

## Isoniazid의 hydrazone을 갖는 몇 가지 니켈(II) 착물들의 합성, 자기적 및 전기적 성질, 열적 특성과 항균성에 대한 연구

Surendra Prasad\*<sup>‡</sup> and Ram K. Agarwal\*<sup>‡</sup>

<sup>‡</sup>Division of Chemical Sciences, Faculty of Science, Technology and Environment,  
The University of the South Pacific, Suva, Fiji

<sup>‡</sup>Department of Chemistry, Lajpat Rai Postgraduate College, Sahibabad, Ghaziabad 201005, India

\*E-mail: prasad\_su@usp.ac.fj (S. Prasad), ram\_agarwal54@yahoo.com (Ram K. Agarwal)

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## Synthesis, Magneto-Spectral, Electrochemical, Thermal Characterization and Antimicrobial Investigations of Some Nickel(II) Complexes of Hydrazones of Isoniazid

Surendra Prasad\*<sup>‡</sup> and Ram K. Agarwal\*<sup>‡</sup>

<sup>‡</sup>Division of Chemical Sciences, Faculty of Science, Technology and Environment,  
The University of the South Pacific, Suva, Fiji

<sup>‡</sup>Department of Chemistry, Lajpat Rai Postgraduate College, Sahibabad, Ghaziabad 201005, India

\*E-mail: prasad\_su@usp.ac.fj (S. Prasad), ram\_agarwal54@yahoo.com (Ram K. Agarwal)

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**요약.** 본 연구는 Isoniazid의 hydrazone으로부터 유도된 새로운 리간드를 갖는 몇 가지 새로운 니켈(II) 착물의 합성에 대해 보고한다. 착물의 조성은  $[\text{Ni}(\text{L})_2\text{X}_2]$  또는  $[\text{Ni}(\text{L})_3(\text{ClO}_4)_2]$  {L = N-isonicotinamido-furfuralaldimine (INH-FFL), N-isonicotinamido-3',4',5'-trimethoxybenzaldimine (INH-TMB) 또는 N-isonicotinamido-cinnamalidene (INH-CIN) 및 X = Cl<sup>-</sup>, NO<sub>3</sub><sup>-</sup>, NCS<sup>-</sup> 또는 CH<sub>3</sub>COO<sup>-</sup>} 이다. 리간드 hydrazone 은 카보닐 산소와 아조메틴 질소를 통해서 중성의 두 자리 (N 및 O 주개) 리간드로 작용한다. 육면체 구조를 갖는 새로운 착물들은 원소분석, 분자질량분석, 자화율, 열분석과 적외선 및 전기적 스펙트럼을 이용한 전기화학 및 분광학적 연구를 통해 규명하였다. 니트로벤젠(PhNO<sub>2</sub>)에서의 전기 전도성 측정에 의하면  $[\text{Ni}(\text{L})_2\text{X}_2]$  및  $[\text{Ni}(\text{L})_3(\text{ClO}_4)_2]$  착물들은 각각 비전해질 및 1:2 전해질임을 알았다. 착물의 기하구조를 알기 위한 열적 특성도 역시 연구되었다. 니켈(II) 착물 및 약간의 표준 약품의 항균성 및 항진균성 또한 연구되었고, 이를 통해 착물이 적당한 항균성 활동을 하는 것을 알 수 있었다.

**주제어:** 니켈(II). 착물. Hydrazones. 생물학적 거동

**ABSTRACT.** The synthesis of a novel series of nickel(II) complexes with new ligands derived from hydrazones of isoniazid have been reported in present work. The complexes have general compositions  $[\text{Ni}(\text{L})_2\text{X}_2]$  or  $[\text{Ni}(\text{L})_3(\text{ClO}_4)_2]$  {L = N-isonicotinamido-furfuralaldimine (INH-FFL), N-isonicotinamido-3',4',5'-trimethoxybenzaldimine (INH-TMB) or N-isonicotinamido-cinnamalidene (INH-CIN) and X = Cl<sup>-</sup>, NO<sub>3</sub><sup>-</sup>, NCS<sup>-</sup> or CH<sub>3</sub>COO<sup>-</sup>}. The ligands hydrazones behave as neutral bidentates (N and O donor) through the carbonyl oxygen and azomethine nitrogen. The new complexes with octahedral geometry have been characterized by elemental analysis, molecular weight determinations, magnetic susceptibility/moment, thermogravimetric, electrochemical and spectroscopic studies viz. infrared and electronic spectra. On the basis of conductivity measurements in nitrobenzene (PhNO<sub>2</sub>) solution the  $[\text{Ni}(\text{L})_2\text{X}_2]$  and  $[\text{Ni}(\text{L})_3(\text{ClO}_4)_2]$  complexes have been found to be non-electrolytes

and 1:2 electrolytes, respectively. Thermal properties have also been investigated, which support the geometry of the complexes. Antibacterial and antifungal properties of nickel(II) complexes and few standard drugs have also been examined and it has been observed that the complexes have moderate antibacterial activities.

