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Synthesis and spectroscopic characterization of nickel(II) complexes of 1-benzotriazol-1-yl-[(*p*-X-phenyl)hydrazone]propan-2-one

Nouria Al-Awadi, Nadia M. Shuaib, Ali El-Dissouky*

Chemistry Department, Faculty of Science, Kuwait University, P.O. Box 5969, Safat 13060, Kuwait Received 14 July 2005; accepted 12 September 2005

Abstract

The reaction of NiCl₂·H₂O with 1-benzotriazol-1-yl-[(*p*-X-phenyl)hydrazone]propan-2-one, X = H (HL¹), X = Cl (HL²), X = Br (HL³) and X = Me (HL⁴), gave the complexes [(HL)NiCl₂]·*n*H₂O and [LNi(OH)]₂, where L is the monobasic anion of HL² or HL³. The nature of the products is solvent and ligand dependent. The complexes are characterized by elemental analyses, molar conductivity, magnetic moments and spectroscopic (IR and UV/vis) measurements. The IR showed that the ligands act as neutral bidentate coordinated to the nickel(II) through the azomethine nitrogen and carbonyl oxygen atoms in case of [(HL)NiCl₂]·*n*H₂O. In case of [LNi(OH)]₂, the ligands are monobasic bidentate bonded to the nickel(II) through the azomethine nitrogen and the enolato oxygen atoms. The room temperature magnetic moment values of 1.58–2.49 B.M. for [(HL)NiCl₂]·*n*H₂O and [LNi(OH)]₂ and their electronic spectral data indicate that these complexes have square planar–tetrahedral equilibrium. The values of 1.61 and 1.58 B.M. for the hydroxo-complexes support their dimeric nature. The electronic spectral of [(HL)NiCl₂]·*n*H₂O and [LNi(OH)]₂ in pyridine or α-picoline indicated the formation of six-coordinate adducts. The hydroxo-complexes reacted with different Lewis bases to give the complexes [L₂Ni(L_s)₂], where L_s = Py, 2-Pic, 3-Pic, 4-Pic or *n*-PrNH₂. The relationship between the pK_b of the Lewis base and the *v*_{Ni-O} of the ligand and *v*_{Ni-N} of the Lewis base was studied. The different ligand field parameters are calculated for the parent ligands in solutions and the solid mixed ligand complexes. The data showed that both are associated with a distorted octahedral ligand field around the nickel(II) and the ligand fields in solution are different from that in solid. The extent of distortion for the parent complexes is more than that in the solid adducts. Furthermore, the data showed that the nickel–ligand bonding in [LNi(OH)]₂ is more covalent than in [L₂Ni(L_s)₂]. © 2005 Els

Keywords: Benzotriazole; Hydrazone; Nickel(II); Mixed ligand complexes; Spectra; Structure

1. Introduction

In our previous work, we reported the synthesis and spectroscopic characterization of nickel(II) complexes with different polyfunctional ligands having different donors [1–5]. Nickel(II) complexes are used in different fields of chemistry and industry. (1-Me-indyl)(PPh₃)Ni-CCPh was used as a catalyst for the synthesis of *cis*-poly(1-ethylenepyrene) [6]. (1-Meindyl)Ni(PR₃) was used for dehydrogenative oligomerization of PhSiH₃ [7]. Furthermore, nickel(II) compounds are known to cause respiratory cancer in human and induce tumors in the experimental animals. This is because of its bonding to the proteins and DNA leading to generate reactive oxygen species and other reactive intermediate and changing the cel-

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lular homeostasis [8]. Therefore, if there are polyfunctional ligands that can react with nickel(II) before bonding to proteins or DNA, it will prevent the nickel carcinogenesis. Therefore, it is important to study the bonding of nickel(II) with different polyfunctional ligands with different donors. Furthermore, mixed ligand complexes have a key role in biological chemistry [9] because the mixed chelation occurs commonly in biological fluids as millions of potential ligands are likely to compete for metal ions in vivo [10]. These create specific structures [9–11] and have been implicated in the storage and transport of active substances through membranes. Among these ligands are the triazole and its derivatives where they act as polyfunctional having different donors. Triazole-containing complexes are very important due to their uses in different fields [12-16]. Recently, the triazole derivatives as 4-alkyl-3,5-di(pyridyl)-4H-1,2-triazole [17], 3-phenyl-5-(2-pyridyl)-4-(4-pyridyl)-4H-1,2,4-triazole [18], 4,4'-(1,4-phenylene)bis[3phenyl-5-(2-pyridyl)-4H-1,2,4-triazole] [18] and other related

^{*} Corresponding author. Tel.: +965 6014156; fax: +965 4816482. *E-mail address:* adissouky@yahoo.com (A. El-Dissouky).

