Zn(II), Co(II) AND Ni(II) COMPLEXES OF A PHOSPHORYLTHIOUREA DERIVATIVE OF 4-[$(EtO)_2P(O)CH_2$]-C_6H_4-NHC(S)NHP(O)(O*i*Pr)$_2$

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The reaction of *O,O′*-diisopropyl phosphorisothiocyanatidate, (*i*PrO)$_2$P(O)NCS, with diethyl-(4-aminobenzyl)phosphonate leads to the new *N*-phosphorylated thiourea derivative, 4-[$(EtO)_2P(O)CH_2$]-C_6H_4NHC(S)NHP(O)(O*i*Pr)$_2$ (**HL**). The reaction of its potassium salt **KL** with Zn(II) or Co(II) in aqueous EtOH leads to the complexes of formulae M(L-*O,S*)$_2$ (**ZnL$_2$**, **CoL$_2$**). The metal cation in all complexes is coordinated by two deprotonated ligands through the sulfur atoms of the thiocarbonyl groups and the oxygen atoms of the phosphoryl groups. The reaction of **KL** with Ni(II) leads to the formation of two types of complexes: the blue **Ni(L-*N,S*)$_2$** complex, where the ligand is coordinated through the nitrogen atom of the phosphorylamide group and the sulfur atom of the thiocarbonyl groups and light red **Ni(L-*O,S*)$_2$** complex with the same coordination of L^- anion as it was observed for **ZnL$_2$** and **CoL$_2$**. According to UV/Vis spectral data, it was established that the metal cation of **Ni(L-*N,S*)$_2$** is in a square-planar environment in CH_2Cl_2, whereas the **Ni(L-*O,S*)$_2$** complex shows features of tetrahedral complexes.
Keywords: Coordination chemistry; Zinc complexes; Cobalt complexes; Nickel complexes; *N*-Phosphorylthiourea; Chelates; *N,S*-Ligands; Phosphonates.

The coordination chemistry of polyfunctional ligands, capable of realizing different coordination modes with metal cations[1], is of interest for synthesis of new selective complexing agents and analytical reagents. The reasons that allow such ligands to bind metal ions in the various specific ways are intimately connected with such fundamental problems of chemistry as the nature of chemical bonding and the isomerism of coordination compounds as well as the influence of the ligand structure on regio- and stereoselectivity of the bond formation.

Complexes of Zn(II), Co(II) and Ni(II) with *N*-(thio)phosphorylated (thio)amides and (thio)ureas RC(X)NHP(Y)R′$_2$ (X, Y = O, S) (**HZ**) are of interest because of the diversity in composition of obtained complexes, versatility of the coordination modes around the central ion and different magnetic

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properties[2–9]. An overwhelming majority of these complexes contain ligands with the same donor chalcogen atoms (X = Y)[5–9].

Coordination compounds of Zn(II), Co(II) and Ni(II) cations with **HZ** ligands, containing both sulfur and oxygen donor atoms (X ≠ Y), still remain poorly explored. The presence of the hard-donor carbonyl or phosphoryl oxygen atoms in the coordination sphere of the central ion makes it coordinately unsaturated, which, in turn, might lead to the formation of heteroligand and polynuclear complexes with the central atom having the coordination number 5 or 6, or the formation of different isomers. Hence, amidothiophosphates, containing different donor atoms X and Y, show different coordination properties compared to their dithio analogues RC(S)NHP(S)R′$_2$.

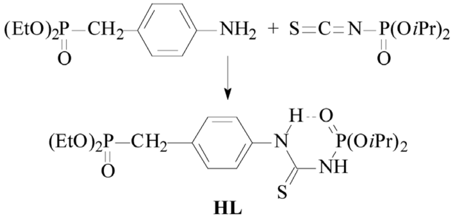
The aim of the present work is to assess the effect of the structure of the amidophosphate ligand 4-[(EtO)$_2$P(O)CH$_2$]C$_6$H$_4$NHC(S)NHP(O)(O*i*Pr)$_2$ (**HL**) on the composition and structure of chelates containing Zn(II), Co(II) and Ni(II) cations.

