



## TRANSITION METAL COMPLEXES WITH THIOSEMICARBAZIDE-BASED LIGANDS

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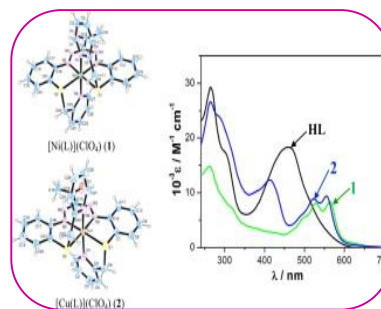
Research Scholar In The Faculty Of Science( Chemistry)

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### ABSTRACT

With the complexes involving the neutral form of PLSC and the monoanionic form of PLTSC, the PL moiety is in the form of a zwitterion. In addition to the above-mentioned techniques, all the complexes were characterized by measuring their molar conductivities, UV-Vis and partial IR spectra.

**KEY WORDS:** Ni(II) complexes; Pyridoxal semi- and thiosemicarbazone; Spectral characteristics .



### 1. INTRODUCTION

For some time, semi- and thiosemicarbazones are a subject matter of interest to researchers of various profiles. Seeable of the very fact that these compounds form with many metals complexes of diverse chemical, physical and structural characteristics, they're of interest group to coordination chemists [1–3]. Additionally, many of those compounds moreover as their metal complexes, especially those with thiosemicarbazones, have shown a large spectrum of biological activity, so they need also become an issue of intense research for pharmacologists [4]. One of the newer semicarbazone ligands, which is that the subject of our research, is pyridoxal semicarbazone (PLSC), whose only complexes reported up to now are those with Cu(II), Fe(III) and Pt(IV) [5–8]. In contrast to PLSC, variety of pyridoxal thiosemicarbazone (PLTSC) complexes, involving not only transition metals (among them Ni(II) too) but also some non-transition metals, are described [9]. As a continuation of our study of the complexing properties of PLSC, we describe here the synthesis and a few physico-chemical and structural characteristics of its first complexes with Ni(II), further as two new Ni(II) complexes with PLTSC.

### 2. EXPERIMENTAL

All chemicals used for the synthesis and measurements were commercial products, except for the ligands, which were prepared according to the previously described procedures [6].

Elemental (C, H, N) analysis of air-dried samples was carried out by standard micromethods in the Center for Instrumental Analysis, Faculty of Chemistry, Belgrade.

#### 2.1. Syntheses of complexes

2.1.1. Ni(PLSC) $X_2 \cdot nH_2O$  (1–3); (X = Cl, n = 3.5 (1); X = NO<sub>3</sub>, n = 3 (2), X = NCS, n = 4 (3))

To a warm suspension of 0.26 g (1.0 mmol) of PLSC · 2H<sub>2</sub>O in 10 cm<sup>3</sup> of EtOH 1.2 mmol of solid NiX<sub>2</sub> · 6H<sub>2</sub>O (X = Cl, NO<sub>3</sub>) was added and the content heated until the reactants were completely dissolved. In the case of the reaction with Ni(NCS)<sub>2</sub> · 2H<sub>2</sub>O use was made of aqueous solutions of the reactants. The green solutions were left to evaporate at room temperature. The crystals were filtered and washed with EtOH. Yield: 50–70%.

### 2.1.2. [Ni(PLSC-2H)NH<sub>3</sub>] · 1.5H<sub>2</sub>O (4)

To a warm suspension of 0.26 g (1 mmol) of PLSC · 2H<sub>2</sub>O in 10 cm<sup>3</sup> of EtOH, a warm EtOH (5 cm<sup>3</sup>) solution of 0.35 g (1.2 mmol) of Ni(NO<sub>3</sub>)<sub>2</sub> · 6H<sub>2</sub>O was added, and the content heated to complete dissolution of the ligand. To the green solution NH<sub>3</sub>(aq.) (1 cm<sup>3</sup>) was added and the content heated for 2–3 min, whereby the solution became red. After 10 h the orange microcrystalline precipitate was filtered and washed with EtOH. Yield: 0.28 g (86%).

### 2.1.3. [Ni(PLTSC-H)py]NO<sub>3</sub> (5)

A mixture of 0.15 g (0.5 mmol) of PLTSC · 3H<sub>2</sub>O and 0.17 g (0.6 mmol) of Ni(NO<sub>3</sub>)<sub>2</sub> · 6H<sub>2</sub>O was dissolved by heating in MeOH (10 cm<sup>3</sup>), and pyridine (0.5 cm<sup>3</sup>) was added to the solution. The red solution was left at room temperature for 24 h. The obtained red monocrystals were filtered and washed with MeOH. Yield: 0.10 g (44%).

### 2.1.4. [Ni(PLTSC-H)NCS] (6)

A warm solution of 0.12 g (0.6 mmol) of Ni(NCS)<sub>2</sub> · 2H<sub>2</sub>O in H<sub>2</sub>O (5 cm<sup>3</sup>) was mixed with a warm solution of 0.15 g (0.5 mmol) of PLTSC · 3H<sub>2</sub>O in DMF (2 cm<sup>3</sup>) and heated mildly for 2–3 min. The complex started to crystallize immediately from the warm solution. After 10 h brown crystals were filtered and washed with H<sub>2</sub>O and EtOH. Yield: 0.10 g (55%).

Data of microanalysis and measurements of magnetic susceptibility, molar conductivity, along with the description of colors and geometry of all the complexes, are given in Table 1.

