

SYNTHESIS AND SPECTRAL CHARACTERIZATION OF NICKEL(II) COMPLEXES

7.1. Introduction

Nickel(II) (d^8) forms a large number of complexes with coordination numbers 3 to 6. The coordination number of Ni(II) rarely exceeds 6 and its principal stereochemistries are octahedral and square planar with rather few examples of trigonal bipyramidal, square pyramidal and tetrahedral. Of the four coordinate complexes of Ni(II), those with the square planar stereochemistry are the most numerous. Although less numerous than the square planar complexes, tetrahedral complexes of nickel(II) also occur.

There are reports on the preparation and spectral characterization of Ni(II) complexes of 2-formylpyridine 4N -methyl, 4N -dimethyl, 4N -diethyl-and 4N -dipropyl thiosemicarbazones [1]. Further studies of Ni(II) complexes of 2-acetylpyridine thiosemicarbazones [2,3] as well as 2-acetylpyridine 4N -alkyl, 4N -dialkyl thiosemicarbazones [4,5] have also been reported.

We have prepared complexes of 2-benzoylpyridine $N(4)$ -cyclohexyl thiosemicarbazone (HL^1) and 2-benzoylpyridine $N(4)$ -phenylthiosemicarbazone (HL^2) using nickel chloride and nickel nitrate. This Chapter describes the synthesis and spectral characterization of the three Ni(II) complexes.

7.2. Experimental

7.2.1. Materials

All the nickel salts used were of analar grade and were used without further purification. The solvents were purified by standard methods. The methods used for the synthesis of HL¹ and HL² are given in Chapter 2.

7.2.2. Synthesis of Ni(II) complexes

$[NiL^1Cl]$ (19)

A methanolic solution of NiCl₂·6H₂O (2 mmol, 0.475 g) and a hot methanolic solution of HL¹ (2 mmol, 0.676 g) were mixed and refluxed for 5 hrs. The blue colored solids, which separated on keeping overnight, were filtered, washed with water, hot ethanol, then ether and dried *in vacuo* over P₄O₁₀.

$[Ni(HL^1)_2(NO_3)_2] \cdot 2H_2O$ (20)

Ni(NO₃)₂·6H₂O (2 mmol, 0.457 g) dissolved in methanol and HL¹ (2 mmol, 0.676 g) dissolved in hot methanol were mixed and refluxed for 6 hrs. The brown colored solids, which separated on keeping overnight, were filtered, washed with water, hot ethanol, then ether and dried *in vacuo* over P₄O₁₀.

$[Ni(HL^2)(L^2)(NO_3)]$ (21)

A methanolic solution of Ni(NO₃)₂·6H₂O (2 mmol, 0.457 g) and a hot methanolic solution of HL² (2 mmol, 0.664 g) were mixed and refluxed for 5 hrs. Brown colored solids separated on cooling. The crystals separated were filtered, washed with water, hot ethanol, then ether and dried *in vacuo* over P₄O₁₀.

7.3. Results and discussion

7.3.1. Physical measurements

The colors, partial elemental analyses, stoichiometries, molar conductivities and magnetic moments of the complexes are presented in Table 7.1. The complex NiL^1Cl is blue crystal and the other two Ni(II) complexes are brown colored crystals. They are insoluble in methanol and ethanol and soluble in chloroform, dimethylformamide and dimethylsulphoxide.

In the complex, NiL^1Cl , the ligand coordinates as the deprotonated L^1 , which is a tridentate ligand bonding *via* the pyridine nitrogen, the azomethine nitrogen and the sulfur atom. The non-electrolytic nature of the compound **19** in DMF shows that the chloride ion is coordinated to the Ni(II) ion. The molar conductivity measurements of the two Ni(II) complexes $[\text{Ni}(\text{HL}^1)_2(\text{NO}_3)_2]\cdot 2\text{H}_2\text{O}$ and $[\text{Ni}(\text{HL}^2)(\text{L}^2)(\text{NO}_3)]$ showed their non electrolytic nature which confirm that the nitrate ions are coordinated to the Ni(II) ion.