**Keywords:** Nickel(II). Complexes. Hydrazones. Biological activity

## INTRODUCTION

The multifarious role of the transition metal complexes in biochemistry have been playing potentially for the development of new chemistry with metal ligand system. This has stimulated enormous interest in synthesis of transition metal complexes with Schiff bases of nitrogen and oxygen donor due to the wide range of pharmacological activities of such compounds.<sup>1</sup> Schiff bases derived from condensation of primary amines and carbonyl group of an aldehyde or ketone by elimination of water molecule, are known to have a nitrogen atom with a lone pair of electrons in its functional group ( $>C=N-$ ), and used as ligands with a variety of metal ions. Many of these complexes may serve as models for biologically important species. In addition, they present a vast variety of biological activities ranging from anti-tumour, fungicide, bactericide, anti-inflammatory and anti-viral activities.<sup>2</sup> We have recently published some lanthanide(III) complexes of semicarbazones<sup>3</sup> and oxovanadium(IV),<sup>4,5</sup> platinum(II),<sup>6</sup> cobalt(II) and nickel(II)<sup>2,7</sup> complexes of thiosemicarbazones derived from 4-aminoantipyrine. The antibacterial and antifungal properties of the thiosemicarbazone ligands and their cobalt(II),<sup>2,7</sup> nickel(II)<sup>7</sup> and oxovanadium(IV)<sup>5</sup> complexes have also been examined.

The remarkable biological activity of acid hydrazides  $R-CO-NH-NH_2$ , their aryl hydrazones,  $R-CO-NH-N=CH-R'$  and their mode of chelation with transition metal ions present in the living systems had been of significant interest in past.<sup>8,9</sup> It is believed that the  $-CO-NH-N=C<$  moiety of hydrazone imparts biological characteristics to this class of compounds. The coordination compounds of arylhydrazones have been reported to act as enzyme inhibitors and are useful due to their pharmacological applications.<sup>10-12</sup> Isoniazid is a drug of proven therapeutical importance and is used against a wide

spectrum bacterial ailments *viz.* tuberculosis. Hydrazones derived from the condensation of isoniazid with pyridine aldehydes have been found to show better antitubercular activity than isoniazid.<sup>13</sup> Thus in the past we and other researchers have reported transition metal coordination compounds of hydrazones of isoniazid.<sup>14-16</sup> In continuation of our most recent work on hydrazones of isoniazid complexes of cobalt(II),<sup>17-18</sup> the present work describes the synthesis, magneto-spectral, electrochemical, thermal and biological studies of a novel series of fifteen Ni(II) complexes of N-isonicotinamido-furfuralaldimine (INH-FFL) (Fig. 1), N-isonicotinamido-3',4',5'-trimethoxybenzalimine (INH-TMB) (Fig. 2) and N-isonicotinamido-cinnamalidene (INH-CIN) (Fig. 3).

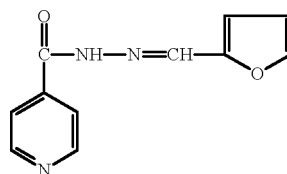


Fig. 1. N-Isonicotinamido-furfuralaldimine (INH-FFL).

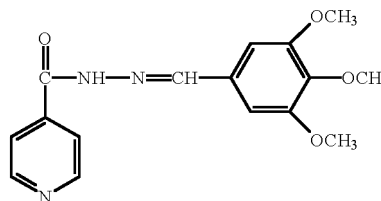


Fig. 2. N-Isonicotinamido-3',4',5'-trimethoxybenzalimine (INH-TMB).

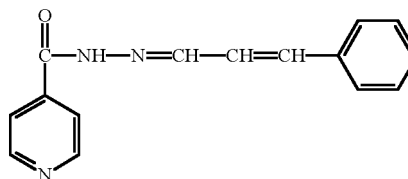


Fig. 3. N-Isonicotinamido-cinnamalidene (INH-CIN).

## EXPERIMENTAL SECTION

### Materials

All the nickel(II) salts, *i.e.*,  $\text{NiX}_2 \cdot n\text{H}_2\text{O}$  ( $\text{X} = \text{Cl}^-, \text{NO}_3^-$  or  $\text{CH}_3\text{COO}^-$ ) were obtained from BDH and were used as received.  $\text{Ni}(\text{NCS})_2$  was prepared by mixing  $\text{NiCl}_2$  (in ethanol) and ethanolic solution of potassium thiocyanate in 1:2 molar ratio. The precipitated KCl was filtered off and the filtrate having  $\text{Ni}(\text{NCS})_2$  was used immediately for complex formation.<sup>7</sup>  $\text{Ni}(\text{ClO}_4)_2$  was prepared by the addition of an ethanolic solution of sodium perchlorate into  $\text{NiCl}_2$  solution. White precipitate of NaCl was filtered off and the filtrate containing  $\text{Ni}(\text{ClO}_4)_2$  was used as such for complex formation.<sup>7</sup>

### Synthesis of schiffs bases; INH-FFL, INH-TMB and INH-CIN

All the three hydrazones of isoniazid *viz.* INH-FFL, INH-TMB and INH-CIN were synthesized by the following general method reported elsewhere.<sup>16</sup> Isonicotinic acid hydrazide (INH) (0.01 mol) was dissolved in 10 mL of 95% ethanol. To this solution respective aromatic aldehyde, *i.e.*, furfural, 3',4',5'-trimethoxybenzaldehyde or cinnamaldehyde (0.01 mmol) was added in 95% ethanol (10 mL). The mixture was refluxed on a water bath for ~ 2 h. The partial removal of solvent on a water bath followed by cooling produced crystalline product, which was suction filtered, washed with cold ethanol and dried over  $\text{P}_2\text{O}_{10}$  under vacuum (yld. 80%).

