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## Synthesis and Properties of Coordination Compounds of Co(II) and Ni(II) with Some Hydrazone Derivatives

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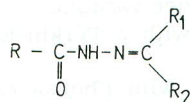
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Reaction of some aroylhydrazones with Co(II) and Ni(II) salts were investigated and the corresponding complexes were isolated. Magnetic and spectral data showed that in the case of metal chloride and nitrate octahedral complexes were formed, with ligands coordinated as neutral molecules. In the case of Ni(II) acetate square planar complexes and with Co(II) acetate paramagnetic complexes were obtained, all of them with deprotonated ligands.

### INTRODUCTION

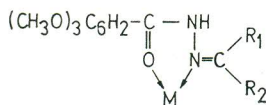
The aroylhydrazones were reported to possess physiological activity<sup>1,2</sup> and their action was attributed to formation of complexes with transition metals present in the vivid cell. This process inhibits many vital enzymatic reactions catalyzed by these metal ions<sup>3,4</sup> and, therefore, coordination chemistry of aroylhydrazones and corresponding compounds was object of many studies<sup>5-7</sup>.

In continuation of our studies on the coordinating properties of aroylhydrazones, the present work is devoted to a fairly detailed study of the interaction of nickel(II) and cobalt(II) salts with some bidentate aroylhydrazones obtained by the reaction of 3,4,5-trimethoxybenzoylhydrazine and carbonyl component — acetone, benzaldehyde and *N,N*-*p*-dimethylaminobenzaldehyde.

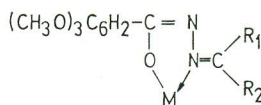


(1)

Aroylhydrazones of type I were found to react with these divalent transition metal ions forming either neutral (IIa) or cationic (IIb) metal complexes in which the aroylhydrazone molecule refers to the neutral and mononegative ligands, respectively.



(11a)



(11b)

## EXPERIMENTAL

*Preparation of Organic Ligands<sup>8</sup>*

*N*<sup>1</sup>-acetone-3,4,5-trimethoxybenzoylhydrazone (HLA). — A solution of 11.3 g (0.05 mol) 3,4,5-trimethoxybenzoylhydrazine (HL) in 30 cm<sup>3</sup> acetone was heated in a water-bath for 3 hrs. After cooling, the crude hydrazone was filtered, washed with acetone and dried. The yield of pure product, *T*<sub>m</sub> = 388 K, was 65%.

*N*<sup>1</sup>-benzaldehyde-3,4,5-trimethoxybenzoylhydrazone (HLB). — A solution of 11.3 g (0.05 mol) of HL and 5.6 cm<sup>3</sup> (0.05 mol) benzaldehyde in 40 cm<sup>3</sup> 96% ethanol was refluxed for 3 hrs. The reaction mixture was kept at room temperature and then water was gently added by stirring when the clear solution became turbid. After a short time, a white precipitate was obtained. The product was filtered and the obtained solid was dried. Recrystallization of the crude product from 96% ethanol gave pure hydrazone in a good yield (60)%, with *T*<sub>m</sub> = 416 K.

*N*<sup>1</sup>-*N,N*-*p*-dimethylaminobenzaldehyd-3,4,5-trimethoxybenzoylhydrazone (HLBD). — 7.46 g (0.05 mol) of *p*-dimethylaminobenzaldehyde was added by stirring to a solution of 11.3 g (0.05 mol) HL in 80 cm<sup>3</sup> methanol. The reaction mixture was refluxed for 4 hrs. After cooling, the formed light yellow crystals of the hydrazone were collected, dried and recrystallized from methanol. The yield was 58%, *T*<sub>m</sub> = 489 K.

*Preparation of Cobalt(II) and Nickel(II) Complexes*

*Bis(aroylhydrazone)cobalt(II) and nickel(II)-chloride or nitrate complexes.* — A hot aqueous solution of cobalt(II) or nickel(II)-chloride hexahydrate (0.01 mol) was treated with a hot solution of (0.02 mol) HLA in acetone (30 cm<sup>3</sup>), HLB in 96% ethanol (30 cm<sup>3</sup>) or HLBD in methanol (30 cm<sup>3</sup>), respectively. The reaction mixture was refluxed for 1/2 hr. On cooling, the precipitates of bis(aroylhydrazone) cobalt(II) complexes were filtered, washed with acetone, 96% ethanol or methanol, respectively, depending on the used aroylhydrazone and then dried under vacuum.