## 2.2. Physical methods

Magnetic susceptibilities were measured at room temperature using a magnetic susceptibility balance MSB-MKL (Sherwood Scientific Ltd. Cambridge, England). Molar conductivities of the freshly prepared 1 × 10<sup>-3</sup> M aqueous or methanolic solutions were measured on a Jenway 4010 conductivity meter.

IR spectra (KBr disk) were recorded on a Thermo Nicolet (NEXUS 670 FT-IR) instrument.

Electronic spectra were recorded on a Secomam (Anthelie 2, Advanced, for the range 200–900 nm) and on a Thermo Nicolet instrument (NEXUS 670 FT-IR, for the range 900–1400 nm) in (2–4) × 10<sup>-4</sup> mol dm<sup>-3</sup> MeOH and DMF solutions of the complexes.

## 2.3. Crystal structure determination

Single crystals of the title compounds 2 (green) and 5 (dark red) were selected and glued on glass threads. Diffraction data were collected on a Bruker PLATFORM three-circle goniometer equipped with SMART 1K CCD detector for 2 and on a Nonius Kappa CCD diffractometer for 5. The crystal to detector distances were 5.4 and

**Table 1**  
**Partial elemental analysis and some physical characteristics of the complexes**

Complex	Found (calculated) %			Color	$\mu_{\text{eff}}$ (BM)	$\lambda_{\text{M}}$ (S cm <sup>2</sup> mol <sup>-1</sup> ) (solvent)	Geometry
	C	H	N				
Ni(PLSC)Cl <sub>2</sub> ·3.5H <sub>2</sub> O (1)	26.22 (25.93)	4.63 (4.59)	13.40 (13.44)	green	3.18	194 (H <sub>2</sub> O) 156 (MeOH)	octahedral
[Ni(PLSC)(H <sub>2</sub> O) <sub>3</sub> ](NO <sub>3</sub> ) <sub>2</sub> (2)	23.72 (23.45)	4.01 (3.93)	18.10 (18.24)	green	3.07	201 (H <sub>2</sub> O) 162 (MeOH)	octahedral
Ni(PLSC)(NCS) <sub>2</sub> · 4H <sub>2</sub> O (3)	28.25 (28.04)	4.25 (4.28)	17.74 (17.84)	green	3.12	203 (H <sub>2</sub> O) 120 (MeOH)	octahedral
[Ni(PLSC-2H)NH <sub>3</sub> ] 1.5H <sub>2</sub> O (4)	33.27 (33.26)	4.91 (4.96)	21.51 (21.56)	orange diamagnetic		6.7 (DMF)	square- planar
[Ni(PLTSC-H)py]NO <sub>3</sub> (5)	38.01 (38.29)	3.74 (3.67)	18.90 (19.14)	red diamagnetic		64 (DMF)	square- planar
[Ni(PLTSC-H)NCS] (6)	33.94 (33.73)	3.18 (3.11)	19.58 (19.67)	brown diamagnetic		18 (DMF)	square- planar

3.0 cm for 2 and 5, respectively. Graphite monochromated Mo K $\alpha$  radiation ( $\lambda = 0.71073\text{\AA}$ ) was employed in both measurements. Frame widths of  $0.3^\circ$  and  $2^\circ$  in  $\omega$ , with 10 and 200 s were used to acquire each frame for 2 and 5, respectively. More than hemispheres of three-dimensional data were collected in both measurements. The data were reduced using the Bruker program SAINT for 2 and Nonius program COLLECT for 5. A semiempirical absorption-correction based upon the intensities of equivalent reflections was applied, and the data were corrected for Lorentz polarization and background effects. Scattering curves for neutral atoms, together with anomalous dispersion corrections, were taken from the International Tables for X-ray Crystallography [10]. The structures were solved by direct methods [11], and the figures were drawn using ORTEP [12]. Refinements were based on  $F^2$  values and done by full-matrix least-squares [13] with all non-H atoms anisotropic. The positions of hydrogen atoms were found from the inspection of the difference Fourier maps. The final refinement included atomic positions and displacement parameters for all atoms. The non-H atoms were refined anisotropically, while all H sites were refined with isotropic displacement parameters. The crystal data and refinement parameters for the title compounds are listed in Table 2.

### 3. RESULTS AND DISCUSSION

#### 3.1. Syntheses, physico-chemical characteristics and geometric structures of the complexes

Reactions of warm EtOH or H<sub>2</sub>O solutions of PLSC and NiX<sub>2</sub> · nH<sub>2</sub>O (X = Cl, NO<sub>3</sub>, NCS) in a mole ratio of 1:1 yielded the paramagnetic green monoligand complexes of the general formula Ni(PLSC)X<sub>2</sub> · nH<sub>2</sub>O (1, 2, 3) (Table 1). In the presence of NH<sub>3</sub>(aq.) and pyridine (py), Ni(NO<sub>3</sub>)<sub>2</sub> · 6H<sub>2</sub>O forms with PLSC and PLTSC, respective diamagnetic complexes [Ni(PLSC-2H)NH<sub>3</sub>] · 1.5H<sub>2</sub>O (4), and [Ni(PLTSC-H)py]NO<sub>3</sub> (5). The other, also diamagnetic, complex with PLTSC, viz. [Ni(PLTSC-H)NCS] (6) was obtained in the reaction of an H<sub>2</sub>O solution of Ni(NCS)<sub>2</sub> and DMF solution of PLTSC. The isolated complexes are crystalline substances that are stable in air. With the exception of [Ni(PLSC-2H)NH<sub>3</sub>] · 1.5H<sub>2</sub>O, which is slightly soluble only in DMF, the other PLSC complexes, in addition to being soluble in DMF, are also soluble in H<sub>2</sub>O, but are somewhat less soluble in MeOH and EtOH. The PLTSC complexes are soluble in DMF but dissolve poorly in H<sub>2</sub>O and alcohols.

