STUDIES ON NICKEL(II) COMPLEX COMPOUNDS WITH 2-BENZOTHIAZOLYL HYDRAZONES

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Six new Ni(II) complex compounds with 2-aminobenzaldehyde-2-benzothiazolyl hydrazone (HL[a]) and 4-methoxybenzaldehyde-2-benzothiazolyl hydrazone (HL[b]) have been prepared and characterized by elemental and thermogravimetrical analyses, magnetic susceptibility measurements, infrared and electronic spectra. The complex compounds have various composition and stereochemistry, depending on the reaction conditions and the metal salt used. The ligand HL[a] acts as neutral tridentate NNN donor in the complex [Ni(HL[a])Cl]Cl, monobasic bidentate donor in the complexes $[Ni_2L_2{}^a(CH_3COO)_2(H_2O)_2]$ and $[NiL^a(CH_3COO)(H_2O)]\cdot2H_2O$ and monobasic tridentate donor in $[Ni_2L_2{}^a(CH_3COO)_2]$. The ligand HL[b] coordinates as neutral bidentate NN donor; for its complexes, $[Ni(HL^b)_2(H_2O)_2](NO_3)_2\cdot3H_2O$ and $[Ni(HL^b)_2(H_2O)_2]I_2$, which have distorted octahedral symmetry, ligand field parameters were calculated from the electronic transitions.

INTRODUCTION

The interest in the study of hydrazones possessing potential donor sites has been intensively increasing last years because of their pharmacological activity, attributed to their ability to form stable chelates with transition metals present in the vivid cell.[1,2] This process inhibits many vital enzymatic reactions catalyzed by the metal ions. It has been also observed that the biological activity of the hydrazones increases by complexation to metal ions, like copper, nickel, cobalt or iron. Thus, a considerable number of hydrazones and their metal complexes have been reported as tuberculostatic,[3,4] antitumor,[5,6] antibacterial and antifungal[7-9] agents. The thiazole and benzothiazole hydrazones, which have sulphur-nitrogen donor sites, have also been reported to show various pharmacological importance.[10,11] A series of hydrazones obtained by the condensation of 2-hydrazinobenzothiazole with aromatic aldehydes have been demonstrated to possess tuberculostatic and anticonvulsant activity.[12-14] A great number of transition metal complexes with these ligands have been prepared in view of their potential application as antibacterial and antifungal drugs,[15,16] but also for the various bonding and stereochemical possibilities that they offer.[17,18] In continuation of our work on the synthesis of 2-benzothiazolyl hydrazone metal complexes,[19-22] we report here on the synthesis and the characterization of six new Ni(II) complex compounds with 2-aminobenzaldehyde-2-benzothiazolyl hydrazone (HL[a]) and 4-methoxybenzaldehyde-2-benzothiazolyl hydrazone (HL[b]).

A series of 2-benzothiazolyl hydrazones, including 4-methoxybenzaldehyde-2-benzothiazolyl hydrazone were prepared by Katz,[12] by condensing the 2-hydrazinobenzothiazol with the appropriate aldehydes.

Gheorghiu and coworkers have prepared thiazole and benzothiazole derivatives as potential antituberculous agents.[14] Thus, by condensation of 2-hydrazinobenzothiazole with *o*-aminobenzaldehyde they have obtained the corresponding hydrazone, m.p.=262 ^{0}C.

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Hamman and co-workers reported the synthesis and spectral properties of such Co(II), Ni(II) and Cu(II) complexes with 4-methoxybenzaldehyde-2-benzothiazolyl hydrazone; for all these complexes they proposed a pseudo-tetrahedral symmetry.[17]

RESULTS AND DISCUSSION

The hydrazone ligands may exist in two tautomeric forms, (I) and (II) (Fig. 1):
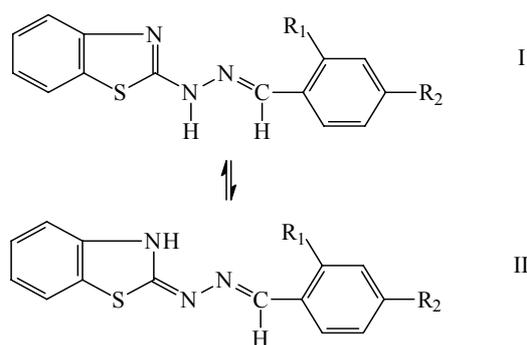
R_1: -NH_2, R_2: H (HL^a) and R_1: H, R_2: -OCH_3 (HL^b)

Fig. 1 – Tautomeric forms of the ligands.