### Synthesis of nickel(II) complexes; $[\text{Ni}(\text{L})_2\text{X}_2]$ and $[\text{Ni}(\text{L})_3](\text{ClO}_4)_2$

A general method has been used for the synthesis of the nickel(II) complexes.<sup>7</sup> A hot ethanolic solution of the corresponding nickel(II) salt was mixed with a hot ethanolic solution of the corresponding hydrazone (in molar ratio 1:2 and 1:3 for  $[\text{Ni}(\text{L})_2\text{X}_2]$  and  $[\text{Ni}(\text{L})_3](\text{ClO}_4)_2$  complexes, respectively). The reaction mixture was refluxed on a water bath for ~ 2 h. On cooling at room temperature, the coloured complexes precipitated out in each case. They were filtered, recrystallized, washed with ethanol and dried over  $\text{P}_2\text{O}_{10}$  under vacuum.

### Instrumentation, analysis and physico-chemical measurements

Nickel contents of the complexes were determined complexometrically with EDTA using erichrome black-T as an indicator after decomposing the complexes with conc.  $\text{H}_2\text{SO}_4$  and  $\text{H}_2\text{O}_2$ .<sup>7</sup> The chlorine was estimated by Volhard's method.<sup>19</sup> The thiocyanate was estimated by titrating slightly acidic solution of the complex with standard silver nitrate solution. The perchlorate was estimated by the method reported in our previous work.<sup>7</sup> The percentage of nitrogen was determined by Kjeldahl method. The molecular weight of the complexes was determined cryoscopically in freezing nitrobenzene using a Beckmann thermometer of accuracy of  $\pm 0.01$  °C.

The conductivity measurements were performed using a Toshniwal conductivity bridge with a dip type cell operated at 220 volts. All the measurements were done at room temperature in nitrobenzene. The magnetic measurements on powder form of the complexes were carried out at room temperature on Evans magnetic balance using anhydrous copper sulfate for calibration. The infrared spectra of the complexes were recorded on a Perkin Elmer FT-IR infrared spectrophotometer model 521 in CsI in the range of  $4000 - 200 \text{ cm}^{-1}$ . Diffused reflectance spectra of the solid complexes were recorded on a Beckmann DK-2A spectrophotometer at CDRI Lucknow, India. Thermogravimetric analyses of the complexes were performed on Perkin Elmer Pyris Diamond in static air with unlined small platinum boat sample holder at IIT Roorkee, India. The heating rate was  $6 \text{ }^\circ\text{C min}^{-1}$ . The antibacterial and antifungal activities of the representative nickel(II) complexes and standard drugs (ampicillin and tetracycline) were screened by following the methods reported elsewhere.<sup>2,7</sup>

## RESULTS AND DISCUSSION

The reaction of nickel(II) salts with INH-FFL, INH-TMB and INH-CIN, resulted in the formation of  $[\text{NiX}_2(\text{L})_n]$  ( $\text{X} = \text{Cl}^-, \text{NO}_3^-, \text{NCS}^-$  or  $\text{CH}_3\text{COO}^-$ ,  $n = 2$  and  $\text{L} = \text{INH-FFL}, \text{INH-TMB}$  or  $\text{INH-CIN}$ ) and  $[\text{Ni}(\text{L})_n]\text{X}_2$  ( $\text{X} = \text{ClO}_4^-$ ,  $n = 3$ , and  $\text{L} = \text{INH-FFL}$ ,

INH-TMB or INH-CIN. The analytical data of present complexes are presented in *Table 1*. The complexes were quite stable and could be stored for several weeks without any appreciable change. The complexes did not have sharp melting points, but decomposed on heating beyond 250 °C. The complexes were generally soluble in common organic solvents.

The molar conductance of the nickel(II) complexes in nitrobenzene are presented in *Table 1*. The chloro, nitrate, isothiocyanato and acetato com-

plexes of the type  $[\text{NiX}_2(\text{L})_n]$  were essentially non-electrolytes in nitrobenzene, while the perchlorato complexes of the type  $[\text{Ni}(\text{L})_n]\text{X}_2$  dissociated in nitrobenzene and behaved as 1:2 electrolytes. The molecular weights determined cryoscopically in nitrobenzene are also given in *Table 1*. The results are in good agreement with conductance data.

#### Magnetic susceptibility

Nickel(II) has the electronic configuration  $3d^8$  and should exhibit magnetic moment higher than

*Table 1.* Analytical, conductivity, molecular weight and magnetic moment data of nickel(II) complexes of hydrazones of isoniazid.