The same procedure was adopted for the preparation of bis(aroylhydrazone)cobalt(II) or nickel(II)-nitrate complexes.

*Bis(aroylhydrazonato)cobalt(II) or nickel(II) complexes.* — A hot solution of cobalt(II) or nickel(II) acetate dihydrate (0.01 mol) in 50% aqueous ethanol was added to a boiling solution of the corresponding aroylhydrazone (0.02 mol) in 30 cm<sup>3</sup> either acetone, or 96% ethanol and methanol, respectively. The reaction mixture was refluxed for 1 hr and after cooling the precipitated complex was filtered, washed with ethanol and dried under vacuum.

*Infrared spectra* were taken with a Perkin-Elmer 580 spectrophotometer with KBr discs.

*Electronic spectra* were taken with Photoacoustic spectrometer Gilford R-1500.

*Magnetic measurements* were made at 300 K by the Faraday method, using Hg[Co(NCS)<sub>4</sub>] as calibrant. Conventional diamagnetic corrections were made using Paskal's constants.

*Thermogravimetric analyses* were made with thermoanalysis apparatus NETZSCH, Geratebau GmbH Selb, with Al<sub>2</sub>O<sub>3</sub> as standard.

*The molar conductance* of DMF solution (10<sup>-3</sup> mol dm<sup>-3</sup>) at 298 K was obtained with a conductometer type MA 5962, Iskra Kranj.

## RESULTS AND DISCUSSION

The reaction of aroylhydrazones of type (I) (HLA = *N*<sup>1</sup>-acetone-3,4,5-trimethoxybenzoylhydrazone, HLB = *N*<sup>1</sup>-benzaldehyd-3,4,5-trimethoxybenzoylhydrazone, HLBD = *N*<sup>1</sup>-*N,N*-*p*-dimethylaminobenzaldehyd-3,4,5-trimethoxybenzoylhydrazone) with Co(II) and Ni(II) chloride and nitrate gave the bis ligand complexes of the general formula  $M(\text{HL-Hon})_2\text{X}_2 \cdot m\text{H}_2\text{O}$ , where HL-Hon refers to the corresponding neutral aroylhydrazone molecules HLA, HLB and HLBD.

The cobalt complexes had a pink colour, while the nickel complexes were from light green to yellow. These chelates are hardly soluble in water, ethanol and methanol but well soluble in DMF and acetonitril.

Elemental analyses are listed in Tables I and II.

On the other hand, the reaction of Co(II) and Ni(II) acetate dihydrate with the corresponding aroylhydrazones afforded the complexes. The cobalt complexes are pink and those of nickel are red to violet. The isolated complexes are insoluble in water, ethanol, methanol and dioxane, while soluble in DMF with exception of Ni(LB)<sub>2</sub> and Ni(LBD)<sub>2</sub>.

In accordance with elemental analyses (Table III), these complexes can be represented by the formula  $M(\text{L-Hon})_2$  where L-Hon refers to a deprotonated molecule of the corresponding aroylhydrazone ligand.

The prepared aroylhydrazones and the corresponding Co(II) and Ni(II) complexes were characterized by their infrared spectra, magnetic measurement data and electronic spectral data.

In the spectrum of the HLA, HLB and HLBD the bands which originated from the stretching NH vibrations, Amide I, Amide II and Amide III were observed at different frequencies, depending on the used aroylhydrazone<sup>9</sup> (Table IV).