The interaction of 2-aminobenzaldehyde-2-benzothiazolyl hydrazone (HL^a) with nickel chloride yields a monomeric complex compound, [Ni(HL^a)Cl]Cl (**1**) in which the ligand acts as neutral tridentate NNN donor. In reaction of the same ligand with nickel acetate, nickel iodide and nickel nitrate (in the two last cases in the presence of sodium acetate) we obtained the complexes corresponding to the formulas: [$Ni_2L_2^a(CH_3COO)_2(H_2O)_2$] (**2**), [$NiL^a(CH_3COO)(H_2O)$]·$2H_2O$ (**3**) and [$Ni_2L_2^a(CH_3COO)_2$] (**4**), respectively, HL^a acting as monobasic bidentate (in the compounds **2** and **3**) and monobasic tridentate ligand (in the complex **4**).

The two complex compounds with 4-methoxybenzaldehyde-2-benzothiazolyl hydrazone (HL^b) were prepared in the reaction of the ligand with nickel nitrate and nickel iodide, respectively and correspond to the formulas: [$Ni(HL^b)_2(H_2O)_2$](NO_3)$_2$·$3H_2O$ (**5**) and [$Ni(HL^b)_2(H_2O)_2$]I_2 (**6**).

The complexes **1**, **5** and **6** are soluble in moderate polar solvents, such as methanol and ethanol. The complexes **2** and **3** are soluble in non-polar solvents, while the complex **4** is insoluble in all common solvents.

Infrared spectra

IR spectra of the solid benzothiazolyl hydrazones show ν(NH) absorption band at 3184 cm^{-1} (HL^a) and 3189 cm^{-1} (HL^b), due to the NH secondary amine group.[3,23] The presence of this band indicates that the ligands exist in the tautomeric form I in solid state. The assignments of some important infrared bands of the ligands and their nickel(II) complexes are listed in Table 1.

A comparison of the IR spectra of the ligands and those of the complex compounds lead to the following conclusions:

The medium absorption band at 3184-3189 cm^{-1} assigned to ν(N-H) in the IR spectra of the ligands is practically unchanged in the spectra of the complexes **1**, **5** and **6**, but disappears in the spectra of the complexes **2**, **3** and **4**, indicating the tautomerisation and subsequent deprotonation of the ligand at the formation of the last three complexes.[6,24,25]

The two strong bands appearing at 1610-1625 cm^{-1} in the IR spectra of the hydrazone ligands may be assigned to ν(C=N) of the hydrazone function (C=N exocyclic, 1623 cm^{-1} for HL^a and 1618 cm^{-1} for HL^b) and benzothiazole moiety (C=N endocyclic, 1610 cm^{-1} for both the ligands).[10,11,18] These bands shift to lower wave numbers in the IR spectra of the complexes **1**, **5** and **6**, indicating the coordination of the ligands through both the azomethinic nitrogen atoms.[6,23,24] The IR spectra of the complexes **2**, **3** and **4** show only one strong band at 1610-1611 cm^{-1} due to ν(C=N) exocyclic and a very strong band around 1520 cm^{-1}, assigned to skeleton >C=N-N=C<, suggesting deprotonation of the ligand and chelatation through the azomethine nitrogen atoms.[23,24]

The bands assigned to asymmetric and symmetric N-H stretching mode of NH_2 group of the ligand HL^a are shift from their positions in the IR spectra of the complexes **1** and **4**, but remain unchanged for the complexes **2** and **3**. These observations are in accordance with the implication of NH_2 group in the coordination to the metal ion only in the complexes **1** and **4**.[26]

A broad band in the ranges 3300-3600 cm^{-1} and a weak band in the range 615-619 cm^{-1} in the IR spectra of the complexes **2**, **3**, **5** and **6** are attributed to ν(OH) and $ρ_r(H_2O)$ modes of coordinated water, respectively.[10,24]

In the IR spectrum of the complex **5** the new very strong band, appearing at 1383 cm^{-1} is due to the stretching vibration of ionic nitrate group.[27]

Table 1

Characteristic bands in IR spectra of the ligands and their metal complexes ν_{max},cm^{-1}

