Redox properties of N_2S_2-type nickel complexes with aromatic ligands. Crystal structure of $[1,2\text{-}C_6H_4(SMe)NH_2]_2Ni^{2+}(MeCN)_2 \cdot 2ClO_4^-$

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The redox properties of six chelate N_2S_2-type Ni(II) complexes containing two aromatic NS or one N_2S_2 ligands, such as 2-aminothiophenol, 2-aminothiophenolate anion, 2-amidothiophenolate dianion, 2-amidothioanisole, 2,2´-diaminodiphenyl disulfide dianion, and 8-quinolinethiolate anion, were studied by cyclic voltammetry at a glassy-carbon electrode in DMF. Some free ligands were also studied for comparison. A new Ni^{II} complex with the 2,2´-diamidodiphenyl disulfide dianion was synthesized. The crystal and molecular structures including the square planar $Ni(N_2S_2)$ center with two MeCN molecules as additional axial ligands were established for the Ni^{II} complex with 2-aminothioanisole $[1,2\text{-}C_6H_4(SMe)NH_2]_2Ni^{2+}(MeCN)_2 \cdot 2ClO_4^-$ using X-ray diffraction. The most part of the studied compounds are irreversibly oxidized and reduced; however, bis(2-amidothiophenolato)nickel(IV) and bis(8-quinolinethiolato)nickel(II) show a quasi-reversible behavior in the reduction region. The electrochemically generated anionic form of the 8-thioquinoline complex is rapidly alkylated in the presence of Bu^nBr or Bu^nI to form, probably, the corresponding butylnickel(III) complex.

Key words: nickel chelate complexes, aromatic NS and N_2S_2 ligands, synthesis, electrochemistry, crystal structure of the Ni^{II} complex with 2-aminothioanisole, electrochemical alkylation, organic compounds of Ni^{III}.

Enzymes containing one or two nickel atoms in the active center are known.[1—4] Some of them react *via* the electron transfer mechanism (redox enzymes): Ni—A hydrogenase from *Desulfovibro gigas* controls the equilibrium $H_2 \rightleftharpoons 2H^+ + 2e^-$, carbon monoxide dehydrogenases (CODH) catalyze the reaction of CO with water ($CO + H_2O \rightleftharpoons CO_2 + 2\ H^+ + 2e^-$) and conjugated synthesis of acetyl-*S*-CoA, and methyl-*S*-CoM reductase transforms the methyl coenzyme M into methane and disulfide.[1] In these redox enzymes, when they are ready to work, the nickel center usually has a square planar configuration and is coordinated to four sulfur atoms (designated as S_4), nitrogen (N_4), or two nitrogen atoms and two sulfur atoms (N_2S_2).

In the catalytic cycle, the Ni^{II}-containing metallocenters in CODH/MeCOS-CoA synthases and MeS-CoM reductases undergo reduction to Ni^I and then methylation at nickel to form the organometallic Ni^{III}—Me compounds, which are transformed, in the case of CODH/MeCOS-CoA synthase, into the acetyl Ni^{III}—COMe compounds. These organic compounds of trivalent nickel are carriers of the Me group from the sulfur atom of the MeS—CoM or MeCO group to the thiol sulfur atom in HS—CoA.

Organometallic complexes containing the Ni^{III}—C bond are labile kinetically and readily dissociate through the metal—carbon bond ($Ni^{III}\text{—}R \rightarrow Ni(II) + R^{\bullet}$). Stability of such compounds strongly depends on the nature

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of polydentate ligands bound to the metal (see, *e.g.*, Ref. 4 and references cited therein). The anionic $[2,6\text{-}(\mathrm{Me_2NCH_2})\mathrm{C_6H_3}]^-$ ligand is unique in stabilization of the $\mathrm{Ni^{III}}$ organometallic compounds,[5–7] strongly decreasing the $\mathrm{Ni^{II}/Ni^{III}}$ redox potential.[8] The formation of labile intermediates with the $\mathrm{Ni^{III}}$—C bond in metal complex catalysis and biology is postulated by many authors.[3,4,9–13]