compounds [19–21] are used as chelating agents for different metal ions, among them is the nickel(II). Furthermore, Haasnoot has reported a review on the coordination chemistry of many triazole derivatives with different metal ions [22]. We have reported the copper(II) complexes of the new chelating agents 1-benzotriazol-1-yl-[(p-X-phenyl)hydrazone]propan-2one, I [23]. The ligands give copper(II) complexes with unique stereochemical, magnetic and spectral properties. It is found that the nature of copper-ligand bonding in the complexes of HL¹, HL⁴ and HL⁵ is covalent in nature while for the complexes of HL^2 and HL^3 is ionic. This is due to the different electronic effects of the *p*-substituent. Due to the importance of these types of ligands, the mixed ligand complexes, the absence of their nickel(II) complexes in literature and our interest in the ligating behavior of the triazole-containing organic compounds, we aim to synthesize and characterize nickel(II) complexes of 1benzotriazol-1-yl-[(p-X-phenyl)hydrazone]propan-2-one, I, as well as the products of the reaction of these complexes with different nitrogen-containing Lewis bases.



 $X = H (HL^{1}), CI (HL^{2}), Br (HL^{3}), Me (HL^{4}), OMe (HL^{5})$ (I)

2. Experimental

All chemicals were reagent grade quality obtained from BDH or Aldrich and used without further purification.

2.1. Synthesis of the ligands

The ligands were synthesized according to the method reported by Al-Awadi and co-workers [24].

2.2. Synthesis of the nickel(II) complexes

- (a) $[(HL)NiCl_2] \cdot nH_2O$; $HL = HL^1$, HL^2 , HL^3 and HL^4 ; n = 1-3. These complexes were synthesized by the addition of a hot ethanolic solution (20 cm³) of NiCl_2·H_2O (0.001 mol) to a hot ethanolic solution (20 cm³) of the corresponding ligand (0.0022 or 0.001 mol) in the same solvent (30 cm³). The reaction mixture was then refluxed for 2–3 h and cooled to room temperature. The solid formed in each case was filtered off, washed several times with EtOH, Et₂O and dried in vacuum over P₄O₁₀ (yield 52–63%).
- (b) $[LNi(OH)]_2$; L = anion of HL² or HL³.

They were synthesized according to the method (a) but using CH_3CN as a solvent. Only HL^2 and HL^3 gave the hydroxo-complexes.

(c) $[L_2Ni(L_s)_2]; L_s = Py, 2-Pic, 3-Pic, 4-Pic \text{ or } n-PrNH_2.$

The adduct complexes were prepared by dissolving [LNi(OH)] in the least amount of the corresponding L_s . The resulting solution was filtered off to remove any undissolved solid and the filtrate was refluxed for 1–2 h. After cooling to room temperature, H₂O was added dropwise until the first turbidity. The mixture was left overnight at room temperature and the isolated solid was filtered off, washed several times with EtOH–H₂O mixture (30:70, v/v), followed by Et₂O until the filtrate become uncolored and dried.

2.3. Physical measurements and analysis

CHN analysis was obtained from LECO-CHNS 932 Analyzer. FT-IR spectra were recorded as KBR discs with Schimadzu 2000 FT-IR spectrophotometer. Electronic spectra were accomplished by Carry Varian 5 UV/vis/NIR spectrophotometer. The room temperature magnetic susceptibility measurements for the complexes were determined by a Gouy balance using Hg[Co(CN)₄] as the calibrant. Molar conductance of the complexes was measured for 1.00×10^{-3} M DMF solutions at room temperature using a systronic conductivity bridge type 305.

3. Results and discussion

3.1. General

The interaction of HL¹–HL⁴ with NiCl₂·H₂O (Scheme 1) in EtOH in a mole ratio 1:1 or 1:2 (Ni²⁺:HL) all gave only complexes [(HL)NiCl₂]·*n*H₂O, HL = HL¹–HL⁴ and *n* = 1–3. In CH₃CN as solvent HL² and HL³ gave [LNi(OH)]₂ while HL¹ and HL⁴ gave [(HL)NiCl₂]·*n*H₂O. All complexes are air stable, partially soluble in EtOH but freely soluble in Lewis bases such as pyridine (Py) or 2-picoline (2-Pic) with color change. The color change could be taken as an evidence for the interaction of these complexes with Py or α -Pic. The molar conductivity values of the complexes as 1.00×10^{-3} M DMF solutions at 298 K (Table 1) indicate their non-electrolytic nature [25]. Only [LNi(OH)] gave solid base adducts complexes [L₂Ni(L_s)₂], L_s = Py, 2-Pic, 3-Pic, 4-Pic or *n*-PrNH₂ (Scheme 2), which are decomposed within 3–4 days to give [L₂Ni], where L is the monobasic anion of HL² and HL³.