Complex	Yield (%)	Analysis: Found (calcd.) (%)					m.wt. Found (calcd.)	$\Omega_m$ (ohm <sup>-1</sup> cm <sup>2</sup> mole <sup>-1</sup> )	$\mu_{\text{eff}}$ (BM)
		Ni	C	H	N	Anion			
$[\text{Ni}(\text{INH-FFL})_2\text{Cl}_2]$	72	10.47 (10.53)	47.00 (47.14)	3.18 (3.21)	14.90 (15.00)	12.55 (12.67)	555 (560)	3.1	3.1
$[\text{Ni}(\text{INH-FFL})_2(\text{NO}_3)_2]$	75	9.57 (9.62)	42.98 (43.06)	2.89 (2.93)	18.19 (18.27)	- -	608 (613)	2.6	2.9
$[\text{Ni}(\text{INH-FFL})_2(\text{NCS})_2]$	68	9.69 (9.75)	47.48 (47.60)	2.93 (2.97)	18.45 (18.51)	19.06 (19.17)	600 (605)	3.3	3.2
$[\text{Ni}(\text{INH-FFL})_2(\text{OAc})_2]$	70	9.66 (9.71)	51.27 (51.40)	2.93 (2.96)	13.76 (13.83)	- -	602 (607)	2.7	2.6
$[\text{Ni}(\text{INH-FFL})_3](\text{ClO}_4)_2$	65	6.48 (6.53)	43.73 (43.85)	2.96 (2.99)	13.89 (13.95)	21.89 (22.03)	899 (903)	51.8	3.2
$[\text{NiCl}_2(\text{INH-TMB})_2]$	70	7.70 (7.76)	50.38 (50.52)	4.43 (4.47)	10.98 (11.05)	9.25 (9.34)	756 (760)	2.7	3.1
$[\text{Ni}(\text{INH-TMB})_2(\text{NO}_3)_2]$	70	7.19 (7.25)	47.11 (47.23)	4.14 (4.18)	13.68 (13.77)	- -	808 (813)	2.9	2.7
$[\text{Ni}(\text{INH-TMB})_2(\text{NCS})_2]$	65	7.26 (7.32)	50.53 (50.68)	4.15 (4.22)	13.79 (13.91)	14.30 (14.40)	800 (805)	2.3	3.0
$[\text{Ni}(\text{INH-TMB})_2(\text{OAc})_2]$	70	7.25 (7.31)	53.40 (53.53)	4.89 (4.95)	10.30 (10.40)	- -	803 (807)	3.1	2.9
$[\text{Ni}(\text{INH-TMB})_3](\text{ClO}_4)_2$	65	4.84 (4.90)	47.69 (47.88)	4.19 (4.23)	10.37 (10.47)	16.40 (16.54)	400 (403)	52.3	2.8
$[\text{Ni}(\text{INH-CIN})_2\text{Cl}_2]$	70	9.29 (9.33)	56.79 (56.96)	4.06 (4.11)	13.19 (13.29)	11.10 (11.23)	628 (632)	2.7	3.2
$[\text{Ni}(\text{INH-CIN})_2(\text{NO}_3)_2]$	68	8.56 (8.61)	52.43 (52.55)	3.75 (3.79)	16.23 (16.35)	- -	680 (685)	2.2	2.8
$[\text{Ni}(\text{INH-CIN})_2(\text{NCS})_2]$	65	8.65 (8.71)	56.57 (56.72)	3.80 (3.84)	16.41 (16.54)	17.00 (17.13)	673 (677)	2.8	3.1
$[\text{Ni}(\text{INH-CIN})_2(\text{OAc})_2]$	70	8.54 (8.60)	59.93 (60.08)	4.67 (4.71)	12.27 (12.37)	- -	676 (679)	2.9	3.1
$[\text{Ni}(\text{INH-CIN})_3](\text{ClO}_4)_2$	65	5.78 (5.83)	53.27 (53.41)	3.81 (3.85)	12.36 (12.46)	19.52 (19.68)	340 (342)	51.9	2.8

OAc:  $\text{CH}_3\text{COO}^-$

expected for two unpaired electrons in octahedral (2.8 - 3.2 BM) and tetrahedral (3.4 - 4.2 BM) complexes, whereas its square planar complexes would be diamagnetic. This increase the magnetic moment value from that of the spin only value has been

considered it to be due to some 'mixing in' of upper state *via* spin-orbit coupling. The paramagnetism observed for the present series of complexes ranges from 2.6 - 3.2 BM (Table 1) which is consistent with the octahedral stereochemistry of the complexes.<sup>7</sup>

Table 2. Key infrared bands ( $\text{cm}^{-1}$ ) of nickel(II) complexes of hydrazones of isoniazid.