HL^a	(1)	(2)	(3)	(4)	HL^b	(5)	(6)	Assignments
3462 s	3388 m	3462 m	3460 s	3346 w	-	-	-	ν_{asym}(NH) NH$_2$
3347 m	3265 m	3346 m	3351 m	3300 w	-	-	-	ν_{sym}(NH) NH$_2$
3184 m	3188 m	-	-	-	3189 m	3198 m	3190 w	ν(NHsec)
-	-	3636 m	3419 s	-	-	3397 m	3408 m	ν(OH)
1623 vs	1602 m	1611 s	1611 s	1610 s	1618 s	1607 s	1615 m	ν(C=N) exocyclic
1610 vs	1552 s	-	-	-	1610 s	1560 m	1567 s	ν(C=N) endocyclic
-	-	1521 vs	1520 vs	1522 vs	-	-	-	ν(>C=N-N=C<)
-	-	-	-	-	-	1383 vs	-	ν(NO$_3^-$)
-	-	615 w	619 w	-	-	615 w	637 w	ρ_r(H$_2$O)

The IR spectra of the complexes **2**, **3** and **4** show a new medium absorption band at 1369-1371 cm^{-1}, which may be assigned to ν_{sym}(COO) of acetate group. The strong absorption band at 1480 cm^{-1} in the spectrum of the complex **3** is due to ν_{asym}(COO), the value of $\Delta = \nu_{asym}$(COO) - ν_{sym}(COO) being in the range of bidentate acetate ligand.[27] For the complexes **2** and **4**, ν_{asym}(COO) probably overlaps to the strong absorption of the skeleton >C=N-N=C< and the values of Δ suggest bridged bidentate acetate.[27] It is interesting to observe the presence of these bands in the spectra of the complexes **3** and **4** (obtained from nickel iodide and nickel nitrate, respectively, in presence of sodium acetate) and the absence of a strong band around 1380 cm^{-1}, due to nitrate group for the complex **4**. We can conclude that iodide and nitrate are not presented in the complexes **3** and **4,** respectively.

Thermogravimetric analysis

The observation of the TG curve of the complex (**1**) indicates that it is stable upon 360 ^{0}C. An endothermic process, with maximum at 375 ^{0}C, is due to the loss of anionic and coordinated halide.[28] In the TG curves of the compounds (**3**) and (**5**), a first weight loss at around 100 ^{0}C corresponds to the elimination of the crystalline water.[29] For the complexes (**2**), (**3**), (**5**) and (**6**) the endothermic peak at 175^{0}C, 200 ^{0}C, 210 ^{0}C and 180 ^{0}C respectively, is due to the loss of coordinated water,[29] which is in agreement with the results obtained from the IR spectra. The thermogravimetric curves for the complexes (**2**), (**3**) and (**4**) show an exothermic peak at 320-380 ^{0}C, due to the loss of coordinated acetate.[29] For the complexes (**5**) and (**6**) the exothermic peaks observed at 270 ^{0}C and 300 ^{0}C, respectively,

correspond to the removal of the anionic nitrate and anionic iodide, respectively.[28]

All the complexes lose the organic ligand in a large exothermic process, in the range of 400-800 ^{0}C.

Based on the analytical, IR and thermogravimetrical analyses we can conclude on the composition of the complex compounds and on the behaviour of the two hydrazone ligands in coordination. Thus, the ligand HL^a acts as neutral tridentate ligand in the complex **1**, monobasic bidentate in the complexes **2** and **3** and monobasic tridentate in the complex **4**. The ligand HL^b acts as neutral bidentate ligand in both its complexes.

The dimeric nature of the complexes (**2**) and (**4**) is also supported by the low values of magnetic moments. The determinations of molar weight using the cryoscopy method with chloroform as solvent give for the complexes (**2**) and (**3**) values corresponding to a dimeric, respectively monomeric compounds.

Magnetic and Electronic Spectral Data

The electronic spectral bands of the complex compounds, in solid state, with their assignments, are given in the Table 2. The last column of this table contains the values of magnetic moments.

The magnetic moment for the complex (**1**) is in agreement with a tetrahedral geometry around the metal ion, this symmetry being supported by the electronic transitions.[30]

The electronic spectrum of the complex (**2**) and other results presented above suggest a square pyramidal geometry around metal ion.[31-33] The low magnetic moment is in accordance with the dimeric structure proposed for this complex.