3.2. Electronic spectral and magnetic data

3.2.1. $[(HL)NiCl_2] \cdot nH_2O$, n = 1-3, and $HL = HL^1$, HL^2 , HL^3 or HL^4

The room temperature magnetic moment values of these complexes (Table 3) are in the $1.59-2.57 \text{ cm}^{-1}$ range. These values are lower than these of octahedral, tetrahedral or high spin five-coordinate nickel(II) complexes. Therefore, the complexes may be low spin five-coordinate nickel(II) complexes. According to the molar conductivity values, elemental analy-



Scheme 1.

sis, IR and the nature of the ligands, these complexes could be assigned to be four-coordinate nickel(II) complexes. Furthermore, these magnetic values are similar to that reported for [NiX₂PR₃], bis(salicylaldiminato)nickel(II) and [NiCl(H₂O)L], L = azo-nitrosoresorcinol derivatives complexes which exist in a square planar-tetrahedral mixture in the solid state [1–5,26].

The nujol mull electronic spectra of all complexes are recorded in the range of 5000–30,000 cm⁻¹. The spectra of [(HL)NiCl₂]·*n*H₂O and [LNi(OH)] are similar and exhibit two bands at 6700–6900 and 18,300–18,900 cm⁻¹ (Table 2), characteristic of square planar–tetrahedral nickel(II) complexes [2–5]. The band at 6700–6900 cm⁻¹ could be assigned to ${}^{3}T_{1} \rightarrow {}^{3}T_{1}(P)$ transition for the tetrahedral nickel(II) complexes while that at 18,300–18,900 cm⁻¹ due to ${}^{1}A_{1}g \rightarrow {}^{1}B_{1}g$ transition in the square planar nickel(II) complexes [27]. This assignment of the electronic transitional bands is made evident by comparing with the spectra of similar complexes [1–3].

The percentage of tetrahedral (N_t) in these complexes could be obtained by applying Eq. (1)

$$N_{\rm t} = \frac{100(\mu_{\rm obsd})^2}{(3.3)^2} \tag{1}$$

where μ_{obsd} is the measured room temperature magnetic moment and 3.3 is the magnetic moment for ideal tetrahedral nickel(II) complexes. The values of N_t of [(HL)NiCl₂]·*n*H₂O are in the order of: Ph (HL¹)>*p*-Cl (HL²)>*p*-Br (HL³)>*p*-Me (HL⁴), which is the reverse of the bulkiness effect of the *p*substituted phenyl moiety. This sequence means that the large steric requirement enhances the planar form and therefore low N_t value. The lower N_t values for [LNi(OH)]₂ relative to those of [(HL)NiCl₂]·*n*H₂O can be referred to the increased planarity of the hydroxo-containing complexes due to their dimeric forms.

The values of $N_{\rm t}$ are used to calculate the molar extinction coefficient ($\varepsilon_{\rm max}$) of the tetrahedral in the 6700–6900 cm⁻¹ region, where the planar forms do not absorb, using Eq. (2)

$$\varepsilon_{\max} = \frac{42N_t}{100} \tag{2}$$

where 42 is the molar extinction coefficient of the band at 6700–69,500 cm⁻¹ for pure tetrahedral nickel(II) complexes. The values of ε (Table 2) are shown to be in the same order of N_t . The spectral data for the solid complexes showed the significant property of the ligand field in the existence of a clear trend between the energies of the bands at 6700–6900 cm⁻¹

Table 1	
Elemental analysis, % found (% calcd.), color, molar conductivity of the ligands and their nickel(II) complex	es