The stoichiometry $[\text{Ni}(\text{HL}^1)_2(\text{NO}_3)_2]\cdot 2\text{H}_2\text{O}$ of the complex suggests the coordination of the neutral ligand *via* the pyridine and azomethine nitrogen atoms with octahedral coordination achieved with the two nitrate ions. In the complex $[\text{Ni}(\text{HL}^2)(\text{L}^2)(\text{NO}_3)]$, as the stoichiometry suggests the two ligand molecules are coordinated to the Ni(II) ion; one as the neutral molecule and the other as the anion. These proposed structures are supported by infrared spectral studies.

7.3.2. Magnetic susceptibilities

For the vast majority of four-coordinate nickel(II) complexes, square planar geometry is preferred. The square planar geometry causes one of the *d* orbitals, $d_{x^2-y^2}$ to be uniquely high in energy and the eight electrons can occupy the other

four d orbitals but leave this strongly antibonding $d_{x^2-y^2}$ vacant. Almost all the planar complexes of Ni(II) are thus diamagnetic. However, weakly paramagnetic nickel (II) planar complexes have also been reported [6.7] but of low spin. Theoretical and experimental results have proved that these paramagnetic complexes have neither octahedral nor tetrahedral geometry. To explain this paramagnetic behaviour of the square planar complexes, equilibrium between spin free and spin-paired configuration is suggested [8].

In tetrahedral complexes (T_d symmetry) the d^8 configuration gives rise to a ${}^3T_1(F)$ ground state. Because the ${}^3T_1(F)$ ground state has much inherent orbital angular momentum, the magnetic moment of truly tetrahedral Ni(II) should be ~ 4.2 B.M. at room temperature [9]. The magnetic moment of a tetrahedral d^8 complex ($e^4 t_2^4$) should have contributions from spin-orbit coupling. In general, orbital contributions are expected in those complexes in which the ground state is triply degenerate (T term) and the values approximating the spin only value are obtained for non-degenerate and doubly degenerate ground states (A and E terms). However, even slight distortions reduce this markedly by splitting the orbital degeneracy. Thus fairly regular tetrahedral complexes have moments of 3.5 to 4.0 B.M. [10].

From both the d orbital splitting and the energy level diagram it is clear that, octahedral Ni(II) complexes have two unpaired electrons. An octahedral Ni(II) complex has the ${}^3A_{2g}$ ground state term that has a considerable mixing with the ${}^3T_{2g}$ excited state. The spin only magnetic moment is therefore modified by the spin-orbit coupling. Thus octahedral Ni(II) complexes have magnetic moments ranging from 2.9 to 3.4 BM.

The compound NiL^1Cl is found to be diamagnetic and so it is a square planar complex. The two Ni(II) complexes $[\text{Ni}(\text{HL}^1)_2(\text{NO}_3)_2] \cdot 2\text{H}_2\text{O}$ and $[\text{Ni}(\text{HL}^2)(\text{L}^2)(\text{NO}_3)]$ have magnetic moment values of 3.2 and 2.91 which is an evidence for the octahedral nature of these complexes.

7.3.3. Infrared spectra

The significant bands obtained in the vibrational spectra of the two ligands HL¹ and HL² and their Ni(II) complexes and their tentative assignments are presented in Table 7.2. Coordination of the azomethine nitrogen has been proposed for the majority of thiosemicarbazone ligands with the evidence for this coordination based on a shifting of the $\nu(\text{C}=\text{N})$ band expected for both the neutral and anionic ligands. This shifting has been reported both to higher [11,12] and to lower energies [13,14]. It appears that both types of shifts can occur due to the differences in the energies of the bands with which $\nu(\text{C}=\text{N})$ is in combination [15]. The $\nu(\text{C}=\text{N})$ band of HL¹ at 1582 cm⁻¹ is found to be shifted to lower energies and appear at 1545 and 1553 cm⁻¹ respectively in compounds **19** and **20** which indicate the coordination *via* the azomethine nitrogen. Two other bands are found at 1649 and 1628 cm⁻¹ in the spectra of compounds **19** and **20** respectively, which are due to the newly formed $\nu(\text{C}=\text{N})$ during the formation of the complex. *via* enolisation. The coordination of azomethine nitrogen to nickel can be confirmed by assigning the $\nu(\text{Ni}-\text{N})$ band at *ca.* 465 cm⁻¹ in the far IR spectra of the complexes [16].