Compounds	Assignments asym & sym	Amide-I	$\nu(\text{C}=\text{N})$ (azomethine)	Amide-II + $\delta(\text{NH})$	$\nu(\text{Ni-N}) /$ $\nu(\text{Ni-O})$
INH-FFL	3300 m 3220 m	1705 vs 1632 s	1585 s	1540 m 1532 m	-
$[\text{Ni}(\text{INH-FFL})_2\text{Cl}_2]$	3305 m 3200 m	1650 m 1620 m 1600 s	1545 m, br	1530 m 1505 w	480 m 390 m
$[\text{Ni}(\text{INH-FFL})_2(\text{NO}_3)_2]$	3305 m 3202 m	1625 s 1600 s	1535 m	1530 m 1505 w	485 m 392 w
$[\text{Ni}(\text{INH-FFL})_2(\text{NCS})_2]$	3300 m 3205 m	1635 m 1615 m	1540 m	1532 m 1505 w	492 m 400 m
$[\text{Ni}(\text{INH-FFL})_2(\text{CH}_3\text{COO})_2]$	3305 m 3200 m	1630 m 1610 m	1542 m	1530 m 1510 w	485 m 398 w
$[\text{Ni}(\text{INH-FFL})_3(\text{ClO}_4)_2]$	3300 m 3205 m	1650 m 1612 m	1535 m	1530 m 1510 m	480 m 390 w
INH-TMB	3300 m 3210 w	1655 s	1588 vs	1540 sh 1520 s	-
$[\text{Ni}(\text{INH-TMB})_2\text{Cl}_2]$	3305 m 3200 w	1670 vs 1605 vs	1525 m	1510 s	487 m 402 w
$[\text{Ni}(\text{INH-TMB})_2(\text{NO}_3)_2]$	3302 m 3205 w	1665 s 1600 s	1530 s	1525 m 1510 m	490 m 410 w
$[\text{Ni}(\text{INH-TMB})_2(\text{NCS})_2]$	3300 m 3200 w	1670 s 1600 s	1555 s	1510 sh 1500 s	495 m 405 w
$[\text{Ni}(\text{INH-TMB})_2(\text{CH}_3\text{COO})_2]$	3300 m 3205 w	1660 s 1600 s	1525 m	1520 s 1510 s	490 m 408 w
$[\text{Ni}(\text{INH-TMB})_3(\text{ClO}_4)_2]$	3300 m 3200 w	1660 s 1605 m	1525 m	1530 s	485 m 410 w
INH-CIN	3290 m 3200 sh 3185 m	1698 s 1640 s	1590 vs	1570 sh 1540 m	-
$[\text{Ni}(\text{INH-CIN})_2\text{Cl}_2]$	3292 m 3200 w 3190 m	1632 s 1620 m	1550 s 1530 m	1520 m 1505 w	490 m 405 w
$[\text{Ni}(\text{INH-CIN})_2(\text{NO}_3)_2]$	3290 m 3202 w 3192 m	1630 s 1615 m	1552 s 1525 m	1522 m 1505 w	495 m 410 w
$[\text{Ni}(\text{INH-CIN})_2(\text{NCS})_2]$	3292 m 3200 sh 3190 m	1628 m 1615 s	1548 s 1528 m	1520 m 1515 w	492 m 398 w
$[\text{Ni}(\text{INH-CIN})_2(\text{CH}_3\text{COO})_2]$	3290 m 3200 sh 3192 m	1627 m 1618 s	1545 s 1540 w	1527 m 1515 sh	487 m 399 w
$[\text{Ni}(\text{INH-CIN})_3(\text{ClO}_4)_2]$	3292 m 3200 sh 3192 m	1632 s 1618 sh	1550 m 1530 m	1528 m 1520 sh	485 m 392 w

### Infrared spectra

The infrared data of the ligands, INH-FFL, INH-TMB and INH-CIN, and their nickel(II) complexes are presented in *Table 2*. The infrared frequencies in the present ligands associated with amide group (carbonyl-oxygen), azomethine-nitrogen (C=N) and heterocyclic nitrogen are expected to be influenced on complex formation with metal ion have been discussed. Generally, all amides show two absorption bands: (i) the carbonyl absorption band near  $1640\text{ cm}^{-1}$  known as amide-I band and (ii) strong band in the  $1600 - 1500\text{ cm}^{-1}$  region, known as amide-II band. The amide-I band in INH-derivatives, however, appeared at  $1655\text{ cm}^{-1}$ .<sup>20,21</sup> In the infrared spectra of the complexes, a considerable negative shift in  $\nu(\text{C}=\text{O})$  was observed indicating a decrease in the stretching force constant of (C=O) as a consequence of coordination through the carbonyl oxygen atom of the free base. The amide-II band appeared at the normal position in the NH-deformation rather than C-N link. In all these ligands the absorptions at  $1540 - 1530\text{ cm}^{-1}$  have been assigned to amide-II absorptions. The NH stretching absorption in free ligands occurs at  $\sim 3300$  and  $3220\text{ cm}^{-1}$  which remain unaffected after complexation. This precludes the possibility of coordination through imine-nitrogen atom. Another important band occurs in  $1590 - 1585\text{ cm}^{-1}$  range is attributed to  $\nu(\text{C}=\text{N})$  (azomethine) mode.<sup>22,23</sup> In spectra of all the complexes this band is shifted to lower wave number and appears in  $1550 - 1525\text{ cm}^{-1}$  region, respectively indicating the involvement of N-atom of the azomethine group in coordination.<sup>22,24</sup> The strong bands observed at  $1575 - 1520\text{ cm}^{-1}$  and  $1080 - 1000\text{ cm}^{-1}$  are tentatively assigned<sup>25</sup> to asymmetric and symmetric  $\nu(\text{C}=\text{C}) + \nu(\text{C}=\text{N})$  of pyridine ring. The pyridine ring breathings and deformations remained practically unchanged in frequency and band intensities revealing non-involvement of pyridine-nitrogen and metal bond. The overall infrared spectral evidence suggests that the present ligands act as bidentate ligand and coordinate through amide-oxygen and azomethine-nitrogen atoms forming a five membered chelate ring. In far infrared spectral region, the bands in these ligands are practically unchanged