$\label{eq:compound} Compound^a \qquad \mbox{Medium}^b \qquad \mbox{Color} \qquad \mbox{Λ_M^c}(\mbox{S}\mbox{cm^2}\mbox{mol^{-1}})$	С	Н	Ν	Ni	
HL ¹	64.85 (64.52)	4.63 (4.66)	25.21 (25.09)		
HL^2	58.00 (57.74)	4.02 (3.83)	22.53 (22.33)		
HL ³	50.49 (50.28)	3.43 (3.35)	19.76 (19.55)		
HL^4	65.12 (65.52)	4.97 (5.12)	24.05 (23.89)		
$[(HL^1)NiCl_2]\cdot 3H_2O$ EtOH or CH ₃ CN Green-brown 13.0	38.66 (38.89)	3.93 (4.11)	15.06 (15.13)		
$[(HL^2)NiCl_2] \cdot H_2O$ EtOH Green 16.0	39.50 (39.11)	2.99 (2.80)	15.39 (15.20)		
[L ² Ni(OH)] CH ₃ CN Brown 8.0	46.07 (46.37)	3.18 (3.09)	18.21 (18.03)	15.10 (15.12)	
$[L^2_2Ni(Py)_2]$ Py Red 3.2	56.93 (57.03)	4.00 (3.80)	19.81 (19.96)	7.09 (6.98)	
$[L^2_2Ni(2-Pic)_2]$ 2-Pic Red-brown 2.8	57.68 (57.95)	4.02 (4.14)	19.51 (19.32)	7.00 (6.76)	
$[L^2_2Ni(3-Pic)_2]$ 3-Pic Red-brown 3.0	57.66 (57.95)	3.92 (4.14)	19.29 (19.32)	6.88 (6.76)	
$[L^2_2Ni(4-Pic)_2]$ 4-Pic Red-brown 2.0	58.19 (57.95)	4.21 (4.14)	19.23 (19.32)	6.58 (6.76)	
$[L^2_2Ni(PrNH_2)_2]$ PrNH ₂ Brown-yellow 2.7	53.59 (53.88)	4.85 (4.99)	21.02 (20.95)	13.01 (13.13)	
$[(HL^3)NiCl_2]\cdot H_2O$ EtOH Green 14.0	37.20 (3691)	2.61 (2.46)	14.08 (14.35)		
[L ³ Ni(OH)] CH ₃ CN Brown 6.0	41.49 (41.61)	2.86 (2.77)	15.98 (18.18)	13.97 (13.71)	
$[L^3_2Ni(Py)_2]$ Py Red 2.8	47.10 (46.91)	3.09 (3.32)	16.26 (16.42)		
$[L^{3}_{2}Ni(2-Pic)_{2}]$ 2-Pic Red 3.0	47.68 (47.94)	3.78 (3.61)	16.15 (15.98)	11.58 (11.70)	
$[L^3_2Ni(3-Pic)_2]$ 3-Pic Red-brown 2.3	48.1 (47.94)	3.66 (3.61)	15.76 (15.98)	11.80 (11.70)	
$[L_{2}^{3}Ni(4-Pic)_{2}]$ 4-Pic Brown 2.4	47.66 (47.94)	3.72 (3.61)	16.21 (15.98)	11.58 (11.70)	
$[L_{2}^{3}Ni(PrNH_{2})_{2}]$ PrNH ₂ Brown-yellow 2.1	44.19 (43.94)	4.08 (4.27)	17.33 (17.09)	12.01 (11.94)	
$[(HL^4)NiCl_2] \cdot H_2O$ EtOH or CH ₃ CN Green 9.0	43.29 (43.56)	3.63 (3.86)	15.76 (15.88)	. ,	

^a Py: pyridine; 2-Pic: 2-picoline; 3-Pic: 3-picoline; 4-Pic: 4-picoline; *n*-PrNH₂: *n*-propylamine. ^b Medium of the synthesis. ^c Molar conductivity of 1.00×10^{-3} M DMF solution at 25 ± 1 °C.

Table 2 Electronic spectral data and room temperature magnetic moments for the complexes

Complex	$\mu_{ ext{eff}}$	State	Nt	ε_{\max}	\dot{v} (cm ⁻¹)
[(HL ¹)NiCl ₂]·3H ₂ O	2.49	Solid Py 2-Pic	56.9	23.9	6900, 18050 9800, 9980, 11800, 15410, 15620, 23250 9500, 9700, 1200, 15100, 15380, 23000
[(HL ²)NiCl ₂]·H ₂ O	2.35	Solid Py 2-Pic	50.7	21.3	6830, 18300 9830, 11920, 1430, 15900, 23800 9480, 11950, 15020, 15680, 23700
[L ² Ni(OH)]	1.61	Solid Py 2-Pic	23.8	10.0	6850, 19150 10500, 12500, 15240, 15890, 24990 9300, 9400, 12800, 15250, 15550, 23120
$ \begin{split} & [L^2_2 Ni(Py)_2] \\ & [L^2_2 Ni(2\text{-Pic})_2] \\ & [L^2_2 Ni(3\text{-Pic})_2] \\ & [L^2_2 Ni(4\text{-Pic})_2] \\ & [L^2_2 Ni(PrNH_2)_2] \end{split} $	3.20 3.22 3.21 3.30 3.26	Solid Solid Solid Solid Solid			9820, 12700, 16100, 17050, 24060 9420, 10300, 12790, 152800, 16600, 23600 9800, 12000, 12890, 15900, 23800 10100, 12200, 12700, 16300, 24080 10400, 10900, 13000, 16700, 17350, 25000
[(HL ³)NiCl ₂]·H ₂ O	2.26	Solid Py 2-Pic	46.9	19.7	6800, 18780 9640, 11700, 15000, 15500, 23670 9200, 12000, 15000, 23420
[L ³ Ni(OH)]	1.58	Solid Py 2-Pic	22.9	9.6	6850, 19200 10100, 12460, 15280, 14800, 23790 9900, 12900, 15310, 15530, 23700
$ \begin{bmatrix} L^{3}_{2}Ni(Py)_{2} \\ [L^{3}_{2}Ni(2-Pic)_{2}] \\ [L^{3}_{2}Ni(3-Pic)_{2}] \\ [L^{3}_{2}Ni(4-Pic)_{2}] \\ [L^{3}_{2}Ni(PrNH_{2})_{2}] \\ \end{bmatrix} $	3.19 3.24 3.28 3.30 3.30	Solid Solid Solid Solid Solid			9800, 11500, 13000, 16100, 24200 9400, 10600, 12900, 15300, 23600 9770, 10400, 12980, 15900, 16080, 23800 9900, 10800, 13600, 16200, 24000 10350, 11600, 13000, 16850, 24900
[(HL ⁴)NiCl ₂]·H ₂ O	2.19	Solid Py 2-Pic	44.0	18.5	6760, 18900 10125, 13000, 15700, 24000 9660, 13000, 15380, 23140