Electrochemical methods are convenient for the generation of unstable compounds with the $\mathrm{Ni^{III}}$—C bond and complexes containing $\mathrm{Ni^{IV}}$, $\mathrm{Ni^{I}}$, and $\mathrm{Ni^{0}}$. These methods make it possible to identify these species in a solution, if their lifetime is at least comparable with the characteristic time of a given electrochemical method. Previously,[14] we showed the possibility of electrochemical detection of $\mathrm{N_2S_2}$-type methylnickel(III) complex containing α-thiopicolinamide ligands, which is formed by the methylation *in situ* of the electrochemically generated $\mathrm{Ni^{I}}$ complex with methylcobaloxime. This process was used for the electrochemical modeling of one of the main stages in the mechanism of operating of the active center of acetyl-*S*-CoA synthase.[14]

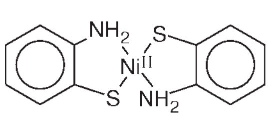
In this work, we electrochemically studied the redox properties of the nickel complexes with aromatic ligands of the $\mathrm{N_2S_2}$ type, *viz.*, benzene or quinoline derivatives, and the possibility of alkylation of their reduced forms containing $\mathrm{Ni^{I}}$.

Results and Discussion

We studied the $\mathrm{Ni^{II}}$ and $\mathrm{Ni^{IV}}$ complexes with aromatic ligands and free ligands: 2-aminothiophenol (**L1**), 2,2′-diaminodiphenyl disulfide (**L5**), and 2-aminothioanisole (**L3**).

The crystal and molecular structures of complex **3** were determined by X-ray diffraction. The molecular structures of compounds **1** and **2** were not established. We failed to prepare crystals of complex **1** appropriate for X-ray diffraction analysis and, therefore, we arbitrarily ascribe the *trans*-configuration to compounds **1** and **2**. Some arguments in favor of this assumption are the results of studying the $[\mathrm{Ni(NHC_6H_4S)_2}]\mathrm{Ph_4As}$ salt containing one complex anion in which Ni exists in a formal oxidation state of +3. According to the X-ray diffraction data, the anion in this compound, which is closest in structure to the complexes studied in this work, is square planar with the *trans*-configuration of the NS ligands.[15]

Synthesis and structure of the complexes. For complex **1** first described in 1949, the authors[16,17] proposed the polymeric structure with bridging sulfur atoms because of its very low solubility in all solvents studied. It was shown later[18] that this compound is diamagnetic. Hence, a square planar monomeric structure was ascribed to it. The absence of the bridging sulfur atoms is also confirmed by the fact of *S*-alkylation of this complex with alkyl halides to form bis(*ortho*-aminoalkylthio)nickel(II) dihalides,[19] which is characteristic of only terminal rather than bridging sulfur atoms.[20]



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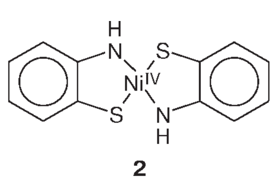

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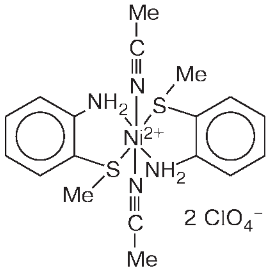

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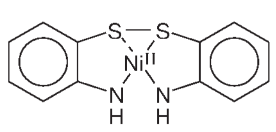

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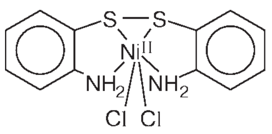

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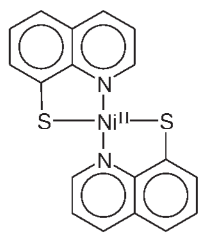

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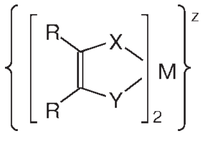
Independent authors gave contradictory descriptions of this complex. For example, the authors[16,17] described nickel bis-2-aminophenyl thiolate as a yellow substance, whereas the others[21,22] described it as green. In addition, it was established[17] the reaction of *ortho*-aminothiophenol with nickel nitrate in a water-alcohol medium affords a light-yellow complex, while the reaction in an aqueous solution of NaOH or treatment of the ready yellow complex with aqueous alkali results in a black-blue product, so that the green color ascribed to complex **1** by several authors is probably due to the presence of an admixture of a dark-blue complex in the yellow substance. Thus, two different complexes can be formed by the reaction of *ortho*-aminothiophenol with nickel(II) salts.

The yellow substance was assumed[23] to be the expected bis(2-aminothiophenolato)nickel(II), whose suspension in a basic medium in air is rapidly oxidized to form a blue complex with the bridging oxygen atoms between two nickel atoms. However, according to the elemental analysis data,[23] this complex contains no oxygen, and the content of other elements is the same as in the yellow compound.

