2\text{O}$ 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 [35, 58].

RESULTS AND DISCUSSION

Analytical

The colours, elemental analysis, stoichiometries of ligand and its complexes are presented in Table 1.1. 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.

Molar conductance

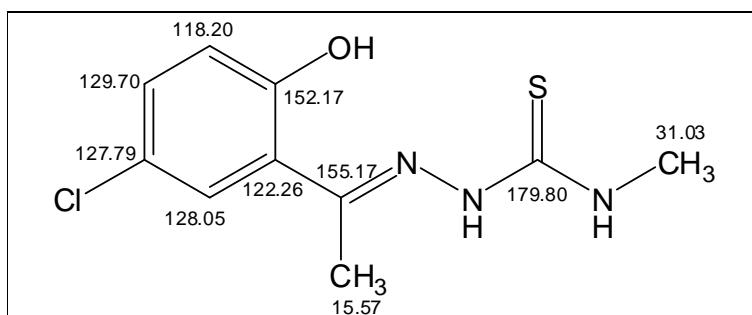
The molar conductances measured in 10^{-3} M DMF solutions, indicating all the formed complexes are non electrolytes in nature [36].

Magnetic susceptibility

The room temperature magnetic susceptibility of all complexes in polycrystalline state showed four coordinate complexes Ni.L.H₂O, Ni.L.B (B- Pyridene, α -Pico, β -Pico) are diamagnetic. Five coordinate high spin complexes have magnetic moments in the range 3.20-3.40 B.M [37]. The observed values of magnetic moment for five coordinate complexes are slightly lower than those calculated for five coordinate trigonal bipyramidal configuration [38]. Lower μ_{eff} values for Ni (II) complexes [39] 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 [40,41].

NMR spectra

The ¹H NMR signals at 10.45 and 3.40 ppm are assigned to –OH and –CH₃ protons respectively. The signals at 2.19 and 2.91 corresponds to –NH and H⁴N-CH₃ respectively. Absence of ²NH protons signal suggests enolization of ²NH-C=S group to ²N=C-SH. The aromatic protons show multiplet at 6.9, 7.325, 7.45 ppm range. ¹³C-NMR (DMSO-D₆): δ ppm 118.20 (C=C); 129.70 (C=C); 127.79 (C=C-Cl); 128.05 (C=C); 122.26 (C=C); 155.17 (C=C-OH), 152.17 (C=C-OH), 179.80 (C=S); 31.03 (NH-CH₃)

**Mass spectra**

ESI-MS m/z ion ligand (L) 243.80 M⁺, ESI-MS m/z ion Ni.L.H₂O 333.09 M⁺, ESI-MS m/z Ni.L.py 393.50 M⁺, ESI-MS m/z ion Ni.L.bipy 470.58 M⁺, ESI-MS m/z ion Ni.L.phen 494.60 M⁺, ESI-MS m/z ion Cu.L. α -pico 407.52 M⁺, ESI-MS m/z ion Cu.L. β -pico 407.52 M⁺. Mass spectra data confirm the structure of ligand as indicated by molecular ion peak (M+1) corresponding to their molecular weight.

Table 1.1 : 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 ₉ H ₁₀ N ₃ SClO			-	44.03 (44.35)	4.36 (4.14)	17.62 (17.24)	13.33 (13.16)
Ni-L.H ₂ O	Brown	C ₁₀ H ₁₂ N ₃ SClO ₂ Ni	31.2	Diamagnetic	17.43 (17.65)	36.40 (36.13)	3.87 (3.64)	12.85 (12.64)	9.98 (9.64)
Ni-L.Py	Brown	C ₁₅ H ₁₅ N ₄ SClONi	93.6	Diamagnetic	14.53 (14.91)	45.13 (45.78)	3.41 (3.84)	14.77 (14.24)	8.47 (8.15)
Ni-L.Bipy	Brown	C ₂₀ H ₁₈ N ₅ SClONi	62.4	3.08	12.78 (12.47)	51.32 (51.04)	3.52 (3.86)	14.64 (14.88)	7.12 (6.81)
Ni-L.Phen	Brown	C ₂₂ H ₁₈ N ₅ SClONi	72.8	3.06	11.62 (11.86)	52.64 (53.12)	3.97 (3.67)	14.47 (14.16)	6.05 (6.48)
Ni.L. α -Pico	Brown	C ₁₆ H ₁₇ N ₄ SClONi	52.0	Diamagnetic	14.11 (14.47)	47.12 (47.39)	3.32 (3.73)	13.51 (13.82)	7.32 (7.91)
Ni-L. β -Pico	Brown	C ₁₆ H ₁₇ N ₄ SClONi	62.4	Diamagnetic	14.53 (14.47)	46.99 (47.39)	3.32 (3.73)	13.67 (13.82)	8.05 (7.91)