and the planar component band at $18,300-19,000 \text{ cm}^{-1}$. The data showed a direct proportionality between N_t and the energy of the band at $6700-6900 \text{ cm}^{-1}$ but inverse relation with the higher energy band ($18,300-19,000 \text{ cm}^{-1}$). The higher energy band (combination band) provides a measure of the frequency trend of the planar d–d transition due to: (i) the intensity increase with decreasing N_t and (ii) the trend of the higher energy band is opposite to that in the lower energy band.

The electronic spectra of the complex in a Lewis base as Py or α -Pic (Table 2) are quite different from the nujol mull. The color change with the new spectral features are taken as evidences for the interaction of the Lewis base leading to ligand field change around the nickel(II). The spectra of all complexes display bands with maxima at 9300–10,100, 11,000–13,000, 15,000–16,000 and 22,400–24,400 cm⁻¹ which are characteristic of tetragonally distorted octahedral nickel(II) complexes [13,14]. The bands at 9300–10,100, 15,000–15,700 and 23,000–24,400 cm⁻¹ are assigned to $v_1[{}^4A_{2g} \rightarrow {}^4T_{2g}]$, $v_2[{}^4A_{2g} \rightarrow {}^4T_{1g}(F)]$ and $v_3[{}^4A_{2g} \rightarrow {}^4T_{1g}(P)]$ transition, respectively. The bands at 11,000–13,000 cm⁻¹ can be attributed to the forbidden ${}^3A_{2g} \rightarrow {}^1E_g(D)$ and ${}^3A_{2g} \rightarrow {}^1E_g(G)$ transition [27]. Furthermore, the splitting of v_2 could be taken as an evidence for the distortion from the ideal symmetry. The interaction of these bases with the complexes to form six-coordinate nickel(II) complexes is presented in Scheme 1.

The ligand field parameters Δ_0 (splitting parameter), B' (Racah parameter of interelectronic repulsion) and β (nephelauxetic ratio) for these nickel(II) complexes are calcu-

