COORDINATION
COMPOUNDS

Nickel(II), Nickel(I), and Nickel(0) Complexes with 1,8-Bis(2'-pyridyl)-3,6-dithiaoctane

V. V. Pavlishchuk*, S. V. Kolotilov*, A. W. Addison**, E. Sinn***, and M. J. Prushan**

* *Pisarzhevskii Institute of Physical Chemistry, National Academy of Sciences of Ukraine, pr. Nauki 31, Kiev, 252039 Ukraine*
** *Chemical Department, Drechsel University, Philadelphia, PA 19104 USA*
*** *Chemical Department, Hull University, Hull, HU6 7RX, Great Britain*
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Abstract—Nickel complexes with 1,8-bis(2'-pyridyl)-3,6-dithiaoctane (Pdto) are synthesized; $Ni(Pdto)(H_2O)_2(ClO_4)_2$ is studied by X-ray diffraction.

The discovery of nickel atoms in the composition of numerous enzymes, such as urease and Ni–CO dehydrogenase and hydrogenase, playing an important biological role, has stimulated a great interest in the biomimetic chemistry of this element [1]. In particular, Ni–CO dehydrogenases are found to catalyze the following reactions [2]: synthesis of acetyl coenzyme A from coenzyme A, CO, and a CH_3^+ donor; exchange reactions of CO of the carbonyl group of acetyl coenzyme A (reactions proceed at the active site of Ni–CO dehydrogenase named center A or Ni–Fe center); reversible CO/CO_2 redox reaction (involving the active site of Ni–CO dehydrogenase named center C).

With the use of various methods, including EXAFS, the Ni–Fe center was found to contain the nickel atom surrounded by nitrogen and sulfur donor atoms and the attached Fe_4S_4 cluster [1]. Upon treatment of dehydrogenase with carbon monooxide, the Ni–Fe center is reduced and attaches CO to produce the so-called Ni–Fe–C center [2]. The spatial arrangement of the donor environment of nickel in the active centers of Ni–CO dehydrogenases have not been clearly identified, and the experimental data may be interpreted in terms of both the four-coordinate nickel atom in the square-planar surroundings and the five-coordinate state of the nickel atom [3]. Besides, the oxidation state of nickel neither in the Ni–Fe center of free Ni–CO dehydrogenase nor in the Ni–Fe center at different stages of the catalyzed reactions is determined definitely. The CO adducts with the Ni(I) compounds may be the intermediates in the aforementioned reactions. The progress in the structural study of these unique proteins is restrained by difficulties of their isolation as individual compounds and by the complex structure of the polypeptide chain. In this context, modeling the structure and spectral and redox properties and functions of the active centers of Ni–CO dehydrogenases with sim-

ple synthetic models is actually a real problem. Nickel complexes with thia and aza ligands are concerned as potential models of the active centers of Ni–CO dehydrogenases. The ligands containing thioether sulfur atoms stabilize low oxidation states of metals, in particular, of nickel [4]. The great contribution to the stabilization of low oxidation states is made by σ- and π-dative bonds [4] formed between the donor sites of the ligand and nickel(I) or nickel(0) atoms.

The purpose of this work was to synthesize and study the structural, spectral, and redox parameters of the nickel(II) complex with 1,8-bis(2'-pyridyl)-3,6-dithiaoctane (Pdto) (Fig. 1) and to examine the possibility of nickel(II) reduction to nickel(I) and nickel(0) and the possibility of preparing a CO adduct with the nickel(I) complex. The ligand contains donor sulfur atoms and pyridine residues that are capable of forming dative bonds with the coordinated nickel atom. That is why it is expected that the nickel(II) complex with Pdto should be easily reduced to nickel(I) and nickel(0)
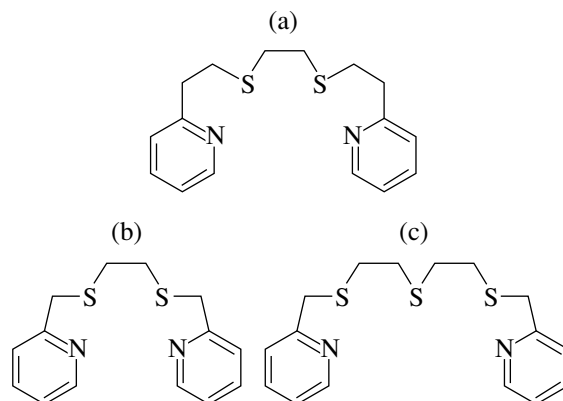

Fig. 1. Ligands (a) Pdto; (b) L1; (c) L2.

complexes. The nickel(II) complexes with 1,6-bis(2'-pyridyl)-2,5-dithiahexane (L1) and 1,9-bis(2'-pyridyl)-2,5,8-trithianonane (L2) (Fig. 1) were prepared recently [4]; however, the literature lacks data on complexes of nickel in low oxidation states with these ligands.