The structure of the square planar $\mathrm{Ni^{II}}$ aminothiolate complex was ascribed[24,25] to the yellow complex from the measurement of the magnetic moment (measured magnetic moment of this complex is equal to zero, which corresponds to the predicted value for the square planar Ni^{II} complex), and the structure of the a Ni^{IV}* iminothiolate complex was ascribed to the blue compound from the elemental analysis data,[24] IR spectroscopy, and measurement of the magnetic moment.[25] It was firmly proved[25] that the reaction of *ortho*-aminothiophenol with Ni^{II} salts under anaerobic conditions affords only the yellow complex, which is readily oxidized to the blue complex in air in a basic medium.

In addition, the authors[25] showed the possibility of deprotonation of the nickel(II) and palladium(II) aminothiophenolate complexes with potassium amide in liquid ammonia to form the corresponding $K_2[M(NHC_6H_4S)_2]$ salts. These salts react with water to regenerate the initial aminothiolate complex.[26] In the case of the deprotonated palladium complex, the reaction product with methyl iodide, *viz.*, $K_2[Pd(MeNHC_6H_4SMe)_2]$, was additionally isolated.

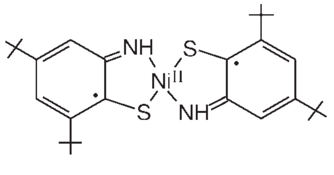
The authors[27,28] discussed the possibility for the complexes with the structure presented below to enter into the reactions of chemical and electrochemical stepwise electron transfer to form species with the charge $z = 0, -1, -2$.



X. Y = NH, O, or S

It was concluded that only the nickel atom in the oxidation state higher than +2 can stabilize the *ortho*-amidothiophenolate ligand. This requires, perhaps, a more basic reaction medium; the acidic properties of the coordinated amino group strongly depend on the charge and size of the central metal atom.

Several reports devoted to the structure of complexes of type **2** appeared recently.[29—31] The iminothionobenzosemiquinonate structure was proposed for the Ni complex of 2-mercapto-3,5-di-*tert*-butylaniline.[29]



According to the data of ^1H NMR spectra in CH_2Cl_2, fast equilibrium between the *cis*- and *trans*-forms of the complex exists in this case.**

The $NiCl_2$ complex with 2,2´-diaminodiphenyl disulfide (**5**) has been known long ago.[23] It is assumed that the disulfide ligand coordinates tridentately to the metal atom through two nitrogen atoms and one sulfur atom. Based on the spectral data and the absence of electric conductivity in solutions, the authors ascribed to complex **5** the octahedral structure with the bridging Cl atoms.

Another diaminodisulfide for which the complexes with nickel(II) and other transition metals are known, namely, 2,2´-dipyridyl disulfide, was described as a bidentate ligand coordinating the metal atom only by the nitrogen atoms (sulfur atom is not involved in coordination); this conclusion was drawn from analysis of the IR spectra.[32,33]

We synthesized new complex **4** by the reaction of complex **5** with NaH.

$$\mathbf{5} \xrightarrow[C_6H_6,\ t^\circ]{2\ NaH} \mathbf{4} + H_2 + 2\ NaCl.$$

Compound **4** forms dark-blue crystals, which being dissolved give a dark-green solution.

Crystal and molecular structure of complex 3. The structure of complex **3** was determined by X-ray diffraction. The crystallographic data, experimental conditions, and refinements of the structure of this complex are presented in Table 1. Some characteristic bond lengths and bond angles for **3** are given in Table 2. The structure of the $(\mathbf{L3})_2(MeCN)_2Ni^{2+}$ dication ($[o\text{-}(MeS)\text{—}C_6H_4\text{—}(NH_2)_2Ni(MeCN)_2]^{2+}$) is presented in Fig. 1. The central nickel atom has an octahedral ligand environment with two MeCN molecules as axial ligands lying in the crystallographic inversion center. The latter results in the situation that the Ni atom lies rigidly in the plane of two N_2S_2 ligands with mutual *trans*-configuration. Examination of the parameters of octahedral Ni^{II} complexes available from the Cambridge Structural Data Bank (November 2000)[34] showed that the distances Ni—N(1) (2.105(1) Å), Ni—S(1) (2.4378(4) Å), and Ni—N(2) (2.065(1) Å) range within the limits character-