Coordination of pyridine nitrogen to the metal in the complexes is indicated by an increase in energy of the out of plane modes of the pyridine ring. The magnitude of the shift is somewhat higher in compound **21**, and this result is consistent with the previous reports on acetylpyridine thiosemicarbazones [15]. The strong bands observed in the far IR spectra of the Ni(II) complexes at *ca.* 280 cm⁻¹ can be assigned to $\nu(\text{Ni}-\text{N})$ of the pyridine ring [17].

The coordination of the sulfur atom to the metal is indicated by the shifts of the two bands considered to have contributions from $\nu(\text{C}-\text{S})$ to lower energies. The $\nu(\text{C}-\text{S})$ bands of HL¹ at 1370 and 833 cm⁻¹ are found to be shifted to 1338 and 742 cm⁻¹ in NiL¹Cl indicating the coordination of the sulfur atom to nickel(II). In

complex **20**, the $\nu(\text{C}=\text{S})$ band of the ligand is found to be slightly shifted to higher energy compared to their position in the spectrum of the free ligand and the band at 833 cm^{-1} suffers marginal shift to lower energy. This indicates non-coordination by the sulfur atom for the neutral ligands HL^1 . In compound **21**, which contains both neutral and anionic ligands, the bands at 823 and 762 cm^{-1} can be assigned to $\nu(\text{C}-\text{S})$. The coordination of sulfur to Ni(II) in complex **19** can be confirmed by a strong band corresponding to $\nu(\text{Ni}-\text{S})$ at 382 cm^{-1} in its far infrared spectrum.

A strong band observed in the spectrum of NiL^1Cl at 302 cm^{-1} can be assigned to the $\nu(\text{Ni}-\text{Cl})$ band. Compound **20** shows a broad band centered at 3449 cm^{-1} in its spectrum indicating hydrate rather than coordinated water [18]. Strong bands at 324 and 322 cm^{-1} in the far IR spectra of compounds **20** and **21** can be assigned to $\nu(\text{Ni}-\text{O})$ for the nitrate ligands [19]. This is in support of the results from conductivity measurements, that the nitrate ion is coordinated to the nickel ion in compounds **20** and **21**.

Table 7.1. Analytical data

Compound	Empirical formula	Color	Found (Calculated) %			Λ_M^* (in DMF)	μ (B.M.)
			C	H	N		
[Ni(L ¹)Cl] (19)	C ₁₉ H ₂₁ N ₄ SClNi	Blue	52.94 (52.88)	5.15 (5.10)	12.72 (12.90)	1.8	Diamagnetic
[Ni(HL ¹) ₂ (NO ₃) ₂].2H ₂ O (20)	C ₃₈ H ₄₈ N ₁₀ SO ₈ Ni	Brown	51.27 (50.96)	5.39 (5.36)	15.50 (15.64)	5.21	3.21
[Ni(HL ²)(L ²)(NO ₃)] (21)	C ₃₈ H ₃₈ N ₁₀ SO ₆ Ni	Brown	57.92 (58.11)	4.08 (3.95)	16.36 (16.07)	4.90	2.94

*Molar conductivity of 10⁻³M solutions, in ohm⁻¹cm² mol⁻²Table 7.2. IR spectral assignments (cm⁻¹) of HL¹ and HL² and their Ni (II) complexes