in these complexes. Some new bonds with medium to weak intensities appeared in the regions  $450 - 380\text{ cm}^{-1}$  in the complexes under study, which are tentatively assigned to  $\nu(\text{Ni}-\text{N})/\nu(\text{Ni}-\text{O})$  modes.<sup>14-16,26</sup>

### Anions

In all the perchlorato complexes, the presence of the  $\nu_3(1100 - 1090\text{ cm}^{-1})$  and  $\nu_4(625 - 620\text{ cm}^{-1})$  bands indicates that the  $T_d$  symmetry of  $\text{ClO}_4^-$  is maintained in these complexes. This observation suggested the presence of  $\text{ClO}_4^-$  outside the coordination sphere in perchlorato complexes.<sup>27</sup> The three fundamental absorption in  $[\text{Ni}(\text{NCS})_2(\text{L})_2]$  (L = INH-FFL, INH-TMB or INH-CIN) complexes i.e. C-N stretching ( $\nu_1$ ), C-S stretching ( $\nu_3$ ) and N-C-S bending ( $\nu_2$ ) were identified at  $2040 - 2035$ ,  $845 - 830$  and  $470 - 465\text{ cm}^{-1}$  region, respectively. These frequencies are associated with the terminal N-bonded isothiocyanate ions.<sup>7,28</sup>

In nitrate complexes, the infrared spectral data indicate the occurrence of two strong absorption bands in the regions  $1555 - 1500\text{ cm}^{-1}$  and  $1310 - 1295\text{ cm}^{-1}$  which are attributed to  $\nu_4$  and  $\nu_1$  modes of vibrations of the covalently bonded nitrate groups, respectively. This suggests that nitrate groups are present inside the coordination sphere.<sup>29</sup> Distinction between monodentate and bidentate nitrate is usually difficult. However, by applying Lever's separation method,<sup>30</sup> a separation of  $15 - 25\text{ cm}^{-1}$  in the combination bands ( $\nu_1 + \nu_4$ ) in the  $1800 - 1700\text{ cm}^{-1}$  region conclude the monodentate nitrate coordination. Other bands appeared at  $\sim 1040$  ( $\nu_2$ ),  $810$  ( $\nu_6$ ) and  $7335\text{ cm}^{-1}$  ( $\nu_3/\nu_5$ ) due to nitrate groups.

The  $\nu_{\text{asym}}(\text{COO}^-)$  of free acetate ions are at  $\sim 1560\text{ cm}^{-1}$  and  $1416\text{ cm}^{-1}$  respectively. In the unidentate complex,  $\nu(\text{C}=\text{O})$  is higher than  $\nu_{\text{asym}}(\text{COO}^-)$  and  $\nu(\text{C}-\text{O})$  is lower than  $\nu_{\text{asym}}(\text{COO}^-)$ . As a result the separation between the two  $\nu(\text{CO})$  is much larger in unidentate complexes than free ion. The opposite trend is observed in the bidentate complexes, the separation between the  $\nu(\text{CO})$  is smaller than that of free ion in this case. In the bridging complexes, however, two  $\nu(\text{CO})$  are close to the free ion values. The present complexes show infrared absorption frequency bands corresponding to  $\nu_{\text{asym}}(\text{COO}^-)$  and

$\nu_{\text{sym}}(\text{COO}^-)$  at  $\sim 1610$  and  $1370 \text{ cm}^{-1}$  respectively. These observations indicate that both the acetate groups in present complexes are unidentate.<sup>7,31</sup>

### Electronic spectra

Six coordinated nickel(II) complexes exhibit a spectrum involving three spin-allowed transitions to  ${}^3T_{2g}(\text{F})$  ( $\nu_1$ ),  ${}^3T_{1g}(\text{F})$  ( $\nu_2$ ) and  ${}^3T_{1g}(\text{P})$  ( $\nu_3$ ) from the ground state  ${}^3A_{2g}(\text{F})$ . These occur in  $7000 - 11000 \text{ cm}^{-1}$  ( $\nu_1$ ),  $15000 - 19000 \text{ cm}^{-1}$  ( $\nu_2$ ) and  $25000 - 29000 \text{ cm}^{-1}$  ( $\nu_3$ ) regions respectively. In the present complexes, the electronic spectra was very similar to each other and consists of bands in  $8200 - 10990$ ,  $15100 - 17700$  and  $20000 - 20800 \text{ cm}^{-1}$  (Table 3), which clearly indicated the octahedral stereochemistry of the complexes<sup>7</sup>. The band maxima, their assignments, the calculated nephelauxetic effect ( $\beta$ ) and the ligand field parameters B and  $D_q$  for some representative chelate complexes are pre-