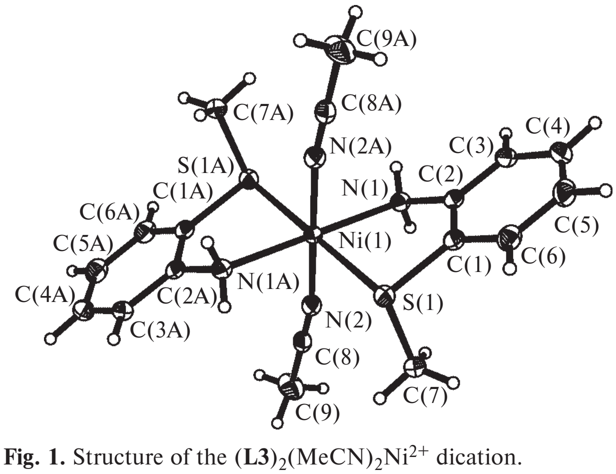


Fig. 1. Structure of the $(\mathbf{L3})_2(MeCN)_2Ni^{2+}$ dication.

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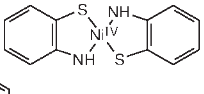
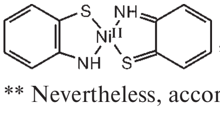
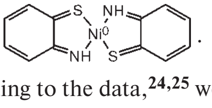
* Note that the available experimental data cannot be a firm proof for a similar structure. For example, the neutral molecule of bis(*ortho*-amidothiophenolato)nickel can be presented *a priori* as either a 14-electron complex of Ni^{IV} or a 16-electron complex of Ni^{II}, or a 18-electron complex of Ni^0:  ,  ,  .

** Nevertheless, according to the data,[24,25] we arbitrarily accept for complex **2** the structure with coordinated Ni^{IV}.

Table 1. Crystallographic parameters of complex **3**

Molecular formula	$C_{18}H_{24}Cl_2N_4NiO_8S_2$
Molecular weight	618.14
Color, habitus	Lilac parallelepipeds
Crystal size/mm^3	0.40×0.20×0.20
System	Orthorhombic
Space group	*Pbca*
Unit cell parameters:	
a/Å	12.7990(3)
b/Å	13.7363(3)
c/Å	14.6747(3)
V/Å^3	2580.0(1)
Z	4
d_{calc}/g cm^{-3}	1.591
F(000)	1272
μ(Mo-Kα)/mm^{-1}	1.171
Intervals of reflection indices	$-9 \le h \le 16$, $-17 \le k \le 16$, $-18 \le l \le 18$
Number of measured reflections	17208
Number of independent reflections	2821 [R_{int} = 0.0304]
Number of reflections with $I > 2\sigma(I)$	2448
Number of refinement variables	208
Quality by F^2	1.107
R factors by $I > 2\sigma(I)$	R_1 = 0.0228, wR_2 = 0.0613
R factors by all data	R_1 = 0.0288, wR_2 = 0.0634
Residual electron density (min/max)/e·Å^{-3}	−0.309/0.325

Table 2. Main interatomic distances (d) and bond angles (ω) for complex **3**

Bond	d/Å	Angle	ω/deg
Ni(1)—N(1)	2.105(1)	N(1)—Ni(1)—N(2)	92.08(5)
Ni(1)—N(2)	2.065(1)	N(1)—Ni(1)—S(1)	82.74(4)
Ni(1)—S(1)	2.4378(4)	N(2)—Ni(1)—S(1)	94.35(4)
S(1)—C(7)	1.816(2)	C(1)—S(1)—C(7)	100.33(7)
S(1)—C(1)	1.786(2)	C(7)—S(1)—Ni(1)	108.31(6)
N(1)—C(2)	1.450(2)	C(1)—S(1)—Ni(1)	94.73(5)
N(2)—C(8)	1.136(2)	C(2)—N(1)—Ni(1)	114.0(1)
C(8)—C(9)	1.459(2)	C(8)—N(2)—Ni(1)	170.7(1)

istic of the bonds Ni—NH_2Ar (2.057—2.268 Å, 18 entries), Ni—S(Alkyl)Ar (2.344—2.575 Å, 48 entries) и Ni—$NCCH_3$ (2.006—2.212 Å, 41 entries). The angles at the metal atom are close to 90°, except N(1)—Ni—S(1) (82.74(4)°), whose small value is related, most likely, to steric demands of the chelating ligand **L3**. Probably, for the same reason, the equatorial plane determined by the N(1), S(1), and Ni atoms is not parallel to the basic plane of the ligand (determined by the N(1), S(1) atoms and carbon atoms of the benzene cycle) and makes an angle of 28.0° with it. In turn, the Ni—NCMe fragment is also nonlinear. The angle at the formally sp-hybridized N(2) atom is 170.7(1)°.