The monomeric complex (**3**), which presents similar IR absorption bands with the complex (**2**) and, as consequence, the same donor groups,

shows an electronic spectrum favoring the high-spin trigonal bipyramidal symmetry.[31,32] Assuming a D_{3h} symmetry, the five observed absorption maxima can be assigned to the spin-allowed transitions given in the Table 2. The absorption band that appears at 26310 cm^{-1} is overlaid upon the ligand absorption.

Table 2

Electronic transitions and magnetic moments for the Ni(II) complexes

Compound	Observed bands (ν_{max}, cm[-1])	Assignments	Symmetry	μ_{eff} (B.M.)
(1)	9020 12500 15500 23809	$^3T_1 \rightarrow {}^3A_2$ $^3T_1 \rightarrow {}^1E^a$ $^3T_1 \rightarrow {}^3T_1(P)$ CT	T_d	3.40
(2)	9090 11627 16600 21413 22779	$^3B_1 \rightarrow {}^3B_2$ $^3B_1 \rightarrow {}^3A_2$ $^3B_1 \rightarrow {}^3E$ (F) $^3B_1 \rightarrow {}^3A_2$ (P) $^3B_1 \rightarrow {}^3E$ (P)	C_{4v}	2.34
(3)	8700 12500 15870 21270 26310	$^3E'$ (F) $\rightarrow {}^3E''$ (F) $^3E'$ (F) $\rightarrow {}^3A_1'', {}^3A_2''$ (F) $^3E'$ (F) $\rightarrow {}^3A_2'$ (F) $^3E'$ (F) $\rightarrow {}^3E''$ (P) $^3E'$ (F) $\rightarrow {}^3A_2'$ (P)	D_{3h}	3.20
(4)	8700 11975 15850 21739 22830	$^3E'$ (F) $\rightarrow {}^3E''$ (F) $^3E'$ (F) $\rightarrow {}^3A_1'', {}^3A_2''$ (F) $^3E'$ (F) $\rightarrow {}^3A_2'$ (F) $^3E'$ (F) $\rightarrow {}^3E''$ (P) $^3E'$ (F) $\rightarrow {}^3A_2'$ (P)	D_{3h}	2.95
(5)	8850 10800 14285 16600 23800	$^3B_{1g} \rightarrow {}^3E_g{}^a$ $^3B_{1g} \rightarrow {}^3B_{2g}$ $^3B_{1g} \rightarrow {}^3A_{2g}{}^a$ $^3B_{1g} \rightarrow {}^3E_g{}^b$ $^3B_{1g} \rightarrow {}^3E_g{}^c, {}^3A_{2g}{}^b$	Distorted O_h (D_{4h})	3.06
(6)	9100 11050 14084 16000 25000 27027	$^3B_{1g} \rightarrow {}^3E_g{}^a$ $^3B_{1g} \rightarrow {}^3B_{2g}$ $^3B_{1g} \rightarrow {}^3A_{2g}{}^a$ $^3B_{1g} \rightarrow {}^3E_g{}^b$ $^3B_{1g} \rightarrow {}^3E_g{}^c$ $^3B_{1g} \rightarrow {}^3A_{2g}{}^b$	Distorted O_h (D_{4h})	3.20

The electronic spectrum of the dimeric complex (4) shows approximately the same absorption maxima as those of the complex (3), despite the important differences due to the coordination of the amino group and the absence of water in the complex compound. The assignments of the observed maxima, presented in Table 2, are also made in a D_{3h} high-spin five-coordinated symmetry.[31,32] We observe here a smaller splitting of the term ^3P.

The electronic spectra of the complexes (5) and (6) are characteristic for a tetragonally distorted octahedral symmetry,[34] with the two hydrazone ligands in the xOy plane and two water molecules in axial positions. The complexes show magnetic moments expected for pseudo-octahedral geometry. Splitting of the first and the second "octahedral" bands is observed for both complexes and permits the calculation of the parameters D_s and D_t [33,34] and hence the splitting of the t_{2g} and e_g orbitals of the metal ion. The third "octahedral" band is split only at the complex (6). A comparison with the position of the first octahedral band for the complex compounds of the type ML_6 (10800 cm^{-1} for $[Ni(NH_3)_6]^{2+}$ and 8500 cm^{-1} for $[Ni(H_2O)_6]^{2+}$) permitted the assignment of the observed bands to the transitions written in Table 2.