EXPERIMENTAL

Infrared spectra (Nujol; ν, cm^{-1}) were recorded with a Specord M-80 spectrometer in the range 400–3600 cm^{-1}. NMR spectra (δ, ppm; *J*, Hz) were obtained on a Varian Unity-300 NMR spectrometer at 25 °C. ^{1}H and ^{31}P{^{1}H} spectra were recorded at 299.948 and 121.420 MHz, respectively. Chemical shifts are referenced to SiMe$_4$ (^{1}H) and 85% H$_3$PO$_4$ (^{31}P{^{1}H}). Electronic absorption spectra of 0.001 M CH$_2$Cl$_2$ solutions were measured on a Perkin–Elmer Lambda-35 spectrometer in the range 200–1000 nm at 5–25 °C. Elemental analyses were performed on a Perkin–Elmer 2400 CHN microanalyser.

4-[(EtO)$_2$P(O)CH$_2$]-C$_6$H$_4$NHC(S)NHP(O)(O*i*Pr)$_2$] (**HL**)

A solution of diethyl(4-aminobenzyl)phosphonate, (EtO)$_2$P(O)CH$_2$C$_6$H$_4$-4-NH$_2$ (0.243 g, 1 mmol), in CH$_2$Cl$_2$ (15 ml) was added dropwise to a solution of *O,O′*-diisopropyl phosphorisothiocyanate, (*i*PrO)$_2$P(O)NCS (0.245 g, 1.1 mmol), in the same solvent (15 ml) (Scheme 1). The mixture was stirred at room temperature for 3 h. The solvent was then re-



HL

SCHEME 1
Preparation of **HL**

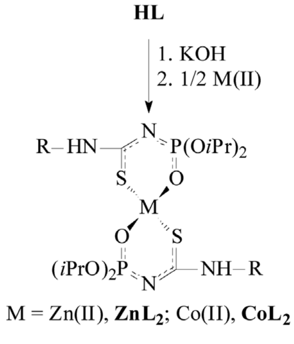
moved in vacuum. The residue was recrystallized from a dichloromethane/*n*-hexane mixture 1:5 (v/v). The product was obtained as a colorless oil. Yield 0.331 g (71%). ^{1}H NMR ($CDCl_3$): 1.23 t, 6 H, $^3J_{H,H}$ = 7.0 (CH_3, EtO); 1.38 d, 12 H, $^3J_{H,H}$ = 6.1 (CH_3, *i*PrO); 3.13 d, 2 H, $^2J_{P,H}$ = 21.9 (CH_2, P(O)CH_2); 4.00 d. quart, 4 H, $^3J_{H,H}$ = 7.2, $^3J_{POCH}$ = 10.9 (OCH_2, EtO); 4.74 d. sept, 2 H, $^3J_{H,H}$ = 6.1, $^3J_{POCH}$ = 7.0 (OCH, *i*PrO); 7.08 d, 1 H, $^2J_{PNH}$ = 8.3 (NH, P(O)NH); 7.21–7.59 m, 4 H (C_6H_4); 10.70 s, 1 H (NH). ^{31}P{^{1}H} NMR ($CDCl_3$): –6.9, 1 P (P(O)NH); 25.5, 1 P (P(O)CH_2). IR: 997, 1013 (POC); 1204 (P=O, P(O)CH_2); 1249 (P=O, P(O)NH); 1562 (SCN); 3139, 3286 (NH). For $C_{18}H_{32}N_2O_6P_2S$ (466.47) calculated: 46.35% C, 6.91% H, 6.01% N; found: 46.42% C, 6.77% H, 6.11% N.