Some physical characteristics of the complexes that are relevant to their geometric structures are presented in

**Table 2**  
**Crystal data and refinement parameters for complexes 2 and 5**

Compound	[Ni(PLSC)(H <sub>2</sub> O) <sub>3</sub> ](NO <sub>3</sub> ) <sub>2</sub>	[Ni(PLTSC-H)py]NO <sub>3</sub>
Empirical formula	C <sub>9</sub> H <sub>18</sub> N <sub>6</sub> O <sub>12</sub> Ni	C <sub>14</sub> H <sub>18</sub> N <sub>6</sub> O <sub>5</sub> SNi
Formula weight	461.00	441.12
Temperature(Å)	293	293
Wavelength	(Å) 0.71073	0.71073
Crystal system	triclinic	monoclinic
Space group	P1	P2 <sub>1</sub> /c
Unit cell dimensions		
a (Å)	9.1392(2)	6.7290(1)
b (Å)	9.0566(2)	15.9620(3)
c (Å)	11.4737(3)	16.6520(3)
α (°)	97.196(1)	
β (°)	102.593(1)	95.064(1)
γ (°)	112.139(1)	
V (Å <sup>3</sup> )	834.89	1781.63
Z	2	4
Dcalc (g/cm <sup>3</sup> )	1.834	1.645
Absorption coefficient (mm <sup>-1</sup> )	1.24	1.25
F(000)	476	921
Crystal size (mm)	0.35 × 0.50 × 0.45	0.45 × 0.25 × 0.05
Color	green	dark red
2θmax for data collection (%)	57.3	55.0
Index ranges: -h +h; -k +k; -l +l	-12 +12; -11 +11; -15 +15	-8 +8; -20 +20; -21 +21
Reflections collected	9676	7868
Independent reflections (R <sub>int</sub> )	3906 (0.0497)	4058 (0.0187)
Refinement methods	full matrix least square on F <sup>2</sup>	full matrix least square on F <sup>2</sup>
Data/restraints/parameters	3906/0/325	4058/0/304
Goodness-of-fit on F <sup>2</sup>	0.979	0.799
Final R indices [F <sub>o</sub> > 4σF <sub>o</sub> ]	R <sub>1</sub> = 0.0251	R <sub>1</sub> = 0.0328
R indices (all data)	R <sub>1</sub> = 0.0306, wR <sub>2</sub> = 0.0671	R <sub>1</sub> = 0.0475, wR <sub>2</sub> = 0.1208
Extinction coefficient	no	no
Largest difference in peak and hole (e/Å <sup>3</sup> )	0.31 and -0.24	0.44 and -0.48

Table 1. First of all, the X-ray analysis of [Ni(PLSC)(H<sub>2</sub>O)<sub>3</sub>](NO<sub>3</sub>)<sub>2</sub> (2) (vide infra) showed that it has an octahedral structure, formed by the tridentate ONO coordination of the PLSC ligand and three H<sub>2</sub>O molecules. The Ni(II) complexes are of the characteristic green color and have the expected μ<sub>eff</sub> values (Table 1). Based on this, the same geometric configuration could also be ascribed to the other two paramagnetic PLSC complexes 1 and 3, this configuration being the most frequently observed for paramagnetic Ni(II) complexes [14]. Therefore, apart from the PLSC ligand, H<sub>2</sub>O molecules or acid residues must participate in coordination. In the case of the Ni(PLSC)(NCS)<sub>2</sub> · 4H<sub>2</sub>O complex, the coordination of the NSC group is also supported by the position of the m(CN) band in the IR spectrum, which appears as a doublet at 2091 and 2104 cm<sup>-1</sup>, i.e. in the region of a coordinated NCS-group [15], bonded through the

nitrogen atom, as is usual with Ni(II) as a representative of medium- hard acids. The weak  $\nu(\text{CS})$  and  $\delta(\text{NCS})$  bands, appearing at lower energies, cannot be located as they are masked by the bands of the organic ligand. On the basis of the IR spectrum of complex 1, it can be supposed that  $\text{Cl}^-$  does not participate in coordination. This assumption is based on the absence of the  $m(\text{Ni}-\text{Cl})$  band. The conclusion is also supported by the great similarity of the IR spectra of the octahedral  $[\text{Ni}(\text{PLSC})(\text{H}_2\text{O})_3](\text{NO}_3)_2$  complex and the Cl-containing complex in the range below  $350\text{ cm}^{-1}$ , i.e. at the wavelengths where one could expect the  $m(\text{Ni}-\text{Cl})$  bands [15,16].

Molar conductivities (kM) of  $\text{H}_2\text{O}$  solutions of the paramagnetic PLSC complexes (Table 1) indicate the presence of a 2:1 type of electrolyte [17]. The same also holds for the MeOH solutions of the Cl- and  $\text{NO}_3^-$ -containing complexes. In contrast to them, the  $\lambda_M$  values of MeOH solutions of the NCS complex correspond to a 1:1 type of electrolyte [17], which suggests partial replacement of the coordinated NCS group with solvent molecules. However, for the same complex in acetone solution  $\lambda_M = 32\ \Omega^{-1}\text{ cm}^2\text{ mol}^{-1}$  was obtained, which is significantly lower than the usual value for a 1:1 electrolyte ( $\Omega_M = 100\text{--}140\ \Omega^{-1}\text{ cm}^2\text{ mol}^{-1}$ ) [17], suggesting the coordination of both NCS groups is preserved in solution.