TABLE I  
Analytical Data and *T<sub>m</sub>* of Co(II) Complexes

Complexes	M/%	C/%	H/%	N/%	Cl/%	H <sub>2</sub> O/%	<i>T<sub>m</sub></i> /K
Co(HLA) <sub>2</sub> Cl <sub>2</sub> (CoC <sub>26</sub> H <sub>36</sub> N <sub>4</sub> O <sub>8</sub> Cl <sub>2</sub> )	9.11 (8.89)*	48.20 (47.14)	5.44 (5.49)	9.01 (8.45)	10.57 (10.70)		over 543
Co(HLA) <sub>2</sub> (NO <sub>3</sub> ) <sub>2</sub> · 3H <sub>2</sub> O (CoC <sub>26</sub> H <sub>42</sub> N <sub>6</sub> O <sub>17</sub> )	8.07 (7.67)	41.14 (40.57)	5.92 (5.50)	11.14 (10.92)		7.20 (7.02)	451
Co(HLB) <sub>2</sub> Cl <sub>2</sub> (CoC <sub>34</sub> H <sub>36</sub> N <sub>4</sub> O <sub>8</sub> Cl <sub>2</sub> )	7.15 (7.74)	53.54 (53.69)	5.00 (4.77)	8.00 (7.36)	9.75 (9.32)		over 543
Co(HLB) <sub>2</sub> (NO <sub>3</sub> ) <sub>2</sub> (CoC <sub>34</sub> H <sub>36</sub> N <sub>6</sub> O <sub>14</sub> )	7.88 (7.26)	50.60 (50.31)	4.29 (4.47)	10.80 (10.35)			504
Co(HLBD) <sub>2</sub> Cl <sub>2</sub> (CoC <sub>38</sub> H <sub>46</sub> N <sub>6</sub> O <sub>8</sub> Cl <sub>2</sub> )	6.89 (6.97)	54.17 (54.03)	5.55 (5.48)	10.15 (9.94)	8.47 (8.89)		490
Co(HLBD) <sub>2</sub> (NO <sub>3</sub> ) <sub>2</sub> (CoC <sub>38</sub> H <sub>46</sub> N <sub>8</sub> O <sub>14</sub> )	6.90 (6.54)	50.74 (50.83)	5.29 (5.16)	12.77 (12.48)			465

\* The values in brackets are calculated.

TABLE II  
Analytical Data and  $T_m$  of Ni(II) Complexes

Complexes	M/%	C/%	H/%	N/%	Cl/%	H <sub>2</sub> O/%	$T_m$ /K
Ni(HLA) <sub>2</sub> Cl <sub>2</sub> (NiC <sub>26</sub> H <sub>36</sub> N <sub>4</sub> O <sub>8</sub> Cl <sub>2</sub> )	8.17 (8.86)*	46.66 (47.15)	5.15 (5.48)	9.10 (8.46)	11.11 (10.70)		over 543
Ni(HLA) <sub>2</sub> (NO <sub>3</sub> ) <sub>2</sub> · 3H <sub>2</sub> O (NiC <sub>26</sub> H <sub>42</sub> N <sub>6</sub> O <sub>17</sub> )	7.97 (7.63)	39.95 (40.58)	5.32 (5.50)	11.43 (10.92)		7.15 (7.02)	456
Ni(HLB) <sub>2</sub> Cl <sub>2</sub> (NiC <sub>34</sub> H <sub>36</sub> N <sub>4</sub> O <sub>8</sub> Cl <sub>2</sub> )	7.17 (7.74)	54.00 (53.87)	5.15 (4.78)	8.01 (7.38)	9.84 (9.35)		over 543
Ni(HLB) <sub>2</sub> (NO <sub>3</sub> ) <sub>2</sub> (NiC <sub>34</sub> H <sub>36</sub> N <sub>6</sub> O <sub>14</sub> )	6.98 (7.23)	51.06 (50.32)	4.33 (4.47)	11.00 (10.35)			520
Ni(HLBD) <sub>2</sub> Cl <sub>2</sub> (NiC <sub>36</sub> H <sub>46</sub> N <sub>6</sub> O <sub>8</sub> Cl <sub>2</sub> )	6.76 (6.95)	53.61 (54.04)	5.22 (5.49)	10.10 (9.95)	8.47 (8.39)		511
Ni(HLBD) <sub>2</sub> (NO <sub>3</sub> ) <sub>2</sub> (NiC <sub>38</sub> H <sub>46</sub> N <sub>8</sub> O <sub>14</sub> )	6.69 (6.54)	51.11 (50.87)	5.00 (5.16)	13.02 (12.48)			487

\* The values in brackets are calculated.