EXPERIMENTAL

Commercially available reagents (ethanol, acetonitrile, benzonitrile, nickel(II) perchlorate hexahydrate) were used without further purification. Pdto (Aldrich) was used without further purification. Elemental analysis for C, H, and N was made with a Carlo Erba 1106 analyzer at the Institute of Physical Chemistry, National Academy of Sciences of Ukraine.

The electronic spectra were recorded on a Specord M40 (Carl Zeiss Jena) spectrometer.

The EPR spectra were recorded on a Varian E-12 spectrometer calibrated with the diphenylpicrylhydrazine radical.

Magnetic susceptibilities were measured on a Johnson Matthey magnetic balance by the Evans method at 293 K.

Electrochemical measurements were carried out at 293 K on a PI-50 potentiostat with a three-electrode system. The working electrode and counter electrode were of platinum. A saturated calomel electrode (SCE) was used as a reference; 0.1 M $NaClO_4$ was used as a supporting electrolyte.

Synthesis of Ni(Pdto)(H$_2$O)$_2$(ClO$_4$)$_2$. A solution of 0.183 g of Ni(ClO$_4$)$_2 \cdot$ 6H$_2$O (0.5 mmol) in 5 ml of 96% ethanol was added to a solution of 0.152 g of Pdto (0.5 mmol) in 5 ml of 96% ethanol at room temperature. In several hours, blue Ni(Pdto)(H$_2$O)$_2$(ClO$_4$)$_2$ began to crystallize from the rich blue solution; after crystallization completed, the product was filtered off and recrystallized from ethanol. The yield was 85%.

For $C_{16}H_{24}O_{10}N_2S_2Cl_2Ni$ anal. calcd. (%): C, 32.13; H, 4.04; N, 4.68. Found (%): C, 32.35; H, 3.91; N, 4.65.

μ_{eff} (cryst) = 2.6 μ_B. For the solution of Ni(Pdto)$^{2+}$ in nitromethane, μ_{eff} = 2.9 ± 0.4 μ_B.

The complex is readily soluble in acetonitrile and benzonitrile and moderately soluble in methanol, 96% ethanol, and nitromethane. A solution of the complex in nitromethane is yellow, unlike solutions in the other solvents.

Reduction of Ni(Pdto)(H$_2$O)$_2$(ClO$_4$)$_2$. Ni(Pdto)(H$_2$O)$_2$(ClO$_4$)$_2$ was reduced by sodium amalgam in a Schlenk flask in an argon atmosphere; the solutions were purged with argon for 20 min. After the reduction, the solutions were removed from mercury by a pipet.

Solution of Ni(Pdto)$^+$ in benzonitrile. A solution of 0.1448 g of Ni(Pdto)(H$_2$O)$_2$(ClO$_4$)$_2$ (0.242 mmol) in 15 ml of benzonitrile was added to the amalgam containing 5.57 × 10^{-3} g (0.242 mmol) of sodium. Within 30–40 s, the color of the solution changed from blue to yellow; then the red-violet shade appeared.

$$Ni(Pdto)^{2+} \xrightarrow[-Na^+]{Na} Ni(Pdto)^+.$$
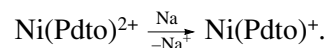
Solution of the adduct of CO and Ni(Pdto)$^+$ in benzonitrile. A solution of Ni(Pdto)$^+$ in benzonitrile (3.5 × 10^{-3} mol/l) was saturated with gaseous CO for 5 min. No change of the color of the solution was observed.

Solution of Ni(Pdto)^0 in acetonitrile. A solution of 0.0963 g of Ni(Pdto)(H$_2$O)$_2$(ClO$_4$)$_2$ (0.161 mmol) in 10 ml of acetonitrile was added to the amalgam containing 7.42 × 10^{-3} g (0.322 mmol) of sodium. The reaction mixture was stirred for 25 min at 50°C; its color changed to red-violet; the black deposit was formed on the amalgam surface.

$$Ni(Pdto)^{2+} \xrightarrow[-2Na^+]{2Na} Ni(Pdto)^0.$$
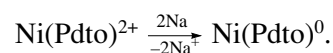
X-ray diffraction study. Crystals of Ni(Pdto)(H$_2$O)$_2$(ClO$_4$)$_2$ are monoclinic with the following unit cell parameters: a = 11.677(5) Å, b = 13.255(2) Å, c = 15.804(4) Å, β = 107.45(3)°, Z = 4, space group $P2_1/c$, V = 2334(2) Å^3, d_{calcd} = 1.70 g/cm^3, μ(MoK_α) = 12.90 cm^{-1}.