Concerning the precise formulas of the octahedral complexes 1 and three, it will be supposed that the structure of complex 1 is analogous to it of complex 2, which is additionally supported by the similarity of the values of their molar conductivities (electrolyte type 2:1). Hence, the probable formula involves a complexation of the sort  $[\text{Ni}(\text{PLSC})(\text{H}_2\text{O})_3]^{2+}$ . However, for complex 3, that a coordination of two NCS groups and one water molecule in crystal is meant, the molar conductivity data indicate that the NCS-group coordination depends on the character of the solvent: within the least polar solvent, acetone, both groups remain coordinated, in MeOH just one is coordinated, whereas in  $\text{H}_2\text{O}$  both are dissociated. Hence, this complex and complexes 1 and a couple of in solution have the identical complex cation, i.e.  $[\text{Ni}(\text{PLSC})(\text{H}_2\text{O})_3]^{2+}$ .

The diamagnetism and color of complex 4 and of two new PLTSC complexes 5 and 6 suggest their structure is square-planar [14]. In the case of 5, this was proved by X-ray analysis (vide infra). In contrast to the other compounds, the PLSC complex 4 contains the ligand in a dianionic form, arising from the deprotonation of not only the enol-form of the semicarbazide moiety but also of the zwitter ion of the PL residue, which also explains its nonelectrolytic nature. Both PLTSC complexes contain the ligand in its monoanionic form, resulting from the deprotonation of the thiol form of the thiosemicarbazide moiety. As is the case with the other complexes containing this ligand [9], both PLTSC complexes involve the ONS set of donor atoms; the fourth coordination site being occupied by a py or NCS group. The  $\nu(\text{CN})$  band of the coordinated NCS group is observed at  $2113\text{ cm}^{-1}$ . The molar conductivity of this complex in DMF (Table 1) suggests partial replacement of the NCS group with solvent molecules.

In the example of the reactions of  $\text{Ni}(\text{NCS})_2$  with these two ligands it can be concluded that the TSC residue is a stronger acid than the SC residue, i.e. that PLTSC is more readily deprotonated than PLSC. The same conclusion can be made on the basis of the reaction of PLTSC with  $\text{Ni}(\text{NO}_3)_2$  too, keeping in mind the fact that in this reaction Ferrari et al. [18] obtained a complex involving the monoanionic form of the ligand of the composition  $\text{Ni}(\text{PLTSC-H})\text{-NO}_3 \cdot 2\text{H}_2\text{O}$ . It should be noted that these authors also described the compound  $\text{Ni}(\text{PLTSC-2H}) \cdot 2\text{H}_2\text{O}$ , obtained from the reaction of PLTSC with  $\text{Ni}(\text{OAc})_2$ .

### 3.2. Electronic spectra

Table 3 summarizes the electronic spectral data for the investigated complexes in two solvents, recorded in the range of 220–1200 nm (MeOH) and 270–1200 nm (DMF). As can be seen, the spectra display several electronic transitions. The strong peak at the blue end of the spectra of the complexes in MeOH (at about 240 nm) can be ascribed to  $\pi \rightarrow \pi^*$  pyridine ring absorptions [19], which are, due to an increased conjugation in the complexes, shifted by about 10–20 nm to higher wavelengths compared to those of the ligands alone [20]. Other spectral characteristics are mainly influenced by the coordinated ligand and its deprotonation and only slightly by solvent effects.

The paramagnetic semicarbazone complexes are characterized by two main bands at about 300 and 400 nm (Fig. 1). Obviously, the bands are complex, each being composed of at least two close bands. The band at 300 nm comprises transitions  $\pi \rightarrow \pi^*$  imine and  $n \rightarrow \pi^*$  of both the imine and pyridine ring, which are also present in this range in the spectra of the ligand alone [21]. The other band (~400 nm) may be due mainly to LMCT transitions. In this spectral range, one would expect LM N! Ni and SCN  $\rightarrow$  Ni charge transfers, but the band for Cl  $\rightarrow$  Ni is usually observed at somewhat higher energies (around 330 nm) [22]. In addition, low intensity d-d dihedral angles between the mean planes of the pyridoxal moiety (A) and six- (B) and five-membered (C) chelate rings are A-B 12.3 $^\circ$ , A-C 15.2 $^\circ$  and B-C 3.5 $^\circ$ . The basal plane of the coordination polyhedron is slightly tetrahedrally deformed, with a maximum distance from the least squares plane of 0.039(1) Å for N3. The nickel atom is displaced towards the apical Ow2 atom by 0.0208(3)Å. Bond distances and bond angles in PLSC are in good agreement with the corresponding values found in the structure of dibromo (pyridoxal semicarbazone- $k^3N^1, O^3, O^{3'}$ ) copper(II) [5]. The geometry of the NO<sub>3</sub> groups do not deviate from the usual literature values. Possible hydrogen bonds are listed in Table 5. The packing (Fig. 3) of this compound is determined by a large network of hydrogen bonds, a few of which are bifurcated among the complex molecules, the nitrate ions and water molecules.