sented in Table 3.<sup>32</sup>

### Thermogravimetric studies

Thermoanalytical results of some representative complexes of the type  $[\text{Ni}(\text{L})_2\text{X}_2]$  where L = INH-FFL and X = Cl<sup>-</sup>, NO<sub>3</sub><sup>-</sup> or NCS<sup>-</sup>, are given in Table 4. Thermal curves clearly suggested the absence of any water molecule in these complexes. During  $160 - 290 \text{ }^\circ\text{C}$  temperature range the weight loss corresponds to 36.32 - 39.34% indicate the loss of one molecule of INH-FFL, while second ligand molecule evaporated off at  $\sim 400 \text{ }^\circ\text{C}$ . Finally, at  $\sim 600 \text{ }^\circ\text{C}$ , NiO formation takes place. Almost similar thermogravimetric curves were obtained with the same end product, NiO, which may be represented by the following equations (cf. Table 4):

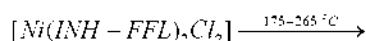


Table 3. Electronic spectral bands ( $\text{cm}^{-1}$ ) and ligand field parameters of nickel(II) complexes of INH-FFL and INH-TMB.

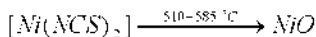
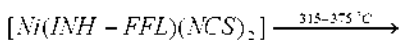
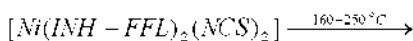
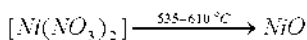
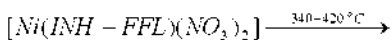
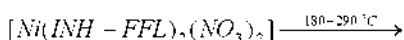
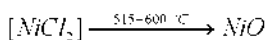
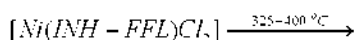
Complex	$\nu_1$ ( $\text{cm}^{-1}$ )	$\nu_2$ ${}^4T_{1g}(\text{F}) \rightarrow {}^4A_{2g}$	$\nu_3$ ${}^4T_{1g}(\text{F}) \rightarrow {}^4T_{1g}(\text{P})$	$D_q$ ( $\text{cm}^{-1}$ )	B ( $\text{cm}^{-1}$ )	$\beta$
$[\text{Ni}(\text{INH-FFL})_2\text{Cl}_2]$	10930	17700	27000	1093	794	0.76
$[\text{Ni}(\text{INH-FFL})_2(\text{NO}_3)_2]$	10990	16950	27400	1099	750	0.73
$[\text{Ni}(\text{INH-FFL})_2(\text{NCS})_2]$	8240 10870	17540	27500	1187	829	0.79
$[\text{Ni}(\text{INH-FFL})_2(\text{CH}_3\text{COO})_2]$	8270 10930	17700	27200	1093	794	0.76
$[\text{Ni}(\text{INH-FFL})_2(\text{ClO}_4)_2]$	8200 10810	17540	26950	1081	804	0.77
$[\text{Ni}(\text{INH-TMB})_2\text{Cl}_2]$	9600	16200	24400	960	1043	0.96
$[\text{Ni}(\text{INH-TMB})_2(\text{NO}_3)_2]$	9900	16660	24390	990	1076	0.99
$[\text{Ni}(\text{INH-TMB})_2(\text{NCS})_2]$	9800	16700	24500	980	1065	0.98
$[\text{Ni}(\text{INH-TMB})_2(\text{CH}_3\text{COO})_2]$	9600	15385	25640	960	1043	0.96
$[\text{Ni}(\text{INH-TMB})_3(\text{ClO}_4)_2]$	9090	15150	25000	909	988	0.91

Table 4. Thermoanalytical results obtained for nickel(II) complexes of INH-FFL.

Complexes	Decomp. temp. (°C)		Decomposition products	Weight loss (%)	
	Initial	Final		Found	Calcd.
[Ni(INH-FFL) <sub>2</sub> Cl <sub>2</sub> ]	175	265	Ni(INH-FFL)Cl <sub>2</sub>	39.34	38.79
	325	400	NiCl <sub>2</sub>	78.32	77.58
	515	600	NiO	88.23	87.06
[Ni(INH-FFL) <sub>2</sub> (NO <sub>3</sub> ) <sub>2</sub> ]	180	290	Ni(INH-FFL)(NO <sub>3</sub> ) <sub>2</sub>	36.32	35.54
	340	420	Ni(NO <sub>3</sub> ) <sub>2</sub>	71.89	71.09
	535	610	NiO	89.06	88.15
[Ni(INH-FFL) <sub>2</sub> (NCS) <sub>2</sub> ]	160	250	Ni(INH-FFL)(NCS) <sub>2</sub>	37.21	36.46
	315	375	Ni(NCS) <sub>2</sub>	74.00	72.93
	510	585	NiO	89.10	87.84

Table 5. Antifungal and antibacterial activities of nickel(II) complexes of INH-FFL and INH-CIN.