Electronic spectra

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 1.2). 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 and 30000 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 [42]. 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 $\pi-\pi^*$ and $n-\pi^*$ transitions cause the lower energy d-d bands and LMCT bands to appear as weak shoulders. The electronic spectra show shoulder band at $39000-41000\text{ cm}^{-1}$ range ($\pi-\pi^*$) and $26000-33000\text{ cm}^{-1}$ range ($n-\pi^*$). This can be assigned to aromatic ring and thiosemicarbazone moiety respectively. The broad bands at $26336-32788$ range are assigned for $n-\pi^*$ transitions [43]. The shift of $\pi-\pi^*$ 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 [44]. Ni.L.Py, Ni.L.H₂O, Ni.L. α -Pico, Ni.L. β -Pico show shoulder bands at $16000-16892\text{ cm}^{-1}$ range. These d-d spectral transitions are assigned to $A_{1g}\rightarrow A_{2g}$. [45]. The d-d bands appearing as weak shoulders centred around 17000 cm^{-1} region are typically of square planer Ni(II) complexes [46]. The presence of intense $\pi-\pi^*$ and $n-\pi^*$ transitions cause the lower energy d-d bands and LMCT bands to appear as weak shoulders. The bands at $23000-26500\text{ cm}^{-1}$ range correspond to $L\rightarrow M$. It is associated with $^1A_{1g}\rightarrow ^1E_g$ 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} [47]. Ni.L. α -Pico, Ni.L. β -Pico show broad band at $23000-26525\text{ cm}^{-1}$ range. This band may be due to tetrahedral complex in addition to square planer complexes. This indicates the possibility of tetrahedral \leftrightarrow square planer equilibrium in these complexes. The electronic spectra of Ni.L.bipy and Ni.L.Phen do not resemble the spectra of five coordinate [41,48], but resemble to pseudo-octahedral Ni(II) complexes [47,49].

Table 1.2: Electronic spectral assignments (cm^{-1})

Compound	Mode	d-d	$L\rightarrow M$	$n\rightarrow\pi^*$	$\pi\rightarrow\pi^*$
L	DMF	-	-	25974(4.05) 28571(3.85)	40860(3.35)
Ni.L.H ₂ O	DMF	16807(2.20)	23697(4.26) 26667(4.38)	30769(4.35)	40000(4.24)
Ni.L.Py	DMF	16807(2.35)	24691(4.33) 26042(4.47)	26667(4.28)	40161(4.22)
Ni.L-Bipy	DMF	17007(2.28)	24096(4.14) 27933(4.25)	28986(4.09) 32788(4.07)	39682(4.05)
Ni.L-Phen	DMF	17123(2.22)	23529(4.26) 25974(4.34)	30769(4.35) 26738(4.22)	40323(4.29)
Ni.L- α Pico	DMF	16807(2.15)	23697(4.12) 26385(4.26)	26455(4.27) 32787(4.31)	40160(4.16)
Ni.L- β Pico	DMF	16863(2.18)	24390(4.37) 25773(4.35)	29586(4.55) 35971(4.40)	34483(4.40) 37313(3.95)

(Absorbance)

Table 1.3: Infrared Spectroscopic Assignment (cm^{-1})

Compounds	νOH	$\nu^2\text{NH}$	νCO	νCN	νCS	$\nu(\text{C}=\text{N}-\text{N}=\text{C})$	νNN	νMO	$\nu\text{MN.H.B}$	νMS	$\nu\text{M}^1\text{N}$	Bands due to heterocyclic bases
L	3225	2925	1288	1638	795,1368	-	1049	-	-	-	-	-
Ni.L.H ₂ O	-	-	1235	1566	671,1286	1577	1113	509	-	309	423	-
Ni.L.Py	-	-	1250	1566	664,1296	1555	1097	509	263	301	423	1296,664,509
Ni.L.Bipy	-	-	1219	1620	1308	1560	1111	514	269	313	425	1404,763,665
Ni.L.Phen	-	-	1227	1582	725,1296	1579	1107	518	278	309	414	1450,725,664
Ni.L. α -Pico	-	-	1234	1631	687,1308	1530	1062	521	288	311	469	1233,698,468
Ni.L. β -Pico	-	-	1234	1625	688,1319	1545	1125	515	280	314	432	1238,688,432