Table 3
Electronic spectral parameters for the octahedral nickel(II) complexes

Complex	Medium ^a	ν_1	ν_2	<i>v</i> ₃	v_2/v_1	D_{q}	B'	β	D_q/B'
[(HL ¹)NiCl ₂]·3H ₂ O	Ру	9800	15515	23250	1.58	980	624	0.60	1.57
	2-Pic	9500	15240	23000	1.60	950	649	0.62	1.46
[(HL ²)NiCl ₂]·H ₂ O	Ру	9830	15665	23800	1.59	983	665	0.64	1.48
	2-Pic	9480	15350	23200	1.62	948	674	0.65	1.41
$[L^2Ni(OH)]$	Py	10500	15565	23900	1.48	1050	531	0.51	1.98
	2-Pic	9900	15400	23120	1.56	990	588	0.56	1.68
$[L^2_2Ni(Py)_2]$	Solid	9820	16100	24060	1.64	982	713	0.68	1.38
$[L^2_2Ni(2-Pic)_2]$	Solid	9420	15280	23600	1.62	942	708	0.68	1.33
$[L^2_2Ni(3-Pic)_2]$	Solid	9800	15900	23800	1.62	980	686	0.66	1.43
$[L^2_2Ni(4-Pic)_2]$	Solid	10100	16300	24180	1.61	1010	678	0.65	1.49
$[L^2_2Ni(PrNH_2)_2]$	Solid	10400	16700	25000	1.61	1040	700	0.67	1.49
[(HL ³)NiCl ₂]·H ₂ O	Ру	9640	15250	23670	1.58	964	666	0.64	1.45
. / 2/2	2-Pic	9200	15000	23420	1.63	920	721	0.69	1.28
$[L^3Ni(OH)]$	Pv	10100	15540	23790	1.53	1010	615	0.59	1.64
//	2-Pic	9900	15420	23700	1.55	990	628	0.60	1.58
$[L^3_2Ni(Py)_2]$	Solid	9800	16100	24200	1.64	980	726	0.70	1.35
$[L^{3}_{2}Ni(2-Pic)_{2}]$	Solid	9400	15300	23600	1.65	930	713	0.68	1.32
$[L^{3}_{2}Ni(3-Pic)_{2}]$	Solid	9770	15900	23800	1.64	967	692	0.66	1.41
$[L^{3}_{2}Ni(4-Pic)_{2}]$	Solid	9900	16200	24000	1.64	990	700	0.67	1.41
$[L_2^3 Ni(PrNH_2)_2]$	Solid	10350	16850	24900	1.63	1035	713	0.68	1.45
[(HL ⁴)NiCl ₂]·H ₂ O	Ру	10125	15700	24000	1.55	1012	621	0.60	1.63
	2-Pic	9660	15680	23140	1.62	966	656	0.63	1.47

lated following Eqs. (3)–(5):

$$\Delta_{\rm o} = \nu_1 \tag{3}$$

$$B' = \frac{\nu_2 + \nu_3 - 3\nu_1}{15} \tag{4}$$

$$\beta = \frac{B'}{B^{\circ}} \tag{5}$$

where $B^{\circ} = 1041 \text{ cm}^{-1}$ for the free Ni²⁺ ion.

The values of D_q for the nickel(II) complexes (Table 3) are found to be in the $920-1010 \text{ cm}^{-1}$ range, indicating the intermediate ligand field position of the ligands in the nephelauxetic series, D_q for octahedral nickel(II) complexes vary between 6400 and 12,700 cm⁻¹. The interelectronic repulsion parameter B' was calculated and found to be in the 531-666 and 588–721 cm⁻¹ for the pyridine and α -picoline-containing complexes, respectively. These values are lower than that for the free Ni^{2+} ion (1041 cm⁻¹) which attributed to the delocalization of the electrons over the molecular orbitals that encompass both the metal and the ligands. Furthermore, the values of B' showed that the e_g -electrons are σ -antibonding and spend some of their time on the ligand. The t_{2g} -electrons may become π -bonding or antibonding and spend some of their time on the ligand. Such delocalization leads to increase in the mean distance between the d-electrons and therefore reduces the interelectronic repulsion parameter B° . The nephelauxetic ratio $\beta = B'/B^{\circ}$ for the complexes (Table 3) indicates the presence of electron delocalization over all the molecular orbitals and therefore a covalent character of nickel(II)–ligand bonding. The ratio v_2/v_1 and D_q/B'

values are further evidences for octahedral with ${}^{3}A_{2g}$ ground state.

3.2.2. $[L_2Ni(L_s)_2], L_s = Py, 2$ -Pic, 3-Pic, 4-Pic or PrNH₂

The formation of the solid complexes $[L_2Ni(L_s)_2]$, $L_s = Py$, 2-Pic, 3-Pic, 4-Pic or *n*-PrNH₂, as a result of interaction of the Lewis base (L_s) with $[LNi(OH)]_2$ was proved from the elemental analysis (Table 1) and can be interpreted on the basis of Eq. (6):

$$[\mathrm{LNi}(\mathrm{OH})]_2 + \mathrm{L}_{\mathrm{s}} \rightarrow [\mathrm{L}_2\mathrm{Ni}(\mathrm{L}_{\mathrm{s}})_2] + \mathrm{Ni}(\mathrm{OH})_2 \tag{6}$$

The room temperature magnetic moments of the solid adducts (Table 2) are in the range of 3.19–3.30 B.M. characteristic of either octahedral or five-coordinate high spin nickel(II) complexes [26]. On the basis of the analytical data, the bidentate and monodentate nature of the anions L^1-L^4 and L_s , respectively, octahedral structure could be assumed for $[L_2Ni(L_s)_2]$.

The electronic spectra of the solid adducts (Table 3) are consistent with that reported for a distorted octahedral nickel(II) complexes [27]. The different ligand field parameters are calculated according to Eqs. (3)–(5) and the results are given in Table 3. The data showed that: (i) the values of D_q are in the order PrNH₂ > 4-Pic > Py > 2-Pic > 3-Pic. The lower values for the pyridines than PrNH₂ could be attributed to the steric effects of the pyridine derivatives and suggest that PrNH₂ behaves as a stronger σ -donor than the pyridine derivatives. (ii) The D_q values for the solid adducts are different from those obtained for the solution spectra of the parent complexes in the corresponding Lewis base. This could be attributed to the formation of different species in solution but both have the octahedral structure.