Compound	ν (C=N)	ν (C-S)	ν (py)	ν (Ni-N)	ν (Ni-N py)	ν (Ni-S)	ν (Ni-X)
HL ¹	1582 m	1370w,833m	607w	--	--	--	--
NiL ¹ Cl (19)	1545s 1649s	1338s,742m	647m	464s	261s	382s	302s
[Ni(HL ¹) ₂ (NO ₃) ₂].2H ₂ O (20)	1553s 1628s	1384s,814w	635m	465s	281s	--	324s
HL ²	1591s	1369s,835m	622m	--	--	--	--
[Ni(HL ²)(L ²)(NO ₃)] (21)	1527s 1596s	1307s,823s,	692m	469s	281s	--	322s

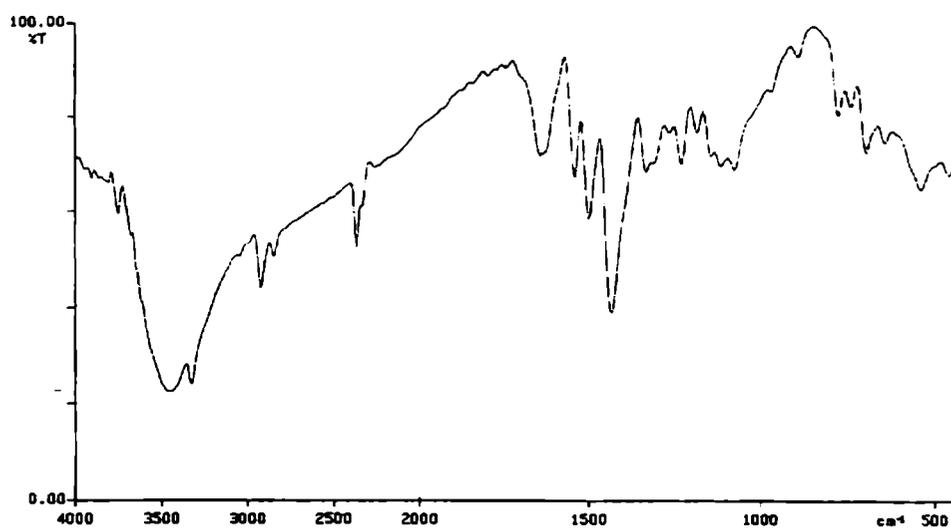


Fig.7.1. IR spectrum of compound 19

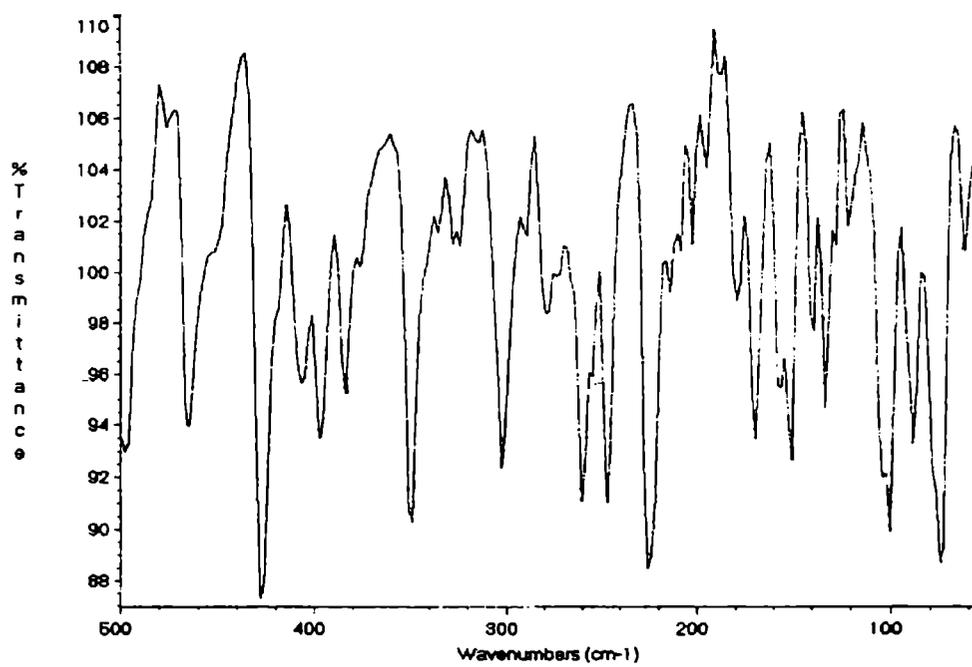


Fig.7.2. Far IR spectrum of compound 19