TABLE III  
Analytical Data and  $T_m$  of Bis(hydrazone)complexes

Complexes	M/%	C/%	H/%	N/%	$T_m$ /K
Co(LA) <sub>2</sub> (CoC <sub>26</sub> H <sub>34</sub> N <sub>4</sub> O <sub>8</sub> )	9.75 (9.99)*	52.12 (52.97)	5.41 (5.81)	10.16 (9.50)	491
Co(LB) <sub>2</sub> (CoC <sub>34</sub> H <sub>34</sub> N <sub>4</sub> O <sub>8</sub> )	8.77 (8.59)	60.00 (59.56)	4.53 (4.99)	8.69 (8.17)	501
Co(LBD) <sub>2</sub> (CoC <sub>38</sub> H <sub>44</sub> N <sub>6</sub> O <sub>8</sub> )	7.55 (7.63)	58.93 (59.14)	5.41 (5.74)	11.01 (10.89)	471
Ni(LA) <sub>2</sub> (NiC <sub>26</sub> H <sub>34</sub> N <sub>4</sub> O <sub>8</sub> )	10.10 (9.96)	53.11 (52.99)	5.61 (5.81)	10.20 (9.50)	535
Ni(LB) <sub>2</sub> (NiC <sub>34</sub> H <sub>34</sub> N <sub>4</sub> O <sub>8</sub> )	8.11 (8.56)	60.12 (59.58)	4.93 (5.00)	8.41 (8.17)	540
Ni(LBD) <sub>2</sub> (NiC <sub>38</sub> H <sub>44</sub> N <sub>6</sub> O <sub>8</sub> )	7.87 (7.61)	59.81 (59.15)	5.59 (5.74)	10.51 (10.89)	over 543

\* The values in brackets are calculated.

The infrared spectra of the complexes, M(HL-Hon)<sub>2</sub>X<sub>2</sub> · mH<sub>2</sub>O, are similar to those of the parent arylhydrazone ligands. The positions of both  $\nu$ (C=O) and  $\nu$ (C=N) bands are generally lower than the values of the parent ligands suggesting bidentate nature of the ligands and formation of five membered chelating rings (Table IV)<sup>10</sup>. These spectra suggest the coordination mode (IIa).

In the infrared spectra of the complexes, M(L-Hon)<sub>2</sub>,  $\nu$ (N-H),  $\delta$ (N-H) and  $\nu$ (C=O) the vibrations disappear, and at least two bands typical of the chelating five membered rings can be observed, due to the deprotonation of

the ligands. These spectra suggest the coordination mode (IIb) in which the aroylhydrazone molecule acts as a mononegative bidentate ligand (Table V).