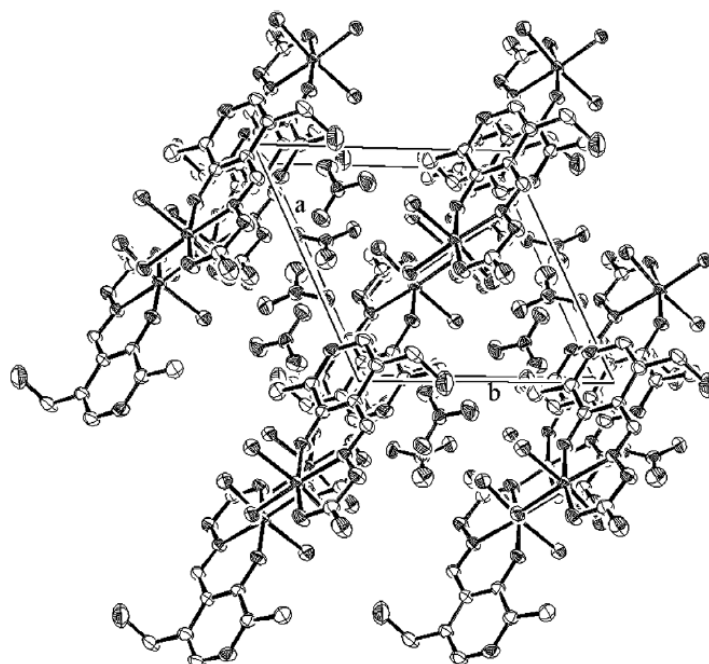


Fig.3.The crystal structure of  $[Ni(PLSC)(H_2O)_3](NO_3)_2$  viewed along the c-axis.



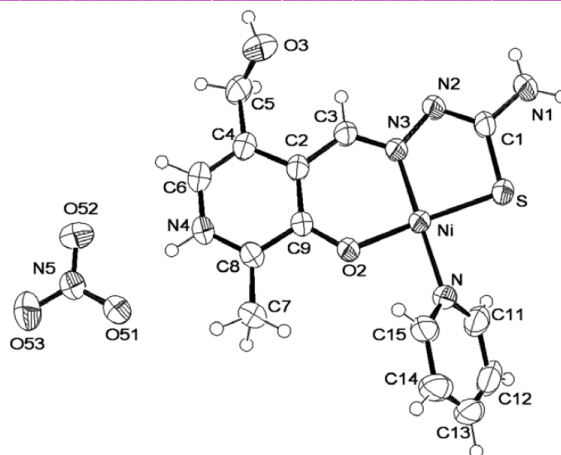


Fig. 4. ORTEP view of  $[\text{Ni}(\text{PLTSC-H})\text{py}]\text{NO}_3$ .

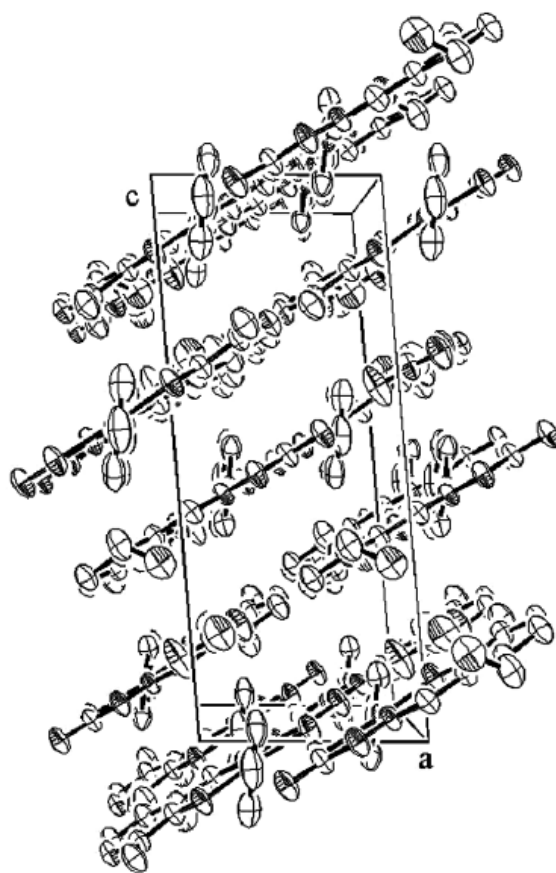


Fig. 5. The crystal structure of  $[\text{Ni}(\text{PLTSC-H})\text{py}]\text{NO}_3$  viewed along the b-axis.

Table 3  
Electronic spectral data for Ni(SCPL) and Ni(TSCPL) complexes in DMF and MeOH