Table 4	
The main IR spectral bands (\dot{v} , cm ⁻¹)	for the ligands and their nickel(II) complexes ^a

Compound	νnh; Oh	vc=0;c-0(Chel) ^b	$v_{C=N(Chel)}^{b}$	$v_{N=N(Chel)}^{b}$	v _{C=N(Base)} ^c	$v_{Ni-N(Chel)}^{b}$	$v_{Ni-N(Base)}^{c}$	$v_{Ni-O(Chel)}^{b}$	pKb ^d
HL ¹	3270–3400 br,m	1698 vs	1600 s						
$[(HL^1)NiCl_2]\cdot 3H_2O$	3456s, 3316 m	1663 s	1587 m			468 w		500 w	
HL ²	3220-3400 br,m	1679 vs	1602 s						
[(HL ²)NiCl ₂]·H ₂ O	3432 s, 3320 m	1648 s	1582 m			470 w		498 w	
[L ² Ni(OH)]	3538 br,m	1441 m		1395 m		487 w		508 w	
$[L^2_2Ni(Py)_2]$		1438 m		1390 m	1558	492 w	422 w	526 w	8.77
$[L^2_2Ni(2-Pic)_2]$		1440 m		1396 m	1555	488 w	432 w	515 w	8.21
$[L^2_2Ni(3-Pic)_2]$		1446 m		1395 m	1558	490 w	428 w	519 w	8.32
$[L^2_2Ni(4-Pic)_2]$		1451 m		1398 m	1560	490 w	440 w	508 w	7.98
$[L^2_2Ni(PrNH_2)_2]$	3488–3518 br,m	1449 m		1392 m		486 w	448 w	500 w	4.26
HL ³	3245–418 br,m	1680 vs	1602 s						
[(HL ³)NiCl ₂]·H ₂ O	3423 vs, 3266 m	1651 s	1581 m			466 w		486 w	
[L ³ Ni(OH)]	3576 s	1440 m		1400 m		475 w		499 w	
$[L_{2}^{3}Ni(Py)_{2}]$		1455 m		1398 m	1550	478 w	424	530 w	8.77
$[L^3_2Ni(2-Pic)_2]$		1449 m		1402 m	1556	480 w	435	520 w	8.21
$[L^{3}_{2}Ni(3-Pic)_{2}]$		1450 m		1396 m	1553	481 w	428	517 w	8.32
$[L^3_2Ni(4-Pic)_2]$		1450 m		1399 m	1552	484 w	441	508 w	7.98
$[L^3_2Ni(PrNH_2)_2]$	3496 br,m	1439 m		1390 m		478 w	448	502 w	4.26
HL^4	3220 br,m	1674 vs	1600 vs						
$[(HL^4)NiCl_2]\cdot H_2O$	3438 s, 3357 m	1649 s	1583 s			466 w		494 w	

^a br: broad; m: medium; s: strong; vs: very strong; w: weak.

^b Chel: chelate or ligand.

^c Lewis base.

^d Base constant for the Lewis base.

(iii) The values of β parameter in case of $[L_2Cu(L_s)_2]$ are lower than that of the free nickel(II) suggesting the covalency of the nickel–ligand bonding. Furthermore, the values for $[L_2Cu(L_s)_2]$ are lower than those of $[LNi(OH)]_2$ suggesting that the covalency in the hydroxo-complexes is more than that in the adducts. (iv) There is direct proportionality between the values of K_b of the L_s and the values of D_q .

3.3. Infrared spectra

The main IR spectra bands with their tentative assignments for the free ligands and their nickel(II) complexes are given in Table 4. The following points arise from the data in Table 4:

- (i) The spectra of all ligands display broad medium band in the 3220–3418 cm⁻¹ range due to the different vibrational modes of −NH− of the hydrazo moiety. The broad band at ca. 3400 cm⁻¹ could be taken as an evidence for the involvement of the −NH− proton in the formation of hydrogen bonding of the −NH···O− type [28].
- (ii) The bands at 3220–3245 cm⁻¹ are not greatly affected in case of [(HL)NiCl₂]·*n*H₂O indicating the unchanged nature of the −NH− group in these complexes, whereas the higher wavenumber band (3400 cm⁻¹) appeared at different positions with different intensities and shapes. This band could be attributed to the water of crystallization or hydrogen bonded water molecules.
- (iii) The triazole moiety displays a medium–strong band at 1554–1592 cm⁻¹ in the spectrum of the free organic compounds. This band is not greatly affected by complex

formation in most cases indicating its non-bonding nature [17–19].