TABLE IV  
*Infrared Spectral Data for Aroylhydrazones and Their Complexes*

Compounds	$\nu(\text{NH})$ $\nu(\text{OH})$	Amide I	$\nu(\text{C}=\text{C})$ $\nu(\text{C}=\text{N})$	Amide II Amide III	
(HLA)	3212s	1630s	1572s	1530s 1338s	
Ni(HLA) <sub>2</sub> (NO <sub>3</sub> ) <sub>2</sub> · 3H <sub>2</sub> O	3450s 3200m	1612m	1570s	1550sh 1345s	$\nu(\text{NO})$ ~ 1382s
Ni(HLA) <sub>2</sub> Cl <sub>2</sub>	3200s	1615m	1574s	1540sh 1342s	
Co(HLA) <sub>2</sub> (NO <sub>3</sub> ) <sub>2</sub> · 3H <sub>2</sub> O	3460s	1618w	1582s	1555w 1350s	$\nu(\text{NO})$ ~ 1388s
Co(HLA) <sub>2</sub> Cl <sub>2</sub>	3210m	1615m	1574s	1540w 1342s	
(HLB)	3180m	1650s	1585s	1555sh 1333s	
Ni(HLB) <sub>2</sub> (NO <sub>3</sub> ) <sub>2</sub>	3200m	1602m	1572s	1550sh 1343s	$\nu(\text{NO})$ ~ 1383s
Ni(HLB) <sub>2</sub> Cl <sub>2</sub>	3220m	1600s	1570s	1340s	
Co(HLB) <sub>2</sub> (NO <sub>3</sub> ) <sub>2</sub>	3200m	1608s	1574s	1340s	$\nu(\text{NO})$ ~ 1380s
Co(HLB) <sub>2</sub> Cl <sub>2</sub>	3195m	1605s	1575s	1340m	
(HLBD)	3200s	1640s	1610w 1570w	1535s 1340s	
Ni(HLBD) <sub>2</sub> (NO <sub>3</sub> ) <sub>2</sub>	3195m	1612w	1588s 1570sh	1340w	$\nu(\text{NO})$ ~ 1380s
Ni(HLBD) <sub>2</sub> Cl <sub>2</sub>	3190m	1610w	1600s 1570sh	1342w	
Co(HLBD) <sub>2</sub> (NO <sub>3</sub> ) <sub>2</sub>	3200m	1605m	1580s 1570sh	1338w	$\nu(\text{NO})$ ~ 1378s
Co(HLBD) <sub>2</sub> Cl <sub>2</sub>	3200w	1610w	1585s 1570sh	1560s 1340w	

Magnetic susceptibility measurements show that all cobalt(II) chloride and nitrate complexes, Co (HL-Hon)<sub>2</sub>X<sub>2</sub> · mH<sub>2</sub>O, are paramagnetic with effective magnetic moments (Table VI) varying from 4.33–5.00  $\mu_B$ , which are within the range reported for high-spin complexes with pseudooctahedral symmetry. The values of the magnetic moments are sensitive to the nature of acid ions (Cl > NO<sub>3</sub>) and therefore the observed low (4.33–4.86  $\mu_B$ ) of the nitrate complexes (chloride complexes have  $\mu_{\text{eff}} = 4.86$ –5.00  $\mu_B$ ) may be due to strong tetragonal distortion resulting from the relatively weak ligand field strength of the nitrate ion<sup>11,13</sup>. The magnetic moments of nickel(II) chloride and

TABLE V  
Infrared Spectral Data for Bis(hydrazone)complexes

Compounds	Bands typical of the chelating ring	
Ni(LA) <sub>2</sub>	1555s	1368s
Co(LA) <sub>2</sub>	1530s	1370s
Ni(LB) <sub>2</sub>	1522s	1370s
Co(LB) <sub>2</sub>	1500s	1368s
Ni(LBD) <sub>2</sub>	1582s	1363s
	1520s	
Co(LBD) <sub>2</sub>	1585s	1370s
	1520s	

nitrate complexes varying from 2.83—3.28  $\mu_B$  and their electronic spectra are quite similar and are clearly indicative of pseudooctahedral structures (Table VI).

TABLE VI  
Magnetic Measurements Data and Molar Conductivity of the Complexes

Complexes	Colour	$\mu_{eff}/\mu_B$	$\lambda$
			S cm <sup>2</sup> mol <sup>-1</sup>
Co(HLA) <sub>2</sub> Cl <sub>2</sub>	pink	4.89	40.11
Co(HLA) <sub>2</sub> (NO <sub>3</sub> ) <sub>2</sub> · 3H <sub>2</sub> O	pink	4.33	145.00
Co(HLB) <sub>2</sub> Cl <sub>2</sub>	pink	4.86	40.11
Co(HLB) <sub>2</sub> (NO <sub>3</sub> ) <sub>2</sub>	pink	4.68	152.80
Co(HLB) <sub>2</sub> Cl <sub>2</sub>	pink	5.00	28.74
Co(HLBD) <sub>2</sub> (NO <sub>3</sub> ) <sub>2</sub>	pink	4.64	145.85
Ni(HLA) <sub>2</sub> Cl <sub>2</sub>	blue	3.28	80.20
Ni(HLA) <sub>2</sub> (NO <sub>3</sub> ) <sub>2</sub> · 3H <sub>2</sub> O	blue	2.83	160.00
Ni(HLB) <sub>2</sub> Cl <sub>2</sub>	greenish blue	3.18	80.20
Ni(HLB) <sub>2</sub> (NO <sub>3</sub> ) <sub>2</sub>	greenish	3.16	160.00
Ni(HLBD) <sub>2</sub> Cl <sub>2</sub>	greenish	3.13	64.17
Ni(HLBD) <sub>2</sub> (NO <sub>3</sub> ) <sub>2</sub>	greenish	2.98	145.85