All measurements were performed on a Rigaku AFC-6S diffractometer (MoK_α radiation, graphite monochromator, ω-2θ scan mode, 2θ$_{max}$ = 54.1°, 295 K) for a single crystal of dimensions 0.75 × 0.35 × 0.30 mm. The unit cell parameters were obtained by the least-squares method from 25 reflections in the range 18.2° < 2θ < 27.5°. A total of 3930 reflections were collected. Equivalent reflections were averaged, which gave 3670 unique reflections (R_{int} = 0.109); of these, 2552 reflections had $F^2 > 3\sigma F^2$, where the $3\sigma F^2$ value was obtained based on counting statistics. The structure was solved by the heavy-atom method in the anisotropic least-squares approximation and refined with the TEXRAY program package (R = 0.038 and R_w = 0.038, GOOF = 2.66). The weighting scheme was based on counting statistics and included the factor (p = 0.001) for lowering the contribution of intense reflections. The dependences of $\Sigma_w(|F_o - F_c|)^2$ on $|F_o|$, the order of the reflections upon data collection, and $\sin(\theta/\lambda)$ were conventional. The influence of the anomalous dispersion was included in F_c. Statistical processing of data, corrections for the Lorentz and polarization factors and absorption, the scattering factors for neutral atoms, the $\Delta f'$ and $\Delta f''$ values were the same as in [5].

Table 1. Atomic coordinates in Ni(Pdto)(H$_2$O)$_2$(ClO$_4$)$_2$

Atom	x	y	z	B_{eq}, Å^2
Ni	−0.02925(6)	0.01128(4)	0.24225(4)	1.82(2)
Cl(1)	−0.2955(1)	0.0635(1)	−0.04707(9)	3.11(6)
Cl(2)	−0.3740(1)	0.1283(1)	0.3875(1)	3.52(7)
S(1)	0.1824(1)	0.0393(1)	0.26822(8)	2.55(6)
S(2)	−0.0108(1)	0.0836(1)	0.38536(8)	2.37(5)
O(1)	−0.0589(3)	−0.0706(2)	0.1229(2)	2.7(1)
O(2)	−0.2202(3)	−0.0026(3)	0.2098(2)	2.7(1)
O(11)	−0.3875(4)	0.0485(3)	−0.1273(2)	5.6(2)
O(12)	−0.1924(4)	0.0048(3)	−0.0452(2)	5.6(2)
O(13)	−0.2657(4)	0.1671(3)	−0.0359(3)	6.4(2)
O(14)	−0.3349(4)	0.0315(4)	0.0258(3)	6.0(2)
O(21)	−0.3260(5)	0.0688(3)	0.3333(3)	7.8(3)
O(22)	−0.3678(6)	0.2276(3)	0.3682(4)	9.7(3)
O(23)	−0.4918(6)	0.1079(6)	0.3748(6)	16.1(6)
O(24)	−0.3224(9)	0.1095(6)	0.4716(4)	18.7(6)
N(1)	−0.0005(4)	−0.1304(3)	0.3054(2)	2.2(2)
N(2)	−0.0460(3)	0.1512(3)	0.1766(2)	2.1(2)
C(2)	0.0902(5)	−0.1952(4)	0.3088(3)	2.5(2)
C(3)	0.0979(5)	−0.2862(4)	0.3517(4)	3.5(3)
C(4)	0.0138(6)	−0.3130(4)	0.3931(4)	4.0(3)
C(5)	−0.0776(5)	−0.2476(4)	0.3905(3)	3.0(2)
ë(6)	−0.0817(4)	−0.1583(4)	0.3472(3)	2.4(2)
C(7)	0.1813(5)	−0.1681(4)	0.2638(3)	3.3(2)
C(8)	0.2603(5)	−0.0785(4)	0.3046(3)	3.3(2)
C(9)	0.2187(5)	0.1123(4)	0.3700(4)	3.7(3)
C(12)	−0.0855(4)	0.2390(4)	0.2019(3)	2.2(2)
C(13)	−0.0796(5)	0.3276(4)	0.1573(4)	3.0(2)
C(14)	−0.0352(5)	0.3279(4)	0.0858(4)	3.3(3)
C(15)	0.0050(5)	0.2397(4)	0.0608(3)	3.0(2)
C(16)	−0.0012(5)	0.1548(4)	0.1069(3)	2.6(2)
C(17)	−0.1352(5)	0.2396(4)	0.2792(3)	2.6(2)
C(18)	−0.0436(5)	0.2177(4)	0.3692(4)	3.0(3)
C(19)	0.1501(5)	0.0808(5)	0.4316(4)	3.5(3)

Final atomic coordinates and thermal parameters (B_{eq}) are given in Table 1.