- (iv) The spectra of the free ligands display bands at 1674–1698 and 1600–1602 cm⁻¹ due to ν (C=O) and ν (C=N), respectively. The position of ν (C=O) is found to be dependent on the electronic nature of the *p*-substituents and can be ordered as HL¹ (H) > HL⁴ (*p*-Me) > HL² (*p*-Cl) > HL³ (*p*-Br), while that due to ν (C=N) is not. This could be taken as an evidence for the involvement of C=O in hydrogen bonding and the presence of the ligands in keto-hydrazo form.
- (v) The spectra of [(HL)NiCl₂]·nH₂O showed that these two bands are shifted to lower wavenumbers relative to the free ligands. Therefore, the ligands act as neutral bidentate bonded to the nickel(II) through the azomethine nitrogen and the keto-oxygen atoms.
- (vi) The spectra of [LNi(OH)]₂ display only a medium band at 3538–3576 cm⁻¹ which could be assigned to ν (OH) with the disappearance of the bands characteristic of ν (NH) and ν (C=O). Furthermore, the spectra of these complexes display another new bands at 1440–1441 and 1395–1400 cm⁻¹ assignable to ν (C–O) and ν (N=N), respectively, suggesting the formation of the azo-enol form with the deprotonation of the enol-OH upon bonding. The appearance of the ν (N=N) at lower wavenumbers relative to the free azo-group in most azo compounds could be taken as an evidence for the bonding of one of the nitrogen atoms to the nickel(II). Accordingly, the ligands act as monobasic bidentate coordinated to the nickel(II) via one of the azo-nitrogen and the enolato-oxygen atoms [19–22].

- (vii) The spectra of $[(HL)NiCl_2] \cdot nH_2O$ and $[LNi(OH)]_2$ exhibit new bands at 486–530 and 466–487 cm⁻¹ characteristic of $\nu(Ni-O)$ and $\nu(Ni-N)_{chel}$, respectively, supporting our suggestion for the monobasic bidentate nature of HL² and HL³ in the hydroxo-complexes.
- (viii) The spectra of $[L_2Ni(L_s)_2]$ display additional bands to those observed in the parent hydroxo-complexes at 1550–1560 and 422–448 cm⁻¹ due to ν (C=N) of the heterocyclic nitrogen ring of pyridine derivatives and ν (Ni–N) of L_s, respectively, supporting the bonding of the L_s via its nitrogen atom. The observation of only one band due to ν (Ni–N) of L_s suggests that the two L_s molecules (as supported from the elemental analysis) are identical in their environments.
- (ix) It is noted that the ν (Ni–O) for the [L₂Ni(L_s)₂] appeared at higher wavenumbers relative to that of [LNi(OH)]₂. Furthermore, apparent shifts accompanying the variation of L_s are observed in the ν (Ni–N) of the L_s and ν (Ni–O) of the parent ligands (Table 4). The ν (Ni–N) of L_s decreases in the order: PrNH₂ > 4-Pic > 2-Pic > 3-Pic > Py, while the ν (Ni–O) of the parent ligands increases in the order: PrNH₂ > 4-Pic > 2-Pic > 3-Pic > Py, corresponding to the decrease in the basicity of the coordinated L_s molecules.

According to the previous results, structures given in Schemes 1 and 2 could be assumed for $[(HL)NiCl_2] \cdot nH_2O$, $[LNi(OH)]_2$ and $[L_2Ni(L_s)_2]$.

4. Conclusion

A new nickel(II) complex is prepared by the reaction of nickel(II) chloride with the benzotriazole hydrazone derivatives. The products were found to be dependent on the solvent and the nature of the ligand. All complexes are found to possess a square planar-tetrahedral in the solid phase based on the electronic spectra and magnetic moment values, in coordinating solvents as Py or α -picoline to give the corresponding tetragonally distorted octahedral complexes. The electronic spectra and the calculated parameters confirmed the formation of the octahedral adducts. Only solid mixed ligand complexes [L₂Ni(L_s)₂] were obtained as a result of the reaction of $[LNi(OH)]_2$ with $L_s = Py$, 2-Pic, 3-Pic, 4-Pic and n-PrNH₂. Their electronic spectral and IR parameters are dependent on the p $K_{\rm b}$ of the Lewis base molecule (L_s) . Furthermore, the electronic transitional energies for the solid adducts were different from that obtained for the solutions of the parent complexes in the different Lewis bases but all were consistent with distorted octahedral nickel(II) complexes. This means the presence of different ligand fields in solutions from those in solids.

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