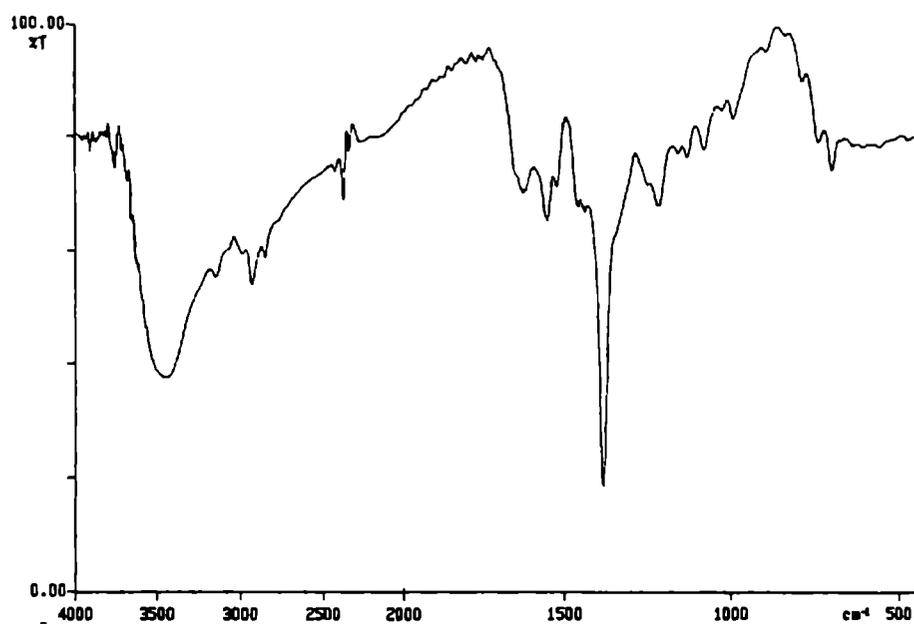


Fig 7.3. IR spectrum of compound 20

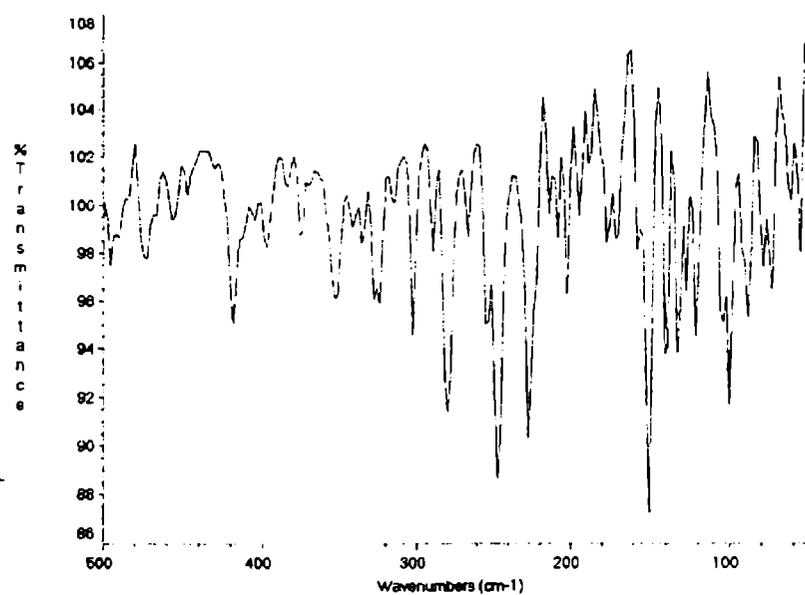


Fig.7.4. Far IR spectrum of compound 20

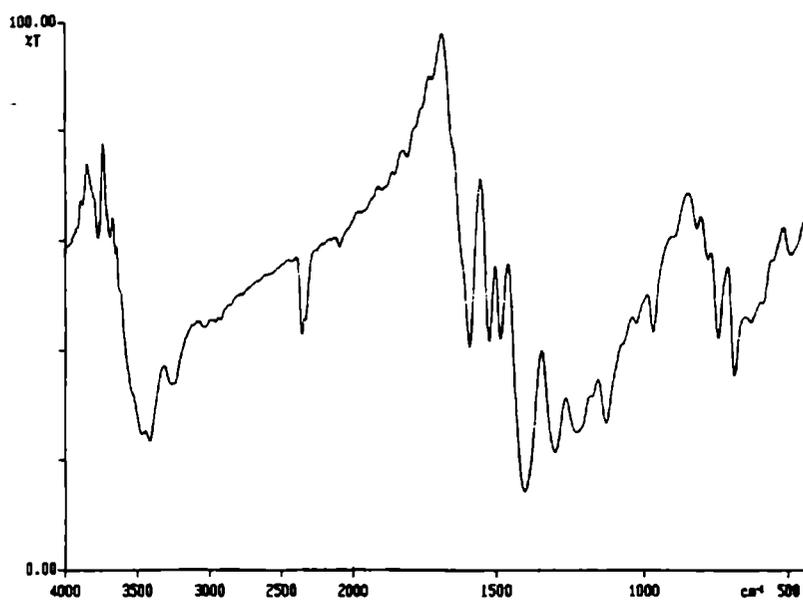


Fig. 7.5. IR spectrum of compound 21

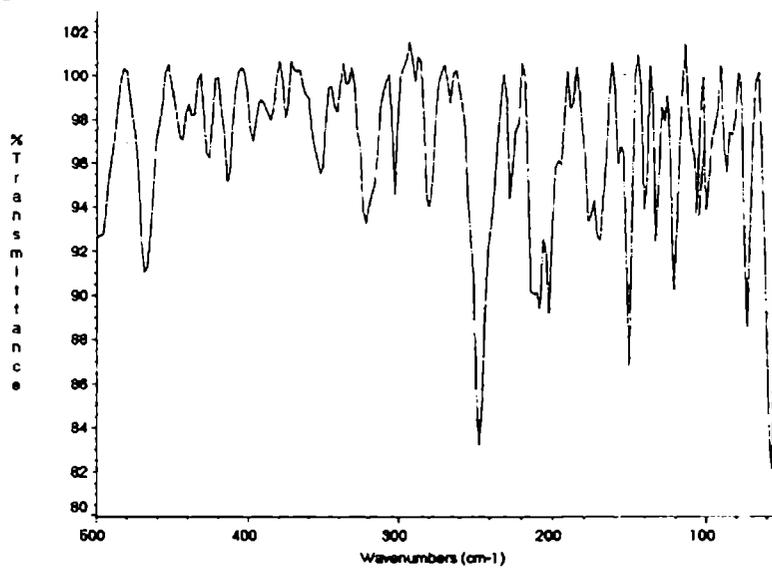


Fig.7.6. Far IR spectrum of compound 21

7.3.4. Electronic spectra

The significant electronic absorption bands recorded in the solid state and in DMF solution are presented in Table 7.3. The electronic spectra of the thiosemicarbazones HL¹ and HL² have absorption bands at *ca.* 340nm due to the $n \rightarrow \pi^*$ transition of the thiosemicarbazone moiety and at *ca.* 259 nm due to $\pi \rightarrow \pi^*$ transitions. These bands suffer marginal shifts on complexation. In the spectra of the three Ni(II) complexes, a high intense broad band is present at *ca.* 420 nm which may be due to the ligand \rightarrow metal charge transfer band. This high intensity charge transfer band may sometimes mask the $d-d$ band [20].