The structure of complex **3** contains one crystallographically independent perchlorate anion (Fig. 2). Of four its oxygen atoms, two atoms (O(2) and O(4)) form

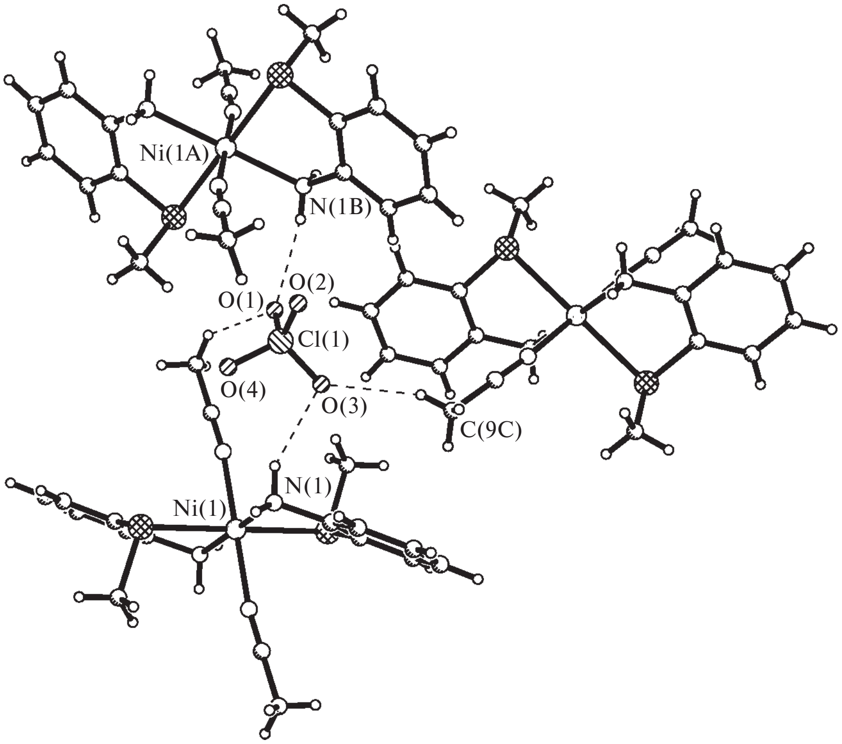


Fig. 2. System of hydrogen bonds formed by the perchlorate anion in the crystal structure of complex **3**.