The electronic spectra of these complexes confirm this assignment. The bands at about 16 000 and 10 000 cm<sup>-1</sup> may be identified as <sup>3</sup>A<sub>2g</sub> → <sup>3</sup>T<sub>1g</sub> and <sup>3</sup>A<sub>2g</sub> → <sup>3</sup>T<sub>2g</sub> transitions. The broadening or splitting of  $\nu_1$  band at about 10 000 cm<sup>-1</sup> in the spectra of Ni(II) complexes indicates some possibly tetragonal distortion (Table VII).

The bands observed in the electronic spectra of the examined cobalt(II) chloride and nitrate complexes (Table VIII) are characterized by the electronic transitions, which suggests a pseudooctahedral environment around the cobalt(II)<sup>13</sup>. The spectra consist of a band in the near infrared which is assigned to the lowest energy transition <sup>4</sup>T<sub>1g</sub> → <sup>4</sup>T<sub>2g</sub> and a band in the visible near 20 000 cm<sup>-1</sup> which is assigned to the <sup>4</sup>T<sub>1g</sub> → <sup>4</sup>T<sub>1g</sub> (P) transition.

TABLE VII

*Electronic Spectral Data (cm<sup>-1</sup>) for Ni(II) Complexes*

Complexes	<sup>3</sup> A <sub>2g</sub> → <sup>3</sup> T <sub>1g</sub> (P)	<sup>3</sup> A <sub>2g</sub> → <sup>3</sup> T <sub>1g</sub>	<sup>3</sup> A <sub>2g</sub> → <sup>3</sup> T <sub>2g</sub>
Ni(HLA) <sub>2</sub> Cl <sub>2</sub>		16 129m	10 121s
Ni(HLA) <sub>2</sub> (NO <sub>3</sub> ) <sub>2</sub> · 3H <sub>2</sub> O		16 260m	10 183s
Ni(HLB) <sub>2</sub> (NO <sub>3</sub> ) <sub>2</sub>	22 222w	15 873w	10 101s
Ni(HLB) <sub>2</sub> Cl <sub>2</sub>	21 505m	14 970m	10 101s
Ni(HLBD) <sub>2</sub> (NO <sub>3</sub> ) <sub>2</sub>	21 276m	15 873w	10 152s
Ni(HLBD) <sub>2</sub> Cl <sub>2</sub>	22 727w	15 432w	10 152s

TABLE VIII

*Electronic Spectral Data (cm<sup>-1</sup>) for Co(II) Complexes*

Complexes	<sup>4</sup> T <sub>1g</sub> → <sup>4</sup> T <sub>1g</sub> (P)	<sup>4</sup> T <sub>1g</sub> → <sup>4</sup> T <sub>2g</sub>
Co(HLA) <sub>2</sub> Cl <sub>2</sub>	19 607m	10 152s
Co(HLA) <sub>2</sub> (NO <sub>3</sub> ) <sub>2</sub> · 3H <sub>2</sub> O	20 833m	10 204s
Co(HLB) <sub>2</sub> (NO <sub>3</sub> ) <sub>2</sub>	21 052s	10 152s
Co(HLB) <sub>2</sub> Cl <sub>2</sub>	20 000s	10 070s
Co(HLBD) <sub>2</sub> (NO <sub>3</sub> ) <sub>2</sub>	19 920s	10 050s
Co(HLBD) <sub>2</sub> Cl <sub>2</sub>	20 833m	10 040s

TABLE IX

*Magnetic Measurements Data and Molar Conductivity for Bis(hydrazonato)complexes*