From the magnetic and infrared spectral studies, NiL¹Cl is considered as a square planar complex. The spectra of NiL¹Cl, exhibit a strong broad band at 417 nm and shoulders at 593 and 662 nm. Assuming D_{4h} symmetry for this solid.

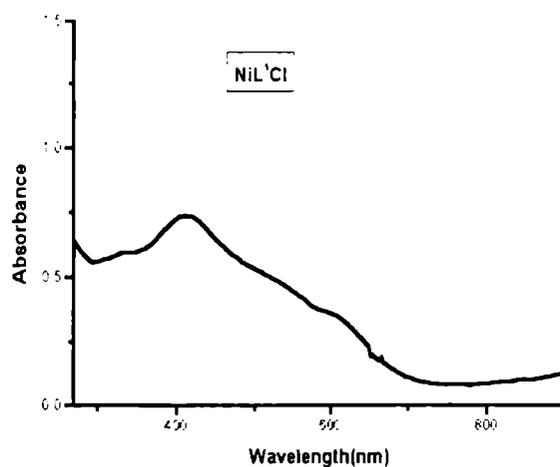


Fig. 7.7. Electronic spectrum of compound 19

Table 7.3 Electronic spectral data (nm) of Nickel (II) Complexes

Compound	State	Intraligand	C.T.	d→d
[NiL ¹ Cl] (19)	Solid DMF	332sh, 275sh 330 (3.81), 274 (3.85)	417 416 (4.25)	593sh, 662sh 596 (1.68), 656 (1.71)
Ni(HL ¹) ₂ (NO ₃) ₂ ·2H ₂ O (20)	Solid DMF	327sh, 272 330 (4.35), 271sh	439 430 (4.72)	513sh, 656sh, 824sh 518 (1.85), 674, 805 (1.5)
[Ni(HL ²)(L ²)(NO ₃)] (21)	Solid DMF	315sh, 292 302 (4.18)	413 415 (4.32)	537sh, 660sh, 762sh 521 (2.01), 640 (1.9)

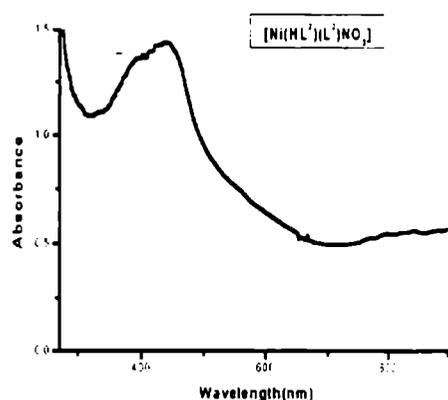


Fig.7.8. Electronic spectrum of compound 21

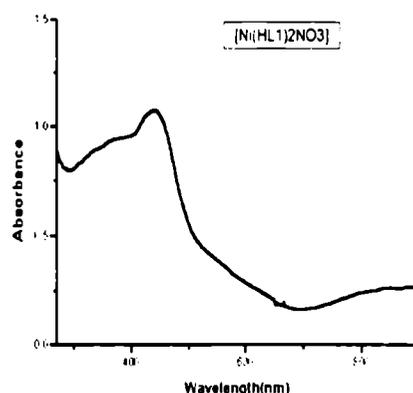


Fig.7.9. Electronic spectrum of compound 20

the three bands can be assigned to ${}^1A_{1g} \rightarrow {}^1E_g$, ${}^1A_{1g} \rightarrow {}^1A_{2g}$ and ${}^1A_{1g} \rightarrow {}^1B_{2g}$ transitions respectively [21]. The absence of bands above 1000 nm confirms its square planar nature. In the spectrum of compound 19, a $d-d$ band appearing as a weak shoulder centered around 500 nm is typical of square planar monoligated Ni(II) complexes [21].