Complex	Solvent	$\lambda_{\max}$ <sup>a</sup> (log $\epsilon$ ) <sup>b</sup> Intraligand and CT kmax	$\lambda_{\max}$ <sup>a</sup> (log $\epsilon$ ) <sup>b</sup> d-d
Ni(PLSC)Cl <sub>2</sub> · 3.5H <sub>2</sub> O(1)	MeOH	243(4.40), 297(3.90), 307(3.93), 321sh(3.80), 394(4.0), 405(4.0)	616(0.95), 720sh(0.70), 930(1.20)
	DMF	301(4.00), 325sh(3.83), 404(4.00)	588(1.07), 1198(1.30)
[Ni(PLSC)(H <sub>2</sub> O) <sub>3</sub> ](NO <sub>3</sub> ) <sub>2</sub> (2)	MeOH	242(4.44), 297(3.92), 305(3.90), 322sh(3.72), 394(4.02), 405(4.01)	606(0.48), 940(1.26), 1053(1.18)
	DMF	301(3.95), 327sh(3.75), 405(3.93)	587(1.09), 720sh(0.78), 980bp(1.04), 1052(0.94), 1199(1.43)
Ni(PLSC)(NCS) <sub>2</sub> · 4H <sub>2</sub> O(3)	MeOH	241(4.46), 298(3.89), 306(3.89) 322sh(3.73), 394(3.94), 405(3.94)	622(0.95), 938(1.18)
	DMF	297bp(4.01), 326sh(3.79), 399(3.86), 410(3.86)	608(1.0), 732sh(0.70), 972(1.32)
[Ni(PLSC-2H)NH <sub>3</sub> ] · 1.5H <sub>2</sub> O(4)	MeOH	241(4.24), 297(3.82), 325(3.76), 393(3.83)	456sh(3.38), ~1195(2.30)
	DMF	305sh(3.86), 319(3.89), 341sh(3.93), 358(4.01)	408(3.78), ~1192(0.95)
[Ni(PLTSC-H)py]NO <sub>3</sub> (5)	MeOH	249(4.41), 293sh(3.92), 327sh(3.79), 407(4.04), 419(4.06)	~870(0.48)
	DMF	295sh(4.02), 325(3.96), 410(4.16), ~425(4.12)	475sh(3.53), ~950(0.5), 1068(0.58), 1200(1.30)
[Ni(PLTSC-H)NCS] (6)	MeOH	249(4.12), 283sh(3.67), 323sh(3.54), 399(3.75), 424(3.66)	476sh(2.95), ~920(1.79), 1200(2.01)
	DMF	302(4.00), ~325(3.92), 410(4.12), 433(4.14)	~500sh(1.81), 1198(1.36)

sh, shoulder; bp, broad peak.

<sup>a</sup>In nm.

<sup>b</sup>In M cm<sup>-1</sup>.

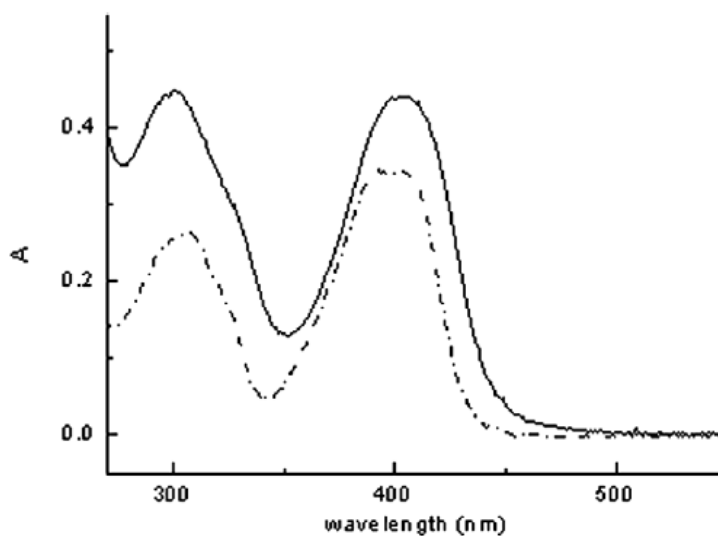


Fig. 1. Electronic spectra of Ni(PLSC)Cl<sub>2</sub> · 3.5H<sub>2</sub>O in MeOH (-----) and DMF (—).



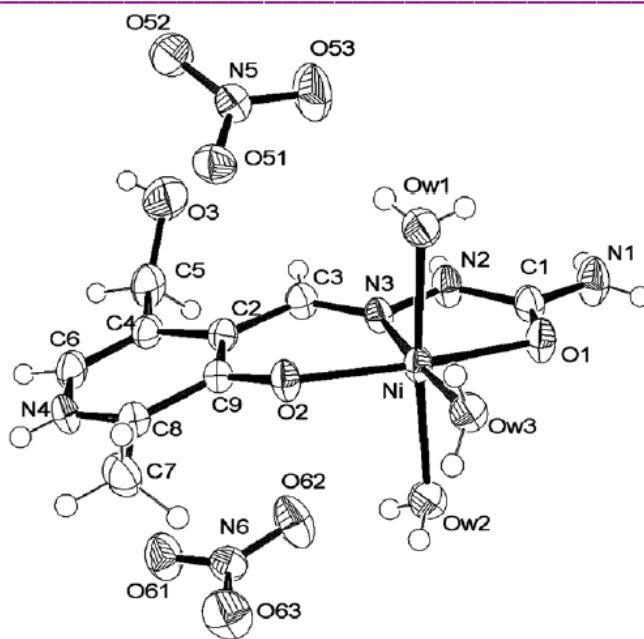


Fig. 2. ORTEP view of  $[\text{Ni}(\text{PLSC})(\text{H}_2\text{O})_3](\text{NO}_3)_2$ .

bands ( $\nu_3$ ) should also be present in this range, but they are masked by the stronger CT absorptions.

Because of their low spectral intensities and the low solubilities of the complexes, the data on d–d transitions are difficult to assign unambiguously. However, having in mind the crystal structure of 2 and the paramagnetic characteristics of the complexes, their light yellow-greenish color of solutions and molar conductivity data, it is reasonable to presume a pseudo-octahedral configuration. Since the PLSC ligand in the crystal occupies three coordination sites in the equatorial plane, the other three sites in the meridional plane are occupied either by three water molecules (1, 2) or, probably, two  $\text{NCS}^-$  and one water molecule (3). In solutions, partial replacement of the anion ( $\text{NCS}^-$ ) with solvent molecules occurs, which was confirmed by the conductivity measurements (see above).