Complexes	Colour	$\mu_{\text{eff}}/\mu_B$	$\lambda$
			S cm <sup>2</sup> mol <sup>-1</sup>
Co(LA) <sub>2</sub>	pink	4.31	8.00
Co(LB) <sub>2</sub>	pink	4.28	4.09
Co(LBD) <sub>2</sub>	pink	4.22	3.37
Ni(LA) <sub>2</sub>	red	diamagnetic	8.00
Ni(LB) <sub>2</sub>	orange	diamagnetic	not soluble
Ni(LBD) <sub>2</sub>	red-violet	diamagnetic	not soluble

On the basis of magnetic, electronic and infrared spectral data it is suggested that the two chloride and nitrate anions are coordinated to the central cobalt(II) or nickel(II) probably in trans axial position completing the pseudo-octahedral symmetry. The molar conductivity determines the nitrate complexes as ternary and the chloride complexes as binary electrolytes<sup>12</sup>. Magnetic susceptibility measurements showed that all the neutral cationic nickel complexes, Ni(L-Hon)<sub>2</sub>, are diamagnetic (Table IX), and because their stoichiometry suggests the apparent coordination number four for the central nickel ion, a square planar structure is accordingly possible.

TABLE X

*Electronic Spectral Data (cm<sup>-1</sup>) for Bis(hydrazonato)Ni(II) Complexes*

Complexes	<sup>1</sup> A <sub>1g</sub> → <sup>1</sup> A <sub>2g</sub> (b <sub>2g</sub> →b <sub>1g</sub> )
Ni(LA) <sub>2</sub>	19 230 s
Ni(LB) <sub>2</sub>	19 047 s
Ni(LBD) <sub>2</sub>	20 000 s 17 482 s

TABLE XI

*Electronic Spectral Data (cm<sup>-1</sup>) for Bis(hydrazonato)Co(II) Complexes*

Complexes			
Co(LA) <sub>2</sub>	19 607s	10 152m	6 747m
Co(LB) <sub>2</sub>	19 230s	10 224m	6 756m
Co(LBD) <sub>2</sub>	20 202s 18 348s	10 172m	6 743m

Their spectra frequently consist of a strong band around 17 482 and 20 000 cm<sup>-1</sup>. These bands are commonly assigned to transitions <sup>1</sup>A<sub>1g</sub>→<sup>1</sup>A<sub>2g</sub>. The planar configuration is stabilized by strong nickel-ligand covalent bonding (both  $\sigma$  and  $\pi$  bonding) and short nickel-ligand bond lengths are frequently observed in planar complexes (Table X).

In the case of neutral cationic cobalt complexes, Co(L-Hon)<sub>2</sub>, the magnetic measurements show that all complexes of this type are paramagnetic (Table IX) with  $\mu_{\text{eff}}$  varying from 4.22—4.31  $\mu_{\text{B}}$ , implying both the square planar and tetrahedral environment around the cobalt(II) ion. Molecular association, however, may give rise to five or six coordinate structures. Thus, a square planar structure can be fairly ruled out<sup>14</sup>.

This range of magnetic moments (high-spin complexes) covers those reported for tetrahedral, pentacoordinate and octahedral structures. On the other hand, electronic spectra showed bands both in the near infrared and the visible region<sup>15</sup> (Table XI). The position of the bands, as well as their intensities, account for the octahedral structure but can be related to either pseudo-octahedral or dimeric pentacoordinate structures.

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### SAŽETAK

#### Sinteza i svojstva koordinacionih spojeva Co(II) i Ni(II) sa nekim hidrazinskim derivatima

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Izolovana su i ispitivana svojstva odgovarajućih kompleksa koji nastaju reakcijom aroilhidrazona sa solima Co(II) i Ni(II). Magnetni i spektralni podaci pokazuju da u slučaju upotrebe klorida i nitrata nastaju oktaedarski kompleksi sa ligandima koordinovanim kao neutralne molekule. U slučaju Ni(II)-acetata stvaraju se dijamagnetni kvadratno-planarni kompleksi, a sa Co(II)-acetatom dobijaju se paramagnetni kompleksi, u oba slučaja sa deprotonovanim ligandima.