IR spectra

The absence of any band in $2600-2800\text{ cm}^{-1}$ region of the IR spectrum of L shows the absence of thiol tautomer in the solid state [50]. Coordination of the azomethine nitrogen $^7\text{C}=\text{N}^1$ shift the frequency to the lower side by $15-25\text{ cm}^{-1}$. The band is shifting from $1624,1638\text{ cm}^{-1}$ in uncomplexed thiosemicarbazone spectra to ca 1582 cm^{-1} in the spectra of complexes. The $\nu(\text{NN})$ shifting to higher wavenumber in spectra of complexes than that of thiosemicarbazones confirm the coordination of azomethine nitrogen [51]. The presence of new band at $40-470\text{ cm}^{-1}$ assignable to $\nu(\text{Ni}-\text{N})$ in the complexes, confirms the coordination of azomethine nitrogen. There is a loss of ^2NH proton on coordination via thiolate sulphur [52]. Decrease in frequency ($10-90\text{ cm}^{-1}$) of the $\nu(\text{C}=\text{S})$ bands found at $758,1311$ in L_1 and $795,1158\text{ cm}^{-1}$ in L_2 . The coordination through sulphur is confirmed by the presence of new band in the $300-325\text{ cm}^{-1}$ range assignable to $\nu(\text{NiS})$. The phenolic oxygen occupies the third coordination on the loss of OH proton, this causes shifting of $\nu(\text{CO})$ to low wavenumbers by $50-60\text{ cm}^{-1}$ from 1281 and 1288 cm^{-1} in the

spectra of L₁ and L₂ respectively. The band at 500-521 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.1.3).

Thermogravimetric analysis (TGA)

The TGA curve of the Ni.L.H₂O complex was carried out within a temperature range from room temperature up to 800°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°C. One coordinated water molecule was lost between the temperature 100-125°C. There are two breaks in curves at 200°C and 378.57°C due to evaporation of organic ligand. NiO was formed and decomposition completed at 800°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 [53].

Differential scanning calorimetry (DSC)

Two sharp peaks were observed in DSC thermogram of Ni.L.H₂O. One peak corresponds to endothermic and another for exothermic. The sharp endothermic peak at 175.0°C corresponds to melting point of the complex. The exothermic peak at 326.46°C corresponds to the decomposition of the complex.

Antioxidant activity by DPPH assay

The antioxidant activity of ligand and complexes was assessed on the basis of the radical scavenging effect of the stable DPPH free radical (Table 1.4). About 100 μ l of each concentrations or standard (from 21 mg/ml to 21 μ g/ml) was added to 2 ml of DPPH in methanol solution (100_M) in a test tube. After incubation at 37 °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. IC₅₀ 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 [57].

Table 1.4: Antioxidant activity data (% Radical scavenging)

μ g/ml	Ni-L.H ₂ O	Ni-L-Py	Ni-L-Bipy	Ni-L. Phen	NiL. α -Pico	Ni-L. β -Pico	Vit C Std
20	10.00	-	72.09	5.55	3.33	70.93	39.53
40	12.50	-	75.58	8.88	20.00	74.41	46.51
60	20.00	10.14	76.24	23.23	22.24	75.58	58.13
80	30.00	15.94	80.23	25.55	27.77	75.58	60.46
100	37.50	23.18	84.88	37.77	34.44	79.06	65.11
IC ₅₀	133.33	215.70	13.87	132.38	145.18	14.09	51.00

CONCLUSION

On the basis of above analytical, molar conductance, magnetic, electronic, thermogravimetric, differential scanning calorimetry and IR, NMR, mass spectral data and keeping view of the preferred geometries, square planer geometry for the four coordinate and a distorted square pyramidal for five coordinate complexes have been proposed. All the synthesized adducts have been found antioxidant particularly adducts with bipyridine and β -picoline showed better antioxidant activity.

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