For a d^8 configuration in octahedral field, three spin-allowed transitions are expected, because of the splitting of the free-ion ground 3F term and the presence of the 3P term. The three transitions are ${}^3A_{2g}(F) \rightarrow {}^3T_{2g}(F)$, ${}^3A_{2g}(F) \rightarrow {}^3T_{1g}(F)$ and ${}^3A_{2g}(F) \rightarrow {}^3T_{1g}(P)$. In the spectra of the two complexes 20 and 21, the bands appearing at *ca.* 526, 657 and 800 nm can be assigned to ${}^3A_{2g}(F) \rightarrow {}^3T_{1g}(P)$, ${}^3A_{2g}(F) \rightarrow {}^3T_{1g}(F)$ and ${}^3A_{2g}(F) \rightarrow {}^3T_{2g}(F)$ respectively [22].

7.3.5. 1H NMR spectrum of $[NiL^1Cl]$

The signal observed in the spectrum of HL^1 at $\delta = 13.48$ (s, 1H) corresponding to the imino proton is found to be absent in the spectrum of $[NiL^1Cl]$, which indicates the deprotonation of the ligand on complexation. In the

spectrum of the complex a signal at 7.70 (s, 1H) corresponds to that of the ^4NH proton. The doublet at 8.60 corresponding to the proton at position 6 (α to pyridyl nitrogen) of the pyridine ring is found to be slightly shifted in the complex confirming the coordination *via* the pyridyl nitrogen. The signals corresponding to the other three protons of the pyridine are also found to be slightly shifted upfield, having δ =7.45, 7.34 and 7.28 respectively. The signals corresponding to the protons of the cyclohexane ring are found to be unshifted in the spectrum of $[\text{NiL}^1\text{Cl}]$. (The position of atoms are based on Fig.2.1)

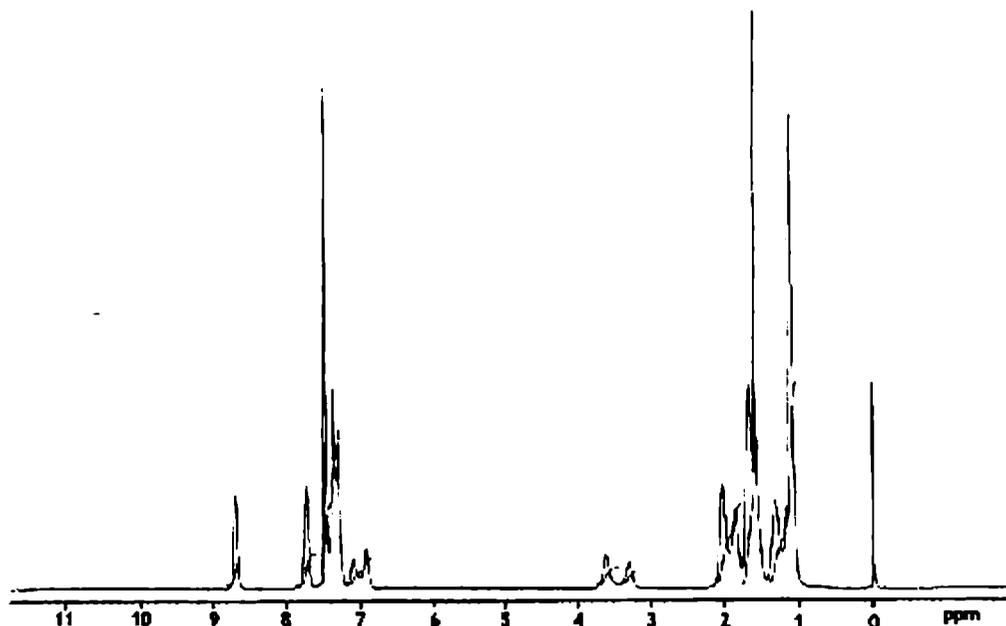


Fig. 7.10. ^1H NMR spectrum of compound 19

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