However, the recorded spectra of all three complexes in d–d range are similar thus suggesting a presumption of a similar geometry of these compounds in solution.

A comparison of the spectral data in the two solvents suggests a red shift of the CT bands in the more polar solvent (DMF), arising as a consequence of a positive solvatochromic effect.

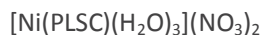
The diamagnetic non-electrolytic complex 4, which is square-planar in the crystal, has probably the same configuration in solution. This assumption is supported by the lack of bands in the visible region. In fact, a d–d band (456 nm,  $\epsilon = 2400 \text{ M cm}^{-1}$ ) appears in MeOH as a shoulder of a stronger CT band, but in DMF these bands overlap. The very poor solubility of this complex in both solvents may be the reason for an apparent absence of weak bands in the region of 900–1000 nm.

The thiosemicarbazone complexes have very broad and unresolved bands in the range 300–350 nm, which are of similar origin to those in the semicarbazone complexes. The other complex band at about 400 nm resulted from

Table 4  
Selected bond distances ( $\text{\AA}$ ) and bond angles ( $^\circ$ )

Compound	$[\text{Ni}(\text{PLSC})(\text{H}_2\text{O})_3](\text{NO}_3)_2$	$[\text{Ni}(\text{PLTSC})\text{py}]\text{NO}_3$
Ni–Ow1	2.0927(19)	

Ni-OW2		2.0539(11)	
Ni-OW3		2.1154(18)	
Ni-O1	Ni(II)	2.0681(14)	
Ni-O2	surrounding	1.9829(12)	1.8483(18)
Ni-N3		2.0161(12)	1.8574(21)
Ni-N			1.9193(21)
Ni-S			2.1345(7)
O1-C1		1.2431(18)	
S-C1			1.7259(25)
O2-C9		1.3036(15)	1.3002(29)
O3-C5		1.4145(32)	1.4194(42)
N1-C1		1.3281(25)	1.3472(34)
N2-N3		1.3675(20)	1.4016(27)
N2-C1		1.3706(20)	1.3100(31)
N3-C3	chelate	1.2886(18)	1.3022(31)
ligand			
N4-C6		1.3434(22)	1.3471(39)
N4-C8		1.3372(18)	1.3351(34)
C2-C3		1.4473(24)	1.4395(33)
C2-C4		1.4199(19)	1.4225(34)
C2-C9		1.4244(19)	1.4057(33)
C4-C5		1.5138(22)	1.4966(38)
C4-C6		1.3632(26)	1.3629(37)
C7-C8		1.4793(25)	1.4871(40)
C8-C9		1.4165(24)	1.4210(34)
N-C15			1.3509(36)
N-C11			1.3394(38)
C11-C12	Py-ring		1.4024(50)
C12-C13			1.3639(65)
C13-C14			1.3461(65)
C14-C15			1.3678(41)



OW1-Ni-OW3	86.95(6)
OW1-Ni-OW2	173.83(6)
OW1-Ni-O1	89.62(5)
OW1-Ni-O2	91.14(5)
OW1-Ni-N3	89.91(6)
OW3-Ni-OW2	87.80(5)
OW3-Ni-O1	98.82(5)
OW3-Ni-O2	92.46(5)
OW3-Ni-N3	176.22(5)
OW2-Ni-O1	87.99(5)
OW2-Ni-O2	92.32(5)
OW2-Ni-N3	95.22(6)
O1-Ni-O2	168.71(5)
O1-Ni-N3	79.06(5)
O2-Ni-N3	89.68(5)

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Ni-O1-C1	112.50(10)
Ni-O2-C9	126.25(10)
N3-N2-C1	115.77(13)
Ni-N3-N2	111.70(10)
Ni-N3-C3	129.28(11)
N2-N3-C3	118.48(13)
C6-N4-C8	124.13(16)
O1-C1-N1	123.59(15)
O1-C1-N2	120.38(16)
N1-C1-N2	116.03(15)
C3-C2-C4	117.43(14)
C3-C2-C9	123.41(13)
C4-C2-C9	119.13(14)
N3-C3-C2	122.27(14)
C2-C4-C5	121.67(15)
C2-C4-C6	119.43(15)
C5-C4-C6	118.90(15)
O3-C5-C4	111.09(17)
N4-C6-C4	120.09(16)
N4-C8-C7	119.79(16)
N4-C8-C9	119.22(14)
C7-C8-C9	120.98(15)
O2-C9-C2	125.70(14)
O2-C9-C8	116.52(13)
C2-C9-C8	117.78(13)

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[Ni(PLTSC)py]NO<sub>3</sub>

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S-Ni-O2	175.49(6)
S-Ni-N	91.65(6)
S-Ni-N3	87.39(6)
O2-Ni-N	85.79(8)
O2-Ni-N3	95.36(8)
N-Ni-N3	176.84(9)
Ni-S-C1	96.24(9)
Ni-O2-C9	127.33(16)
N3-N2-C1	111.49(19)
Ni-N3-N2	121.97(15)
Ni-N3-C3	125.65(17)
N2-N3-C3	112.36(19)
C6-N4-C8	123.83(24)
S-C1-N1	118.76(20)
S-C1-N2	122.90(19)
N1-C1-N2	118.34(23)
C3-C2-C4	119.15(21)
C3-C2-C9	121.45(21)
C4-C2-C9	119.39(22)
N3-C3-C2	125.24(23)
C2-C4-C5	121.85(23)