Some orbital ligand field parameters calculated in the weak field approach are inserted in Table 3. We note that in the weak field approach the positions of the various transitions are expressed in terms of the crystal field parameters Dq, D_s and D_t, with $Dq_{xy} = E(^3B_{2g})$, $D_t = 4/35[E(^3B_{2g}) - E(^3E_g{}^a)]$

and $6D_s - 5/4 \ D_t = [E(^3E_g^b) - E(^3A_{2g}^a)]$.[34] The molecular orbital parameters $d\sigma$ and $d\pi$, calculated with the relations:

$8d\sigma = -12D_s - 15D_t$; $2d\pi = -3D_s + 5D_t$ were also reported in the Table 3.

Some conclusions may be drawn from the values of these parameters:

The Dq_L and Dq_z values indicate that the crystal field strength of the hydrazone is greater that the field created by the water molecules.

Table 3

Ligand field parameters for the complexes (**5**) and (**6**) (cm^{-1})

Parameter	Complex (**5**)	Complex (**6**)
Dq_L	1080	1105
Dq_z	690	715
D_t	223	223
D_s	432	371
$d\sigma$	-1066	-975
$d\pi$	-90	0
Δ_1	181	0
Δ_3	2843	2601
B	538	669

The negative sign for $d\sigma$ is in accordance with a greater σ-bonding power of the hydrazone ligand than water.

The difference in the π-bonding power of the hydrazone and H_2O is very small, practically zero, so we can see from the $d\pi$ parameter values. As a consequence of $d\sigma$ and $d\pi$, the splitting of e_g orbitals, given by Δ_3 is great, but the splitting of t_{2g} orbitals, Δ_1, is very small.

The signs of Δ_1 and Δ_3 parameters imply the following sequence of the d metal orbital energy:

$$d_{xz}, d_{yz} \approx d_{xy} < d_{z^2} < d_{x^2-y^2}$$

Based on these data, the six Ni(II) complexes are proposed to have the conformations shown in Fig. 2.

Antibacterial and antifungal activity was determinated following the cup-plate agar diffusion technique, against bacillus Gram negative (E. *coli, Pseudomonas aeruginosa serotype IV*), bacillus Gram positive (*Staphylococcus coagulase positive, Streptococcus β-hemolytic type A* and *type B*) and fungi (*Candida albicans, Penicillium*). A solution 10^{-4}M of each compound in acetone was used. The disks impregnated with this solution were applied to the surface of inoculated plates. After incubation for 72 h at 37 ^{0}C, the diameter of the zone of inhibition was measured.

The ligands show no significant activity against the tested bacteria and fungi. The complex compounds **1-4** and **6** have a weak antibacterial and antifungal activity, with inhibition diameter between 1 and 3 mm. Interestingly, the complex **5** shows high activity against *Candida albicans* with an inhibition diameter equal to 10 mm.

EXPERIMENTAL

Reagent grade 2-aminobenzaldehyde, 4-methoxybenzaldehyde, 2-mercaptobenzothiazole and hydrazine hydrate were used to prepare the ligands. 2-hydrazinobenzothiazole was prepared by the reaction of 2-mercaptobenzothiazole with hydrazine hydrate, as literature method.[35] The hydrazones were prepared by condensation reactions of 2-hydrazinobenzothiazole with 2-aminobenzaldehyde (for HL^a) and 4-methoxybenzaldehyde (for HL^b), respectively, according to the reported method.[12,14â]

Preparation of the Complexes

[Ni(HL^a)Cl]Cl (**1**), light-green: chloro(2-aminobenzaldehyde 2-benzothiazolyl hydrazone) nickel(II) chloride. A quantity of 1.34 g (5 mmols) of the ligand HL^a was dissolved in 50 mL ethanol, under reflux. To this solution was added 1.19 g (5 mmols) of NiCl$_2$·6H$_2$O, dissolved in 10 mL ethanol and the mixture was stirred under reflux for 2 h. The light-green precipitate formed was filtered, washed with ethanol and ether and dried in air.

Analytical data: exp.%: C: 42.02; H: 2.85; N: 13.78; Ni: 14.60; calc.%: C: 42.21; H: 3.02; N: 14.07; Ni: 14.82. M.p. = 360 ^{0}C (decomp).