M[4-{$(EtO)_2$P(O)CH_2}C_6H_4NHC(S)NP(O)$(OiPr)_2]_2$ (M = Zn(II), Co(II)) (**ML$_2$**)

A suspension of **HL** (0.233 g, 0.5 mmol) in aqueous ethanol (20 ml) was mixed with an ethanolic solution of potassium hydroxide (0.031 g, 0.55 mmol). An aqueous solution of $ZnCl_2$ (20 ml) or $Co(NO_3)_2\cdot 6H_2O$ (0.041 or 0.087 g, 0.3 mmol) was added dropwise under vigorous stirring to the resulting potassium salt solution (Scheme 2). The mixture was stirred at room temperature for another 3 h and left standing overnight. The complex was extracted with dichloromethane, washed with water and dried with anhydrous $MgSO_4$. The solvent was then removed in vacuum. The residue was recrystallized from a dichloromethane/*n*-hexane mixture 1:3 (v/v).

ZnL$_2$. A colorless oil. Yield 0.204 g (82%). ^{1}H NMR ($CDCl_3$): 1.21 t, 12 H, $^3J_{H,H}$ = 7.1 (CH_3, EtO); 1.28 d, 24 H, $^3J_{H,H}$ = 6.0 (CH_3, *i*PrO); 3.09 d, 4 H, $^2J_{P,H}$ = 21.7 (CH_2, P(O)CH_2); 3.89–4.11 m, 8 H (OCH_2, EtO); 4.60 d. sept, 4 H, $^3J_{H,H} \approx {}^3J_{POCH}$ = 6.2 (OCH, *i*PrO); 7.15–7.23, 7.39–7.48 m, 8 H (C_6H_4); 7.79 s, 2 H (NH). ^{31}P{^{1}H} NMR ($CDCl_3$): 5.7, 2 P (P(O)N); 26.4, 2 P (P(O)CH_2). IR: 1012, 1019 (POC); 1209 (P=O, P(O)CH_2); 1167 (P=O, P(O)NH); 1539 (SCN); 3299 (NH). For $C_{36}H_{62}N_4O_{12}P_4S_2Zn$ (996.30) calculated: 43.40% C, 6.27% H, 5.62% N; found: 43.27% C, 6.35% H, 5.57% N.

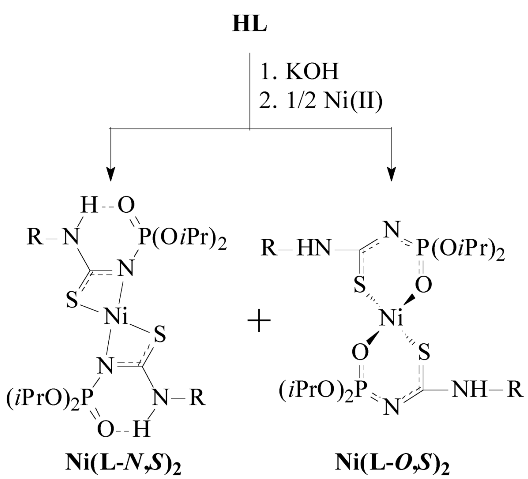
CoL$_2$. A dark blue oil. Yield 0.158 g (64%). IR: 1001, 1007 (POC); 1214 (P=O, P(O)CH_2); 1159 (P=O, P(O)NH); 1564 (SCN); 3316 (NH). UV/Vis (λ_{max}, nm (ε, mol^{-1} dm^3 cm^{-1})): 564 (270); 600 (292); 663 (161). For $C_{36}H_{62}CoN_4O_{12}P_4S_2$ (989.86) calculated: 43.68% C, 6.31% H, 5.66% N; found: 43.81% C, 6.45% H, 5.72% N.



SCHEME 2
Preparation of **ZnL$_2$** and **CoL$_2$** (R = 4-[$(EtO)_2$P(O)CH_2]-C_6H_4)

$Ni[4-\{(EtO)_2P(O)CH_2\}C_6H_4NHC(S)NP(O)(OiPr)_2]_2$ (**NiL$_2$**)