Complex	Antibacterial activity				Antifungal action	
	Zone of inhibition in numbers				<i>A. niger</i>	<i>C. albicans</i>
	<i>B.s.</i>	<i>S.a.</i>	<i>E.c.</i>	<i>S.t.</i>		
[Ni(INH-FFL) <sub>2</sub> Cl <sub>2</sub> ]	12	10	10	9	++	++
[Ni(INH-FFL) <sub>2</sub> (NO <sub>3</sub> ) <sub>2</sub> ]	11	10	9	10	++	++
[Ni(INH-FFL) <sub>2</sub> (NCS) <sub>2</sub> ]	16	15	15	14	+++	+++
[Ni(INH-FFL) <sub>2</sub> (CH <sub>3</sub> COO) <sub>2</sub> ]	14	12	12	11	++	++
[Ni(INH-FFL) <sub>3</sub> ](ClO <sub>4</sub> ) <sub>2</sub>	13	11	12	11	++	++
[Ni(INH-CIN) <sub>2</sub> Cl <sub>2</sub> ]	11	10	10	10	+	+
[Ni(INH-CIN) <sub>2</sub> (NO <sub>3</sub> ) <sub>2</sub> ]	12	11	11	11	+	+
[Ni(INH-CIN) <sub>2</sub> (NCS) <sub>2</sub> ]	15	16	15	14	++	++
[Ni(INH-CIN) <sub>2</sub> (CH <sub>3</sub> COO) <sub>2</sub> ]	13	12	11	12	+	+
[Ni(INH-CIN) <sub>3</sub> ](ClO <sub>4</sub> ) <sub>2</sub>	14	13	12	11	+	+
Ampicillin	24	22	17	16	-	-
Tetracycline	18	17	21	22	-	-
Salicylic acid	-	-	-	-	++++	++++



### Biological properties

The study of the biological i.e. antibacterial and antifungal properties of transition metal complexes with ligands of biological importance have recently been of great interest.<sup>1,2,5,7,33-41</sup> Thus in the present studies, the antibacterial activities of the nickel(II) complexes and standard drugs (ampicillin and tetracycline) were also screened by agar-cup method in DMF solvent at a concentration of 50 µg mL<sup>-1</sup>. The results were checked against gram positive bacteria *B. subtilis* and *S. aureus* and gram negative bacteria *E. coli* and *S. typhi* and reported in Table 5. The diameters of zone of inhibition (in mm) of the standard



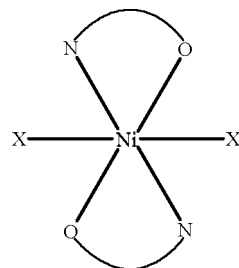
drug ampicillin against gram positive bacteria *B. subtilis* and *S. aureus* and gram negative bacteria *E. coli* and *S. typhi* were found to be 24, 22, 17 and 16 respectively, while tetracycline gave 18, 17, 21 and 22 respectively. Under identical conditions. Table 5 shows that all the nickel(II) complexes of hydrazones of isoniazid have moderate antibacterial activities against these bacteria. These complexes were also screened for their antifungal activities against two fungi (*A. niger* and *C. albicans*). The results are presented in Table 5 which show that almost all the complexes studied showed nearly the same extent of activity but they are less active compared to salicylic acid. These complexes appear to be efficient antifungal agents.

### CONCLUSION AND STEREOCHEMISTRY OF THE COMPLEXES

The conductance, molecular weight determinations and other experimental analyses of the chloro, nitrate, thiocyanato and acetato nickel(II) complexes of INH-FFL, INH-TMB and INH-CIN, suggest that the complexes are non-ionic in nature and do not dissociate in nitrobenzene. Thus in the case of  $[\text{Ni}(\text{L})_2\text{X}_2]$  ( $\text{X} = \text{Cl}^-, \text{NO}_3^-, \text{NCS}^-$  or  $\text{CH}_3\text{COO}^-$ ;  $\text{L} = \text{INH-FFL, INH-TMB}$  and  $\text{INH-CIN}$ ), the coordination number of Ni(II) is found to be six. The 1:2 electrolytic nature of the perchlorato complexes suggests that two perchlorate ions are present outside the coordination sphere and hence, the coordination number of nickel(II) in  $[\text{Ni}(\text{L})_3](\text{ClO}_4)_2$ , is found to be six.

The overall experimental evidences thus show that the studied nickel(II) complexes,  $[\text{Ni}(\text{L})_2\text{X}_2]$  and  $[\text{Ni}(\text{L})_3](\text{ClO}_4)_2$ , display a coordination number six and presumably have an octahedral environment around the metal ion. The proposed structures of these complexes are shown in Fig. 4.

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( $\text{X} = \text{Cl}^-, \text{NO}_3^-, \text{NCS}^-$  or  $\text{CH}_3\text{COO}^-$ )

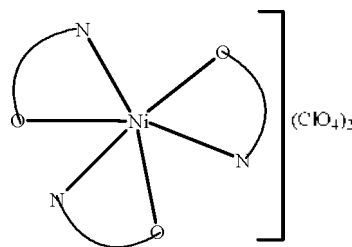


Fig. 4. Probable structures of  $[\text{Ni}(\text{L})_2\text{X}_2]$  and  $[\text{Ni}(\text{L})_3](\text{ClO}_4)_2$ .

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