RESULTS AND DISCUSSION

Molecular structure of Ni(Pdto)(H$_2$O)$_2$(ClO$_4$)$_2$.
The coordination sphere of Ni(Pdto)(H$_2$O)$_2$(ClO$_4$)$_2$ is a distorted octahedron with the N$_2$S$_2$O$_2$ donor environ-

ment of the nickel atom (Fig. 2). The nitrogen donor atoms occupy *trans* positions, and the oxygen and sulfur atoms occupy *cis-, cis* positions. The magnetic moment for Ni(Pdto)(H$_2$O)$_2$(ClO$_4$)$_2$ is consistent with an octahedral structure of the coordination polyhedron [6]. The Ni–N (2.106 and 2.105 Å) and Ni–S (2.409 and 2.406 Å) bonds in Ni(Pdto)(H$_2$O)$_2$(ClO$_4$)$_2$ (Table 2) are, respectively, the same as the Ni–N (2.105, 2.104 Å) bonds and slightly shorter than the Ni–S (2.411, 2.421 Å) bond lengths in NiL1(CH$_3$CN)$_2$(ClO$_4$)$_2$ [7]. In NiL2(H$_2$O)(ClO$_4$)$_2$ · CH$_3$OH, the Ni–N bonds (2.058, 2.084 Å) are slightly shorter, whereas the Ni–S bonds (2.392, 2.426, 2.460 Å) are, on the average, longer than the corresponding bonds in Ni(Pdto)(H$_2$O)$_2$(ClO$_4$)$_2$ [7]. The angles at the nickel atom in Ni(Pdto)(H$_2$O)$_2$(ClO$_4$)$_2$ are close to the value expected for the regular octahedron. In the crystal, the perchlorate ions are united with the complex cation through water molecules by hydrogen bonds. Elongation of the carbon chain between the nitrogen and sulfur donor atoms in Pdto as compared to L1 seems to improve the fit of the spatial arrangement of donor atoms (SADA) [8] as compared to NiL1(CH$_3$CN)$_2$(ClO$_4$)$_2$. Thus, the bonds (Ni–S) may be shortened in Ni(Pdto)(H$_2$O)$_2$(ClO$_4$)$_2$, the deviations of the bond angles at the nickel atom from the values expected for a regular octahedron being similar. Significantly shortened Ni–S bonds in Ni(Pdto)(H$_2$O)$_2$(ClO$_4$)$_2$ as compared to NiL2(H$_2$O)(ClO$_4$)$_2$ · CH$_3$OH (except one Ni–S bond 2.392 Å long) may be explained by a great contribution to the SADA energy from the energy of steric hindrances and hindrances caused by orientation of the orbitals of lone electron pairs of sulfur atoms in the directions of their maximal overlap with the orbitals of the nickel atom. In NiL2(H$_2$O)(ClO$_4$)$_2$ · CH$_3$OH, three bulky sulfur atoms linked by relatively short carbon bridges force out one another from the coordination sphere, whereas the Ni(Pdto)(H$_2$O)$_2^{2+}$ complex contains only two sulfur atoms and does not show this effect.

The Ni–S bond lengths in the nickel(II) octahedral complexes vary in a wide range. For example, the average Ni–S bond length is 2.386 Å in Ni([9]aneS$_3$)$_2$]$^+$ ([9]aneS$_3$ = 1,4,7-trithiacyclononane) [9] and 2.431 Å in Ni([24]aneS$_6$)$_2$]$^{2+}$ ([24]aneS$_6$ = 1,5,9,13,17,21-hexathiacyclotetracosane) [10]. The Ni–S, Ni–N, and Ni–O bond lengths in the thiapyridyl complexes are typical of nickel(II) octahedral complexes; Ni(Pdto)(H$_2$O)$_2$(ClO$_4$)$_2$ by structural properties does not stand out of the series of nickel(II) octahedral complexes.