A suspension of **HL** (0.233 g, 0.5 mmol) in aqueous ethanol (20 ml) was mixed with an ethanol solution of potassium hydroxide (0.031 g, 0.55 mmol). An aqueous solution (20 ml) of $NiCl_2$ (0.039 g, 0.3 mmol) was added dropwise under vigorous stirring to the potassium salt solution (Scheme 3). The mixture was stirred at room temperature for another 3 h and left standing overnight. The complex was obtained by extraction of the reaction mixture with dichloromethane, washed with water and dried with anhydrous $MgSO_4$. The solvent was then removed in vacuum. The residue was extracted using *n*-hexane. The hexane-insoluble residue was recrystallized from a dichloromethane/*n*-hexane mixture 1:3 (v/v), and the **Ni(L-*N,S*)$_2$** complex was isolated as a blue precipitate. Yield 0.063 g (25%), m.p. 62.5–64 °C. ^{1}H NMR ($CDCl_3$): 1.19 t, 12 H, $^3J_{H,H}$ = 7.3 (CH_3, EtO); 1.33 d, 24 H, $^3J_{H,H}$ = 6.2 (CH_3, *i*PrO); 3.13 d, 4 H, $^2J_{P,H}$ = 22.0 (CH_2, P(O)CH_2); 3.94–4.17 m, 8 H (OCH_2, EtO); 4.72 d. sept, 4 H, $^3J_{H,H} \approx {}^3J_{POCH}$ = 6.1 (OCH, *i*PrO); 7.19–7.39, 7.46–7.60 m, 8 H (C_6H_4); 10.59 s, 2 H (NH). ^{31}P{^{1}H} NMR ($CDCl_3$): 2.0, 2 P (P(O)N); 26.7, 2 P (P(O)CH_2). IR: 997, 1004 (POC); 1217 (P=O, P(O)CH_2); 1238 (P=O, P(O)NH); 1541 (SCN); 3171 (NH). UV/Vis, λ_{max}, nm (ε, mol^{-1} dm^3 cm^{-1}) 234 (~32960); 249 (~19080); 428 (1720); 535 (260); 653 (237). For $C_{36}H_{62}N_4NiO_{12}P_4S_2$ (989.61) calculated: 43.69% C, 6.31% H, 5.66% N; found: 43.78% C, 6.21% H, 5.79% N. The hexane soluble **Ni(L-*O,S*)$_2$** complex was isolated as a light red oil. Yield 0.118 g (48%). ^{1}H NMR ($CDCl_3$): 1.28 br. s, 36 H (CH_3, EtO + *i*PrO); 3.06 br. s, 4 H (CH_2, P(O)CH_2); 3.94 br. s, 8 H (OCH_2, EtO); 4.56 br. s, 4 H (OCH, *i*PrO); 7.26 br. s, 8 H (C_6H_4); 6.48 br. s, 2 H (NH). ^{31}P{^{1}H} NMR ($CDCl_3$): –361.7 br. s, 2 P (P(O)N); 34.0 br. s, 2 P (P(O)CH_2). IR: 994, 1018 (POC); 1211 (P=O, P(O)CH_2); 1162 (P=O, P(O)NH); 1571 (SCN); 3293 (NH). UV/Vis (λ_{max}, nm (ε, mol^{-1} dm^3 cm^{-1})): 693 (117); 719 (193); 784 (249). For $C_{36}H_{62}N_4NiO_{12}P_4S_2$ (989.61) calculated: 43.69% C, 6.31% H, 5.66% N; found: 43.54% C, 6.29% H, 5.49% N.



SCHEME 3
Preparation of **Ni(L-*N,S*)$_2$** and **Ni(L-*O,S*)$_2$** (R = 4-[$(EtO)_2P(O)CH_2$]-C_6H_4)