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C2–C4–C6	118.48(23)
C5–C4–C6	119.64(25)
O3–C5–C4	110.45(22)
N4–C6–C4	120.94(26)
N4–C8–C7	119.40(24)
N4–C8–C9	118.34(23)
C7–C8–C9	122.26(24)
O2–C9–C2	124.61(21)
O2–C9–C8	116.52(22)
C2–C9–C8	118.88(21)
Ni–N–C11	122.54(19)
Ni–N–C15	119.27(17)
C11–N–C15	117.85(24)
N–C11–C12	120.87(30)
C11–C12–C13	19.76(34)
C12–C13–C14	119.00(47)
C13–C14–C15	119.95(31)
N–C15–C14	122.55(26)

the overlapping absorptions of two transitions: LMCT ( $S \rightarrow Ni$ ) and the second  $n \rightarrow \pi^*$  of the deprotonated ligand [22]. The data obtained for d–d transitions, with the exception of the band at about 470–490 nm which appears as a shoulder of the stronger CT band, are ambiguous because of the mentioned low solubility and resultant low absorption intensity. However, on the basis of their diamagnetism, orange-to-red color in solutions and very weak bands (shoulders) in the range of 700–900 nm, a distorted square-planar configuration can be suggested. Furthermore, the existence of a mixture of these and pseudotetrahedral complexes cannot be completely excluded, especially in DMF solutions, as was observed in some previous cases [23].

**Table 5**  
Hydrogen-bonding geometry ( $\text{\AA}$ ,  $^\circ$ )

D-H	D.....A	H.....A	D-H.....A	
<b>Hydrogen bonds of 2</b>				
OW1-H1W1	OW1.....O53	H1W1.....O53	OW1-H1W1.....O53	(1)
0.72(3)	3.049(3)	2.36(3)	161(3)	
OW1-H2W1	OW1.....O63	H2W1.....O63	OW1-H2W1.....O63	(2)
0.70(3)	2.958(2)	2.27(3)	170(3)	
OW2-H1W2	OW2.....O62	H1W2.....O62	OW2-H1W2.....O62	(1)
0.73(2)	2.793(2)	2.06(2)	174(3)	
OW2-H2W2	OW2.....O52	H2W2.....O52	OW2-H2W2.....O52	(3)
0.82(2)	2.811(2)	2.02(2)	162(2)	
OW3-H1W3	OW3.....O2	H1W3.....O2	OW3-H1W3.....O2	(4)
0.86(2)	2.788(2)	1.95(2)	163(2)	
OW3-H2W3	OW3.....O52	H2W3.....O52	OW3-H2W3.....O52	(3)
0.78(3)	2.866(2)	2.14(3)	156(2)	
N1-H1N1	N1.....O53	H1N1.....O53	N1-H1N1.....O53	(5)
0.86(2)	3.004(2)	2.26(2)	144(2)	
N2-HN2	N2.....O61	HN2.....O61	N2-HN2.....O61	(6)
0.82(2)	2.839(2)	2.03(2)	164(2)	
N4-HN4	N4.....O51	HN4.....O51	N4-HN4.....O51	(8)
0.78(2)	2.853(2)	2.11(2)	161(2)	
O3-HO3	O3.....O63	HO3.....O63	O3-HO3.....O63	(7)
0.67(4)	2.995(3)	2.33(4)	168(4)	
Equivalent positions: (1) x, y, z; (2) x, +y + 1, +z; (3) x + 1, +y, +z; (4) -x + 1, -y + 1, -z; (5) -x, -y + 1, -z - 1; (6) -x, -y, -z - 1; (7) x - 1, +y, +z; (8) -x, -y, -z				
<b>Selected hydrogen bonds of 5</b>				
N1-H2	N1.....N2	H2.....N2	N1-H2.....N2	(2)
0.75(4)	3.211(3)	2.46(4)	173(4)	
N1-H10	N1.....O53	H10.....O53	N1-H10.....O53	(3)
0.81(3)	3.155(4)	2.38(4)	162(3)	
N4-H14	N4.....O51	H14.....O51	N4-H14.....O51	(1)
0.92(4)	2.814(3)	1.93(4)	161(3)	
N4-H14	N4.....O52	H14.....O52	N4-H14.....O52	(1)
0.92(4)	3.098(3)	2.35(4)	139(3)	
O3-H11	O3.....O51	H11.....O51	O3-H11.....O51	(4)
0.74(5)	2.765(3)	2.06(5)	159(5)	
Equivalent positions: (1) x, y, z; (2) -x + 1, -y, -z + 1; (3) x + 2, -y + 1/2, +z + 1/2; (4) -x - 1, +y - 1/2, -z + 1/2				

moiety (A) and the six- (B) and five-membered (C) chelate rings are A-B 4.71(7)<sup>0</sup>, A-C 6.63(7)<sup>0</sup> and B-C 2.85(4)<sup>0</sup>. The pyridine nitrogen deviates from the ligand best plane by -0.224(2)Å. The dihedral angle between the pyridine and the chelate ligand best plane is about 52<sup>0</sup>. The angle of ~124<sup>0</sup> for C6-N4-C8 suggests the protonation of the nitrogen from the PL moiety [9]. The nitrate group is strictly planar, and the NO<sub>3</sub> plane lies close to the ligand best plane, with a dihedral angle of 3.9(1)<sup>0</sup>. The packing (Fig. 5) is determined by an extended network of hydrogen bonding, as can be seen from Table 5.

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