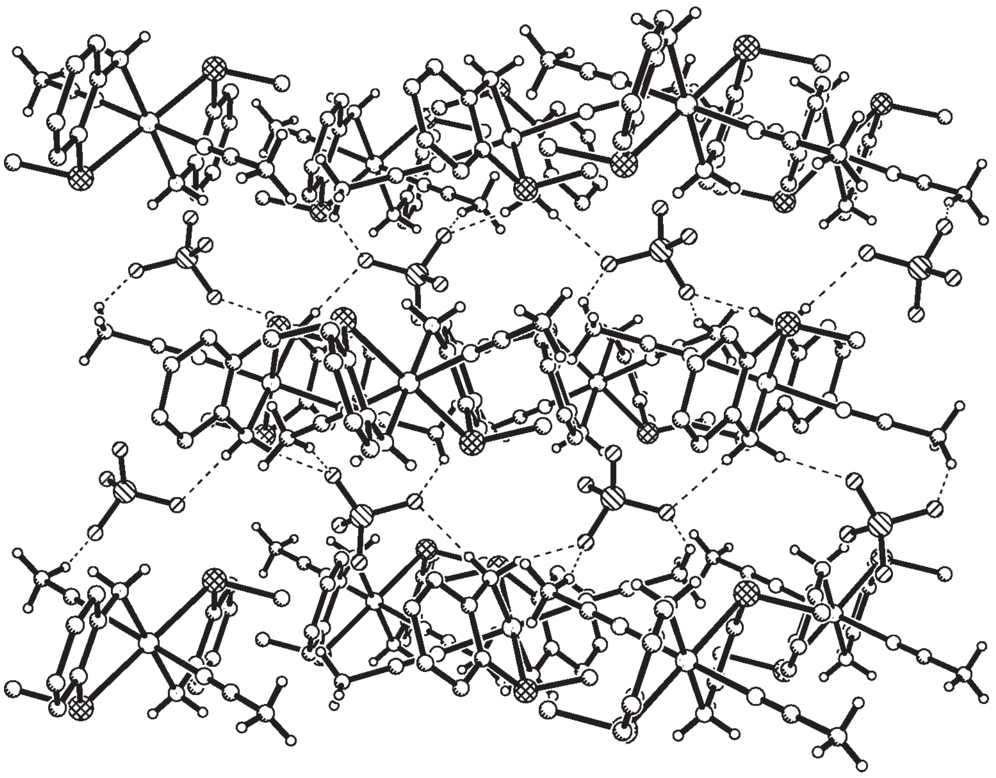


Fig. 3. Crystal structure of complex **3**.

no short contacts, whereas each of two others (O(1) and O(3)) form two almost linear hydrogen bonds with protons of the amine group of ligand **L3** and the methyl group of acetonitrile belonging to the adjacent cations (see Fig. 2). The values of the O—H distances are presented below.

Distance	*d*/Å	Distance	*d*/Å
O(1)—$H_{C(9)}$	2.494	O(3)—$H_{N(1)}$	2.285
O(1)—$H_{N(18)}$	2.333	O(3)—$H_{C(C(9))}$	2.433

In the crystal structure of complex **3** (Fig. 3), the $(\mathbf{L3})_2(MeCN)_2Ni^{2+}$ dications form layers lying in plane [100] and linked to each other by hydrogen bonds formed by the ClO_4 anions. As far as we know, compound **3** is the second example for the structurally characterized metal complex of *ortho*-aminothioanisole **L3**.[35]

Electrochemical study. The synthesized complexes and free ligands were electrochemically studied in a solution of DMF in the presence of 0.05 *M* solution of Bu_4NBF_4, Bu_4NClO_4, or Bu_4NPF_6 at the glassy-carbon or Pt electrode. The potentials of the reduction and oxidation peaks are presented in Table 3. The light-yellow compound **1** is poorly soluble in all tested solvents, including DMF. The cyclic voltammetry (CVA) curve for freshly prepared solutions of complex **1** (Fig. 4, *a*) contains an irreversible peak at –0.58 V in the cathodic region and two irreversible peaks at 0.42 V and 1.16 V in the anodic region. Storage of a solution of complex **1** for 24 h changes its color from yellow through green to intensely blue. The shape of the CVA curve changes sharply: two new peaks appear, which compose two quasi-reversible pairs *A*/*A*′ and *B*/*B*′ (see Fig. 4, *b*). According to the data,[24,25] we can assume that this is caused by the gradual oxidation of complex **1** with oxygen traces containing in the solvent.

$$\mathbf{1} + 1/2\,Q_2 \longrightarrow \mathbf{2} + H_2O.$$

Two quasi-reversible redox transitions found in the reduction of the blue form exactly correspond to two transitions observed for the blue complex with the notorious structure **2**, which was prepared by the treatment of an aqueous suspension of **1** with alkali and air oxygen. These transitions can be identified to the reductions of Ni^{IV} to Ni^{III} and then to Ni^{II}

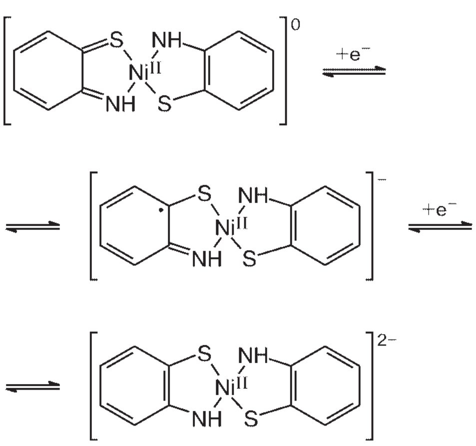
$$(atp)_2Ni^{IV} \underset{-e^-}{\overset{+e^-}{\rightleftharpoons}} [(atp)_2Ni^{III}]^- \underset{-e^-}{\overset{+e^-}{\rightleftharpoons}} [(atp)_2Ni^{II}]^{2-}$$

(atp is *ortho*-amidothiophenolate dianion)

or to ligand reduction with the retention of Ni^{II} in all structures (Scheme 1).