RESULTS AND DISCUSSION

The IR spectrum of **HL** contains a band at 1249 cm^{-1} for vibration of the P=O fragment of the P(O)NH group. It is shifted to low wavenumbers (1159–1167 cm^{-1}) in the spectra of **ZnL_2**, **CoL_2** and **Ni(L-*O*,*S*)$_2$** due to the coordination with the cations. The coordination shift (82–90 cm^{-1}) is in the region characteristic of the 1,5-*O*,*S*-coordination of the deprotonated phosphorylated thioamides and thioureas towards Zn(II), Co(II) and Ni(II) (refs[2,8–11]). The wavenumbers of the P=O group in the IR spectrum of **Ni(L-*N*,*S*)$_2$** also decreases (11 cm^{-1}) relative to that of the free ligand. The absorption occurs in the region characteristic of the 1,3-*N*,*S*-coordination of the Ni(II) cation to deprotonated phosphorylated thioamides and thioureas[2]. The occurrence of the new broad and intense band at 1539–1571 cm^{-1}, due to the conjugated SCN group[8], also proves the formation of complexes. The presence of the substituted POC groups in **HL** and its complexes can be deduced from the IR spectra by their absorption bands at 994–1019 cm^{-1} (refs[8,9]).

Two bands for the arylNH and P(O)NH groups at 3139 and 3286 cm^{-1} are observed in the IR spectrum of **HL**, whereas a simple band at 3293–3316 cm^{-1} corresponding to the arylNH group are present in the spectra of **ZnL_2**, **CoL_2** and **Ni(L-*O*,*S*)$_2$**. It should be noted that the band of the arylNH group in the IR spectra of **ZnL_2**, **CoL_2** and **Ni(L-*O*,*S*)$_2$** is shifted to higher wavenumbers relative to the band of the free ligand **HL**. This confirms the absence of hydrogen bonding in the complexes[8,9]. The NH absorption band in the spectrum of **Ni(L-*N*,*S*)$_2$** is observed at 3171 cm^{-1}, in the characteristic region of amide protons participating in hydrogen bonding[8,9].

It should be noted that in the IR spectra of all complexes, the band corresponding to the P=O fragment of the P(O)CH_2 group occurs between 1209 and 1217 cm^{-1}, practically in the same region as in the free ligand (1204 cm^{-1}), or even shifted to higher wavenumbers. This confirms the absence of coordination of the P=O group, in the P(O)CH_2 fragment.

The $^{31}P\{^1H\}$ NMR spectrum of **HL** in a $CDCl_3$ solution shows two singlet at –6.9 and 25.5 ppm, corresponding to the P(O)NH and P(O)CH_2 phosphorus atoms, respectively. In the $^{31}P\{^1H\}$ NMR spectrum of **ZnL_2**, the resonances for the phosphorylamide and phosphonic ester groups are observed at 5.7 and 26.4 ppm, respectively. The signal corresponding to the P(O)N group in **ZnL_2** is shifted downfield by 12.6 ppm. This fact also confirms the 1,5-*O*,*S*-coordination of **L^-** anion[2,8–11]. The phosphorylamide phosphorus signal in the spectrum of **Ni(L-*N*,*S*)$_2$** is also downfield shifted by 8.9 ppm. This confirms the 1,3-*N*,*S*-coordination of **L^-** anion[2]. The singlet of the $P(O)CH_2$ groups in the spectra of **ZnL_2** and **Ni(L-*N*,*S*)$_2$** are practically in the same region as in the free ligand.

The $^{31}P\{^1H\}$ NMR spectrum of **Ni(L-*O*,*S*)$_2$** also contains two singlets. The signal of the P(O)N group is observed in an extremely high-field region, δ = –361.7 ppm. The $P(O)CH_2$ phosphorus is shifted to a lower field relative to that in the spectrum of **HL**; the shift is 8.5 ppm. Thus, the **Ni(L-*O*,*S*)$_2$** complex in $CDCl_3$ is paramagnetic due to its tetrahedral geometry[12–14].