Electronic absorption spectra. The electronic absorption spectrum of Ni(Pdto)(H$_2$O)$_2$(ClO$_4$)$_2$ in acetonitrile in the range 11 000–35 000 cm^{-1} is typical of nickel(II) high-spin complexes with the octahedral or pseudooctahedral environment of donor atoms. The spectrum reveals two bands at $\nu_1 = 11500$ and $\nu_2 = $
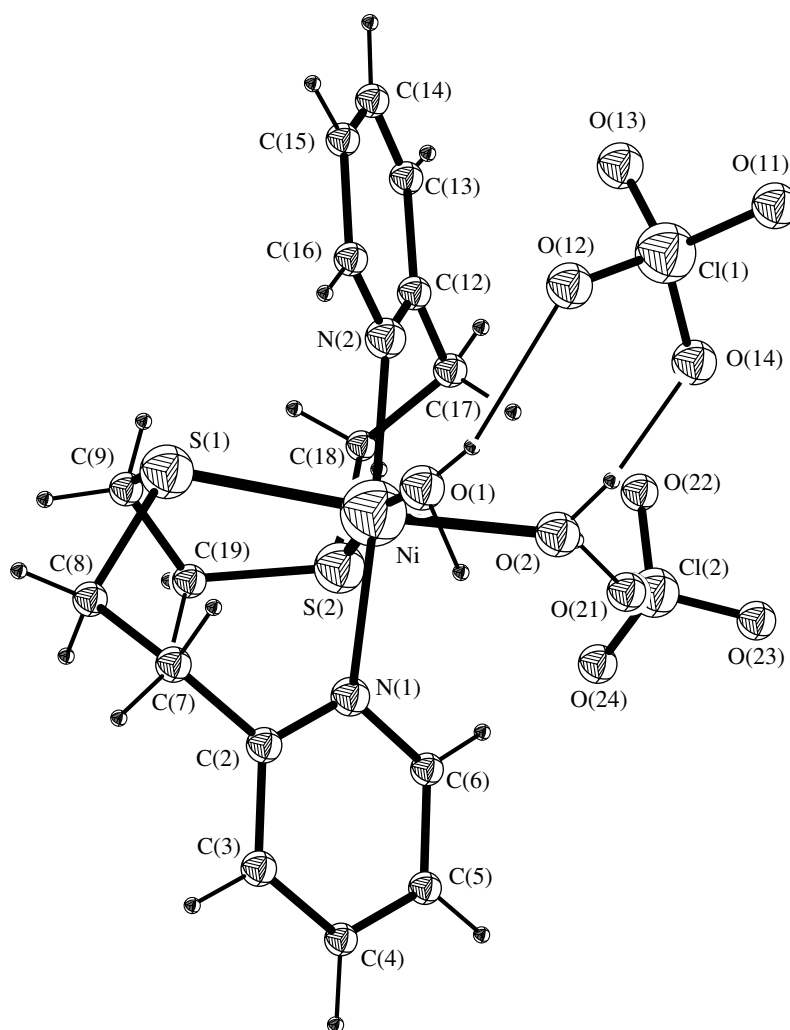
Fig. 2. Molecular structure of $Ni(Pdto)(H_2O)_2(ClO_4)_2$.

17600 cm^{-1}. By analogy with the assignment in [11], these bands may be assigned to the $^3A_{2g} \longrightarrow {}^3T_{2g}$ and $^3A_{2g} \longrightarrow {}^3T_{1g}(F)$ transitions, respectively. The third transition expected for the nickel(II) high-spin atom in the octahedral environment is not observed, because it is overlapped by the intense charge-transfer band at 34100 cm^{-1}. The electronic absorption spectrum of the complex in acetonitrile differs strongly from the diffusion reflection spectrum of $Ni(Pdto)(H_2O)_2(ClO_4)_2$ (Table 3). This indicates a significant change in the nickel environment upon dissolution of the complex in acetonitrile; we suppose that solvent molecules substitute for the coordinated water molecules. Neither the electronic absorption spectrum of $Ni(Pdto)^{2+}$ in acetonitrile nor its diffusion reflection spectrum show the features of a tetragonal distortion of the coordination sphere [12]. That is why the spectra may be interpreted in terms of the octahedral symmetry of the ligand field. For strongly diluted acetonitrile solutions, the values of optical density slightly differ from the Lambert–Bou-guer–Beer law, which may be explained by some dissociation of $Ni(Pdto)^{2+}$.

The 10Dq value (11450 cm^{-1}) for $Ni(Pdto)^{2+}$ in acetonitrile, calculated from the position of the $^3A_{2g} \longrightarrow {}^3T_{2g}$ band [11], slightly differs from the 10Dq values for $NiL1(CH_3CN)_2^{2+}$ and $NiL2(H_2O)^{2+}$ in acetonitrile (11800 and 11400 cm^{-1}, respectively) [7]; the Racah parameter for $Ni(Pdto)^{2+}$ ($B = 722$ cm^{-1} in acetonitrile) calculated as $B_{complex} = (2\nu_1^2 + \nu_2^2 - 3\nu_1\nu_2)/(15\nu_2 - 27\nu_1)$ [7] is less than the Racah parameter for $NiL2(H_2O)^{2+}$ (936 cm^{-1} in acetonitrile) and is nearly the same as the Racah parameter for $NiL1(CH_3CN)_2^{2+}$ (728 cm^{-1} in acetonitrile). The maximal deviation of the Racah parameter for $Ni(Pdto)^+$ from the B value for the gaseous Ni^{2+} ion ($B = 1038$ cm^{-1}) indicates the greatest covalence of the Ni–D bonds (D is a donor atom) in the nickel(II) complex with Pdto as compared to the