[Ni$_2$L$_2^a$(CH$_3$COO)$_2$(H$_2$O)$_2$] (**2**), green-brown: di-μ-acetato-bis[aqua(2-aminobenzaldehyde 2-benzothiazolyl hydrazonato)nickel(II)], [NiL^a(CH$_3$COO)(H$_2$O)]·2H$_2$O (**3**), brown: aquaacetato(2-aminobenzaldehyde 2-benzothiazolyl hydrazonato)nickel(II) dihydrate and [Ni$_2$L$_2^a$(CH$_3$COO)$_2$] (**4**), dark-green: di-μ-acetato-bis[(2-aminobenzaldehyde 2-benzothiazolyl hydrazonato)nickel(II)]. To the same quantity of the ligand dissolved in methanol with heating, the corresponding nickel(II) salt: 1.245 g (5 mmols) of Ni(CH$_3$COO)$_2$·4H$_2$O for the complex (**2**), 1.565 g (5 mmols) of NiI$_2$ for the complex (**3**) and 1.455 g (5 mmols) of Ni(NO$_3$)$_2$·6H$_2$O for the complex (**4**) was added. For the last two syntheses, approximately 0.82 g (10 mmols) of sodium acetate were also added. The resulted solution was refluxed for 2-3 h and then cooled to room temperature, when solid products separated out.

Analytical data: Complex (**2**) exp.%: C: 47.30; H: 3.62; N: 13.72; Ni: 14.43; calc.%: C: 47.64; H: 3.97; N: 13.89; Ni: 14.64. M.p. = 175 ^{0}C (decomp).
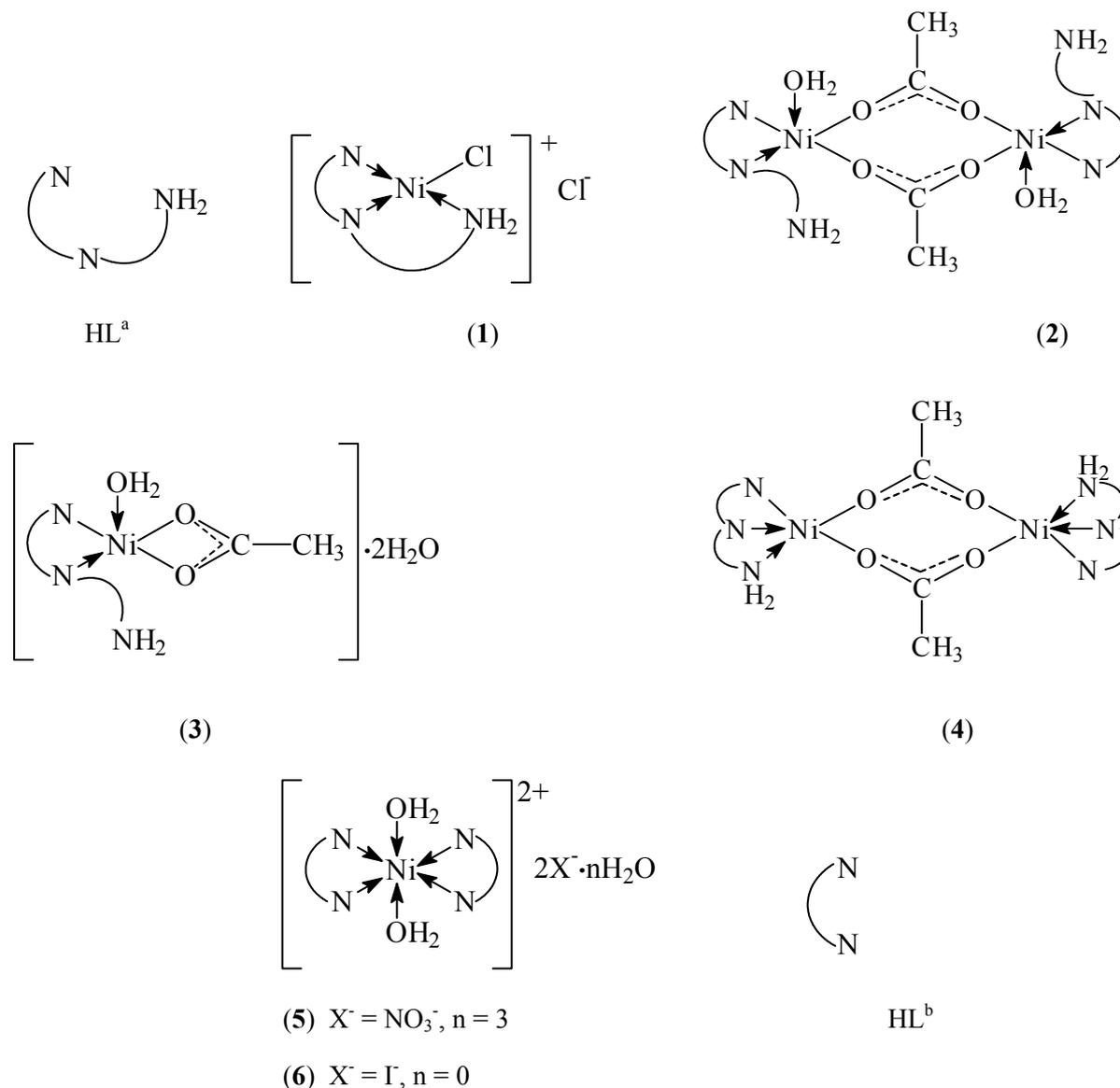
Fig. 2 – Proposed structures of the complexes.