In the ^1H NMR spectra of **HL**, **ZnL_2** and **NiL_2**, the signals of the CH_3 protons in the $(iPrO)_2P(O)$ and $(EtO)_2P(O)$ groups are observed as doublets, triplets or broad singlets at 1.19–1.38 ppm and doublets of septets, doublets of quartets, multiplets or broad singlets at 3.89–4.74 ppm, correspond to the OCH and OCH_2 protons of the groups. The signals of the C_6H_4 protons in the spectra of **HL**, **ZnL_2** and **NiL_2** are multiplets or broad singlets at 7.15–7.59 ppm. The CH_2 proton signals appear at 3.06–3.16 ppm. A doublet and singlet of the P(O)NH and arylNH protons at 7.08 and 10.70 ppm, respectively, are in the spectrum of **HL**, whereas only singlets are observed for the arylNH proton at 6.48–7.79 ppm in the ^1H NMR spectra of **ZnL_2** and **Ni(L-*O*,*S*)$_2$**. The signals are high-field shifted relative to that in the spectrum of **HL**. This confirms the absence of hydrogen bonds in **ZnL_2** and **Ni(L-*O*,*S*)$_2$** (refs[2,8–10]). The arylNH proton resonance in the spectrum of **Ni(L-*O*,*S*)$_2$** appears at 10.59 ppm and is slightly shifted relative to that in the spectrum of **HL**. This confirms the preservation of hydrogen bonds in **Ni(L-*N*,*S*)$_2$** (ref.[2]).

The investigation of **CoL_2** complex by $^{31}P\{^1H\}$ NMR spectrometry was not successful due to the presence of paramagnetic Co(II). The signals in the $^{31}P\{^1H\}$ NMR spectrum of the **CoL_2** complex are absent because of strong contact or pseudocontact interactions between the paramagnetic metal ion and the phosphorus atoms[5]. These pseudocontact interactions are practically absent for the protons where the dipole–dipole interactions predominate.

The 1D ^1H NMR spectrum of **CoL_2** in $CDCl_3$ displays twelve well-resolved isotropically shifted signals a–l (Fig. 1). The ^1H NMR chemical shifts are reported in Table I. All signals display broad signals (as measured at their half-height). The $\Delta\nu_{1/2}$ values are characteristic of a four-coordinated Co(II) complex (S = 3/2)[15–17]. The assignment of signals was done on the basis of ^1H-^1H COSY spectra and chemical shifts.

Signal a, corresponding to the phenylene group, is partly overlapped with the solvent signal. Signals b and c represent two protons each and correspond to the $P(O)CH_2$ groups. The signal of the NH protons (4.7 ppm) is observed in the relatively high-field region. The signals e + f and g–l are due to twelve and thirty six protons, respectively, of the isopropyl (*i*PrO) and ethyl (EtO) groups (Table I). The COSY cross-peaks between signals e and h–j, l, and f and g, k confirm their assignment to the *i*PrO and EtO groups.

It should be noted that all signals in the ^{1}H NMR spectra of **CoL$_2$** and **Ni(L-*O*,*S*)$_2$** are in the diamagnetic region (0–14 ppm); however the signals are extremely broad.

In the UV spectrum of **CoL$_2$**, there is an absorption band (corresponding to the $^4A_2 \rightarrow {}^4T_1(P)$ transition)[11] with peaks at 564 (ε_{max} = 270 mol^{-1} dm^3 cm^{-1}),

TABLE I
^{1}H NMR signals of paramagnetic **CoL$_2$** in $CDCl_3$

Assignment protons	Signal (δ, ppm)	No. of protons
C_6H_4 + solvent	a (7.3)	
CH_2(P(O)CH_2)	b (6.5), c (5.9)	2 (b) + 2 (c)
NH	d (4.7)	
CH(*i*PrO)	e (4.0)	12 (e + f)
CH_2(EtO)	f (3.6)	
CH_3(EtO)	g (2.5), k (1.2)	
	h (2.0), i (1.6)	36 (g–l)
CH_3(*i*PrO)	j (1.4), l (0.8)	