Table 2. Selected bond lengths and angles in Ni(Pdto)(H$_2$O)$_2$(ClO$_4$)$_2$

Bond	d, Å	Bond	d, Å
Ni–S(1)	2.409(2)	Ni–S(2)	2.406(1)
Ni–O(1)	2.112(3)	Ni–O(2)	2.141(3)
Ni–N(1)	2.106(4)	Ni–N(2)	2.105(4)
Angle	ω, deg	Angle	ω, deg
S(1)NiS(2)	88.88(5)	S(1)NiO(1)	96.7(1)
S(1)NiO(2)	174.6(1)	S(1)NiN(1)	92.7(1)
S(1)NiN(2)	83.5(1)	S(2)NiO(1)	171.3(1)
S(2)NiO(2)	93.0(1)	S(2)NiN(1)	87.3(1)
S(1)NiN(2)	94.7(1)	O(1)NiO(2)	82.1(1)
O(1)NiN(1)	85.7(1)	O(1)NiN(2)	92.7(1)
O(2)NiN(1)	92.5(1)	O(2)NiN(2)	91.2(1)
N(1)NiN(2)	175.7(2)		

nickel(II) complexes with L1 and L2. Taking into account the probable substitution of acetonitrile for the coordinated water molecules in Ni(Pdto)(H$_2$O)$_2^{2+}$, the nickel(II) ion in the S$_2$N$_4$ donor environment in Ni(Pdto)(CH$_3$CN)$_2^{2+}$ should be compared to the S$_2$N$_4$ environment in NiL1(CH$_3$CN)$_2^{2+}$ and the S$_3$N$_2$O environment in NiL2(H$_2$O)$^{2+}$. The larger 10Dq value for Ni(Pdto)(CH$_3$CN)$_2^{2+}$ as compared to NiL2(H$_2$O)$^{2+}$ is explained by the effect of the donor surroundings: In this case, the contribution of the nitrogen donor atom to the field created by the coordinated donor atoms is greater than the contribution of the sulfur donor atom; this effect is somewhat compensated for by that the contribution of the oxygen atom of coordinated water

to the field created by the coordinated donor atoms in NiL$_2$(H$_2$O)$^{2+}$ is smaller than the contribution from the nitrogen atom of coordinated acetonitrile in Ni(Pdto)(CH$_3$CN)$_2^{2+}$ [11].

The B value may be expected to be the least in the NiL2(H$_2$O)$^{2+}$ complex, where the nickel(II) atom is coordinated with three sulfur atoms, because the B values for the nickel(II) complexes with the S$_6$ environment are less than for the complexes with the N$_6$ environment [13]. The notably higher B value for NiL2(H$_2$O)$^{2+}$ as compared to Ni(Pdto)$^{2+}$ and NiL1(CH$_3$CN)$_2^{2+}$ may be explained by mutual forcing out of the sulfur atoms from the coordination sphere in NiL2(H$_2$O)$^{2+}$, which results in the elongation of the Ni−S bonds and, hence, in the diminution of the overlap of the nickel d orbitals with the sulfur σ orbitals and the degree of covalence of the Ni–S bonds. The smallest B value for Ni(Pdto)$^{2+}$ indicates the best fit of the SADA parameters for the nickel(II) complex with Pdto in the L1–Pdto–L2 series: The maximal degree of the covalence for the bonds of nickel(II) with the ligand atoms, or the maximal overlap of the nickel d orbitals and the σ orbitals of the donor atoms, can occur upon the smallest distortion of the angles at the nickel atom (for comparable bond lengths) achieved at the optimal geometric and electronic fit of the metal ion to the ligand [8].

The electronic absorption spectrum of Ni(Pdto)$^{2+}$ in nitromethane in the range of 11000–26000 cm^{-1} reveals absorption bands at 21 850 and 16 800 cm^{-1}. The spectrum is not characteristic of the octahedral high-spin nickel(II) complexes [11], and we suppose that the Ni(Pdto)(H$_2$O)$_2^{2+}$ complex cation in CH$_3$NO$_2$ undergoes dissociation with elimination of one or two water molecules or its Ni–S bond (weaker than the Ni–N bond) is ruptured. This leads to lowering the ligand field symmetry from pseudooctahedral to a lower one.

Table 3. Electronic absorption spectra for nickel(II) complexes

Complex	ν_{max}, cm^{-1} (ε, l mol^{-1} cm^{-1})	10Dq, cm^{-1}	B, cm^{-1}
Ni(Pdto)(H$_2$O)$_2$(ClO$_4$)$_2^a$	11450(30.4); 17600(19.6)	11450	722
Ni(L1)(CH$_3$OH)$_2$(ClO$_4$)$_2^b$	10800 (sh); 11800(30); 18000(20)	11800	728
Ni(L2)(H$_2$O)(ClO$_4$)$_2^b$	10150 (sh); 11400(50); 18350(30)	11400	936
Ni(Pdto)(H$_2$O)$_2$(ClO$_4$)$_2^c$	21850(67.5); 16800(12.8)		
Ni(Pdto)(H$_2$O)$_2$(ClO$_4$)$_2^d$	16320; 27200		

^{a} Spectrum in CH$_3$CN.
^{b} Taken from [7].
^{c} Spectrum in CH$_3$NO$_2$.
^{d} Diffusion reflection spectrum.