Complex (**3**) exp.%: C: 43.48; H: 4.38; N: 12.60; Ni: 13.40; calc.% : C : 43.73 ; H : 4.55 ; N : 12.75 ; Ni : 13.43. M.p. = 100 ^{0}C (decomp).

Complex (**4**) exp.%: C: 49.60; H: 3.41; N: 14.33; Ni: 15.05; calc.% : C : 49.87 ; H : 3.63 ; N : 14.54 ; Ni : 15.32. M.p. = 340 ^{0}C (decomp).

[Ni(HL^b)$_2$(H$_2$O)$_2$](NO$_3$)$_2$·3H$_2$O (**5**), green: diaqua bis(4-methoxybenzaldehyde 2-benzothiazolyl hydrazone)nickel(II) nitrate trihydrate and [Ni(HL^b)$_2$(H$_2$O)$_2$]I$_2$ (**6**), yellow-brown: diaqua bis(4-methoxybenzaldehyde 2-benzothiazolyl hydrazone)nickel(II) iodide were prepared by the following method: a hot suspension of 1.415 g HL^b (5 mmols) in 30 mL ethanol was mixed with 0.727 g (2.5 mmols) of Ni(NO$_3$)$_2$·6H$_2$O or 0.782 g (2.5 mmols) of NiI$_2$, respectively. The resulting solutions were heated under reflux for 1 h and the solids formed were filtered off, washed with ethanol and dried at air.

Analytical data: Complex (**5**) exp.%: C: 42.63; H: 3.98; N: 13.02; Ni: 6.82; calc.%: C: 42.90; H: 4.29; N: 13.34; Ni: 7.03. M.p. = 100 ^{0}C (decomp).

Complex (**6**) exp.%: C: 39.03; H: 3.01; N: 8.89; Ni: 6.40; calc.% : C : 39.34 ; H : 3.27 ; N : 9.18 ; Ni : 6.44. M.p. = 180 ^{0}C (decomp).

The purity of the hydrazone Schiff base and its complexes was confirmed by C, H and N analyses. The metal content was determined by standard procedures.

Infrared spectra (in KBr pellets) were recorded on a BIORAD FTIR 135 spectrophotometer, in the range of 4000-400 cm^{-1}. Diffuse reflectance spectra were measured on a Specord M-40 spectrophotometer in the range of 200-900 nm. Thermogravimetric analyses were carried out in static air atmosphere, at a heating rate of 10 ^{0} C/min, using a MOM Q-1500 derivatograph. Magnetic susceptibility measurements were performed by the Faraday method at room temperature using Hg[Co(SCN)$_4$] as a calibrant.

CONCLUSIONS

We have prepared and characterized six new complex compounds of Ni(II) with 2-aminobenzaldehyde-2-benzothiazolyl hydrazone (HL^a) and 4-methoxybenzaldehyde-2-benzothiazolyl hydrazone (HL^b). Using nickel(II) acetate, or nickel(II) nitrate or iodide in the presence of sodium acetate, the tautomerisation and deprotonation of the ligand HL^a takes place.

The values of ligand field parameters, calculated for the complexes with 4-methoxybenzaldehyde-2-benzothiazolyl hydrazone, indicate that such ligands give strong σ-bonding, but weak π-bonding.

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