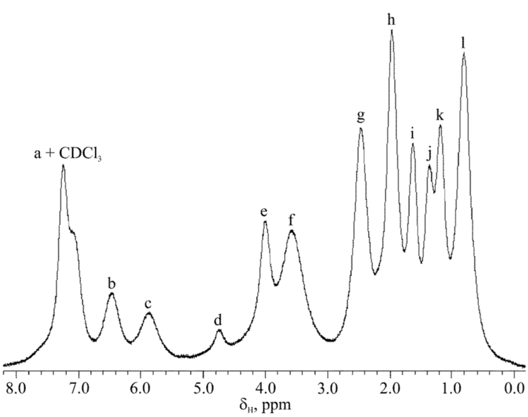


FIG. 1
^{1}H NMR spectrum of **CoL$_2$** in $CDCl_3$

600 (ε_{max} = 292 mol^{-1} dm^3 cm^{-1}) and 663 (ε_{max} = 161 mol^{-1} dm^3 cm^{-1}) nm. The band shape is caused by spin–orbital interaction resulting (i) in a splitting of the state $^4T_1(P)$ state and (ii) in a resolved transitions in the next doublet states with the same intensity. Other possible transitions, $^4A_2 \rightarrow {}^4T_2$ and $^4A_2 \rightarrow {}^4T_1(F)$, are outside of the visible region. UV-spectral data support the tetrahedral environment of the Co(II) cation in **CoL$_2$** (ref.[11]).

In the electronic absorption spectrum of **Ni(L-*N*,*S*)$_2$** in CH_2Cl_2 two bands at 653 and 535 nm, two shoulders at 428 and 249 nm and a band at 234 nm are observed. The last high-energy intensive transitions (ε_{sh} = 19 083 mol^{-1} dm^3 cm^{-1} and ε_{max} = 32 961 mol^{-1} dm^3 cm^{-1}) fall obviously into ligand–ligand and ligand-to-metal transitions[18–20]. The long-wave spectral region shows three bands with ε_{max} = 237, 260 and 1717 mol^{-1} dm^3 cm^{-1}. The bands at 653 and 535 nm of **Ni(L-*N*,*S*)$_2$** assigned to the $^1A_{1g} \rightarrow {}^1B_{1g}$ ($d_{x^2-y^2} \rightarrow d_{xy}$) and $^1A_{1g} \rightarrow {}^1B_{3g}$ ($d_{xz} \rightarrow d_{xy}$) transitions, respectively, of square-planar isomers. The band at 428 nm can be assigned to the $^1A_{1g} \rightarrow {}^1B_{1g}$ ($d_{z^2} \rightarrow d_{xy}$) transition with its high intensity derived from activation by the ligand-to-metal transition[18–20].

In the electronic absorption spectrum of **Ni(L-*O*,*S*)$_2$**, bands at 690–800 nm are assigned to the $^3T_1(F) \rightarrow {}^3T_1(P)$ transition. It supports the presence of the tetrahedral chromophore in **Ni(L-*O*,*S*)$_2$** (refs[12–14]).

The UV/Vis spectra of **Ni(L-*N*,*S*)$_2$** and **Ni(L-*O*,*S*)$_2$** show no temperature dependence in the range 5–25 °C. It shoud be also noted that the spectra exhibit only bands typical of square-planar **Ni(L-*N*,*S*)$_2$** or tetrahedral **Ni(L-*O*,*S*)$_2$** chromophores.

Unfortunately after numerous attempts, we were not successful to obtain single crystals of the complexes suitable for X-ray diffraction study.

CONCLUSION

Novel Zn(II), Co(II) and Ni(II) complexes with **HL** have been synthesized. NMR, UV/Vis and IR spectra showed that the thiourea is a 1,5-*O*,*S*-ligand in **ZnL$_2$**, **CoL$_2$** and **Ni(L-*O*,*S*)$_2$**. The **Ni(L-*O*,*S*)$_2$** complex is the first example of a Ni(II) complex with RNHC(S)NHP(O)(O*i*Pr)$_2$ ligands, containing the –RNHC(S)– group having a 1,5-*O*,*S*-coordination. The central metal ion is in a tetrahedral environment. The Ni(II) cation of **Ni(L-*N*,*S*)$_2$** is in a square-planar environment and the deprotonated thiourea group shows a 1,3-*N*,*S*-coordination mode.

Two isomers with different coordinations of **HL** to Ni(II) and with different polyhedral structures are a novel uniqueness in Ni(II) coordination chemistry with RNHC(S)NHP(X)(O*i*Pr)$_2$ (X = O, S).

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