The value of the magnetic moment for Ni(Pdto)$^{2+}$ in this solution (2.9 ± 0.4 μ_B) indicates that the solution contains Ni(II) in the high-spin state. Suggestions of the formation of the square-planar complex are in conflict with measurements of the magnetic moment in solution: The vast majority of square-planar nickel(II) complexes are diamagnetic. The square-pyramidal, trigonal-bipyramidal, and tetrahedral nickel(II) complexes of C_{4v}, C_{3v}, and T_d symmetry, respectively, are documented, whose electronic spectra are similar to the spectrum of Ni(Pdto)$^{2+}$ in nitromethane [14–16]; that is why we failed to uniquely determine the symmetry of the coordination sphere of Ni(Pdto)$^{2+}$ in nitromethane. Note that Ni(Pdto)(H$_2$O)$_2$(ClO$_4$)$_2$ may be recrystallized from nitromethane quantitatively; therefore, the changes in the spectrum are not caused by any irreversible decomposition of the complex.

Redox behavior of Ni(Pdto)$^{2+}$. Two redox processes are found for Ni(Pdto)$^{2+}$ in an acetonitrile solution at $E_{1/2} = -0.975$ V and $E_a = +0.26$ V against SCE. The quasi-reversible ($\Delta E = 150$ mV, $i_a/i_c \approx 1$) process at -0.975 V is caused by reduction of Ni(Pdto)$^{2+}$ to Ni(Pdto)$^+$, and the process at $+0.26$ V is caused by irreversible oxidation to Ni(Pdto)$^{3+}$. The potential for the Ni^{2+}/Ni$^+$ couple for Ni(Pdto)$^{2+}$ is the most negative as compared to NiL1(CH$_3$CN)$_2^{2+}$ and NiL2(H$_2$O)$^{2+}$ (-0.784 and -0.642 V versus SCE, respectively [7]). For NiL2(H$_2$O)$^{2+}$, this difference may be explained by a better stabilization of lower nickel oxidation states by the L2 ligand including a greater number of softer sulfur donor atoms as compared to L1 and Pdto.

Formation of Ni(I) and Ni(0). Taking into account the negligible dissociation of Ni(Pdto)$^{2+}$ in acetonitrile, the reduction was studied both in acetonitrile and benzonitrile; the solutions in benzonitrile were more stable in storage and toward the action of the atmospheric oxygen. The electronic spectra of the Ni(I) and Ni(0) complexes are given in Table 4. The electronic spectrum in the visible region of Ni(Pdto)$^{2+}$ reduced by two equivalents of sodium amalgam is similar to the spectrum of Ni$_2$(Pdmt)$_2^-$ prepared by electrochemical reduction of Ni(II) in the binuclear complex with Pdmt to Ni(I) [17] (Pdmt^{2-} is pyridine-2,6-bis(methylthiolate)). Hence, the presence of the Ni(Pdto)$^+$ impurity in the solution of Ni(Pdto)^0 may be assumed; therefore, the reduction of Ni(Pdto)$^{2+}$ with the sodium amalgam is not stoichiometric. The non-stoichiometry of the Ni(Pdto)$^{2+}$ reduction may be caused by the concurrent reaction between sodium and water molecules involved in the coordination sphere of Ni(Pdto)(H$_2$O)$_2$(ClO$_4$)$_2$. The similarity of the electronic spectra of the solutions prepared after oxidation of Ni(Pdto)$^+$ by atmospheric oxygen to the spectra of the initial solutions prepared from pure Ni(Pdto)(H$_2$O)$_2$(ClO$_4$)$_2$ indicates the possibility of reoxidation of Ni(Pdto)$^+$ to Ni(Pdto)$^{2+}$ (upon

Table 4. Electronic absorption spectra for nickel(I) and nickel(0) complexes

Complex	ν_{max}, cm^{-1}
Ni(Pdto)$^{+}$ [a]	19400; 11500
Ni(Pdto)$^{+}$ [b]	19500(180); 11500 (sh)
Ni(Pdto)$^{+}$ + CO [b]	19000 (sh); 14600 (sh)
Ni(Pdto)^{0} [a]	26000 (sh); 20000 (sh)
[Ni(Pdmt)]$_2^{-}$ [c]	26300 (sh); 22000 (sh); 16300 (sh)

[a] Spectrum in CH$_2$CN.
[b] Spectrum in C$_6$H$_5$CN.
[c] Taken from [17]; Pdmt is pyridine-2,6-bis(methylthiolate).

oxidation by the atmospheric oxygen, one of the coordination sites seems to be occupied by the OH$^-$ group, which causes some differences in the spectra).

The electronic spectrum of the Ni(Pdto)$^+$ solution saturated with CO differs from the electronic spectrum of initial Ni(Pdto)$^+$ and is similar to the electronic spectrum of Ni(Pdto)^0 by its contour. This difference may indicate the formation of the adduct of the Ni(I) complex with CO. To some extent, the adduct formation may be considered to be a model for one of the stages of CO fixation by Ni–CO dehydrogenases.

The EPR spectrum of the frozen solution of Ni(Pdto)$^+$ in butyronitrile at 77 K with the parameters $g_\parallel = 2.275(4)$ and $g_\perp = 2.081(4)$ is similar to the EPR spectra of the Ni(I) complexes [18]. This fact supports the formation of nickel(I), rather than the pyridyl anion-radicals from Pdto, upon the reduction.

The Ni–Fe–C center of dehydrogenase from *Clostridium thermoacetium* gives the EPR signal with $g_1 = 2.08$, $g_2 = 2.075$, and $g_3 = 2.028$ [2]. This signal is assigned to the entire Ni–Fe–C center, and a significant delocalization of electronic density within the center is proposed. Comparing the parameters of this signal to those of the EPR spectrum of Ni(Pdto)$^+$ permits us to suggest that the unpaired electron of the Ni–Fe–C center of dehydrogenase is appreciably localized at the nickel atom rather than at the Fe$_4$S$_4$ component (note that, in the EPR spectrum of dehydrogenase, the EPR signal of center C containing the Fe$_4$S$_4$ cluster is observed at $g_{av} = 1.94$ [2]).

Our findings indicate that Pdto forms the pseudooctahedral high-spin nickel(II) complex. The best fit of the spatial arrangement of donor atoms for Pdto in the series of the nickel(II) complexes with Pdto, L1, or L2 is supported by comparing structural, spectral, and redox properties of the complexes. Ni(Pdto)$^{2+}$ is reversibly reduced by sodium amalgam in a solution to form nickel(I) and nickel(0) complexes. Upon saturation of the Ni(Pdto)$^+$ solutions with carbon(II) oxide,

Ni(Pdto)$^+$ reacts with CO probably producing an adduct. Formation of the nickel(I) and nickel(0) complexes, reaction of the nickel(I) complex with CO and similarity of the EPR spectral parameters of Ni(Pdto)$^+$ to the Ni–Fe–C center of Ni–CO dehydrogenases permit us to consider the Ni(Pdto)$^{2+}$ complex as a potential model for the nickel fragment of the Ni–Fe center of Ni–CO dehydrogenases.

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REFERENCES

1. Halcrow, M.A. and Christou, G., *Chem. Rev.*, 1994, vol. 94, p. 2421.

2. Shin, W. and Lindahl, P.A., *Biochemistry*, 1992, vol. 31, p. 12870.

3. Bastian, N.R., Diekert, G., Niederhoffer, E.C., *et al.*, *J. Am. Chem. Soc.*, 1988, vol. 110, p. 5581.

4. Yatsimirskii, K.B., *Teor. Eksp. Khim.*, 1997, vol. 33, no. 5, p. 284.

5. Addison, A.W., Rao, T.N., and Sinn, E., *Inorg. Chem.*, 1984, vol. 23, p. 1957.

6. Bersuker, I.B., *Elektronnoe stroenie i svoistva koordinatsionnykh soedinenii* (Electronic Structure and Properties of Coordination Compounds), Leningrad: Khimiya, 1986.

7. Adhikary, B., Liu, S., and Lucas, R., *Inorg. Chem.*, 1993, vol. 32, p. 5957.

8. Yatsimirskii, K.B., *Teor. Eksp. Khim.*, 1980, vol. 16, no. 1, p. 34.

9. Setzer, W.N., Ogle, C.A., Wilson, G.S., and Glass, R.S, *Inorg. Chem.*, 1983, vol. 22, p. 266.

10. Blake, A.J. and Schröder, M., *Adv. Inorg. Chem.*, 1990, vol. 35, p. 2.

11. Lever, A.B.P., *Inorganic Electronic Spectroscopy*, Amsterdam: Elsevier, 1968.

12. Martin, L.Y., Sperati, C.R., and Busch, D.H., *J. Am. Chem. Soc.*, 1977, vol. 99, p. 2968.

13. Cooper, S.R., Rawle, S.C., Hartman, J.R., *et al.*, *Inorg. Chem.*, 1988, vol. 27, p. 1209.

14. Ciampolini, M., *Inorg. Chem.*, 1966, vol. 5, p. 35.

15. Ciampolini, M. and Nardi, N., *Inorg. Chem.*, 1966, vol. 5, p. 41.

16. Sacconi, L. and Gelsomini, J., *Inorg. Chem.*, 1968, vol. 7, p. 291.

17. Krüger, H.-J. and Holm, R.H., *Inorg. Chem.*, 1989, vol. 28, p. 1148.

18. Bowmaker, G.A., Boyd, P.D.W., Campbell, G.K., *et al.*, *Inorg. Chem.*, 1982, vol. 21, p. 1152.