Electrolysis of complex **2** in a special electrochemical cell placed directly in the cavity of an ESR spectrometer showed that in DMF solutions an intense signal (*g* factor is 2.05257 at 20 °C) appears at potentials about –0.6 V

Scheme 1



(after the first reversible reduction peak, see Fig. 4, *b*, peak *A*), which confirms the formation of a fairly stable paramagnetic anion.

The polarographic curve for complex **3**, when scanning the potential from $E = 0$ V to the cathodic side, exhibits the two-electron irreversible reduction peak at −1.32 V (Fig. 5, peak *A*), and when the potential is scanned from $E = 0$ V to the anode side, two irreversible oxidation peaks of **3** appear. The same anode peaks were detected for the inversion of potential scan from cathode to anode after passing a potential of −1.32 V (see Fig. 5, peaks *B* and *C* at 1.08 and 1.58 V). In addition, a high anode peak at 0.12 V (see Fig. 5, peak *A´*), whose intensity increases during electrolysis with the controlled potential more negative than −1.32 V, appears in the CVA curve. The CVA curve (see Fig. 5) exhibits a hysteresis loop; the same hysteresis and inverse peak at 0.09—0.32 V are present in the polarization curve of $Ni(ClO_4)_2 \cdot 6H_2O$ reduction. We believe that the *ortho*-aminothioanisole ligand cannot stabilize the Ni^{I} complex and, hence, reduction proceeds *via* one two-electron step.

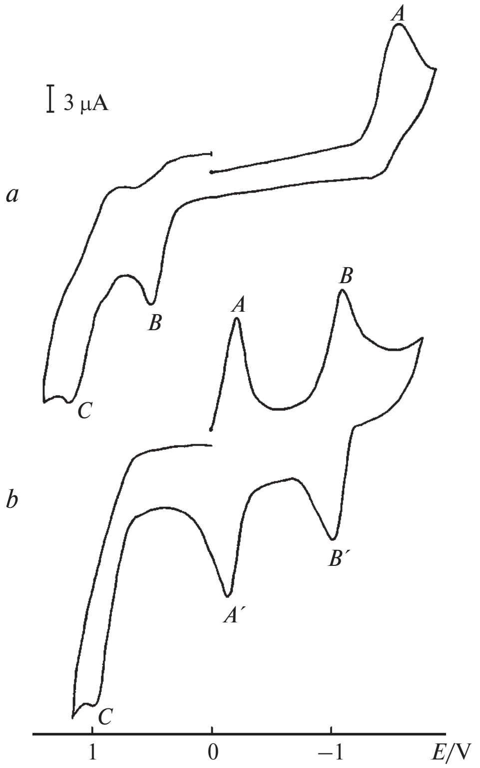


Fig. 4. CVA curves for complex **1** (*a*) immediately after dissolution in DMF containing a 0.05 *M* solution of Bu_4NBF_4 or 0.05 *M* Bu_4NClO_4 and after storage in this solution for 20 h (*b*). The concentration of **1** is $5 \cdot 10^{-4}$ mol L^{-1}.

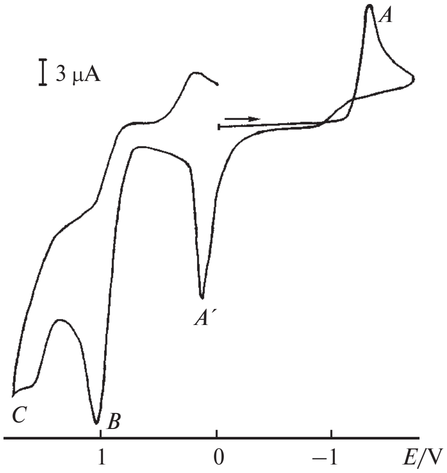
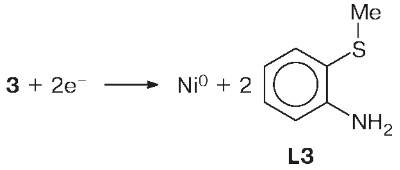


Fig. 5. CVA curves for complex **3** in DMF containing a 0.005 *M* solution of Bu_4NBF_4. The concentration of **3** is ~$5 \cdot 10^{-4}$ mol L^{-1}.



L3

The anode scan of the voltampere curve exhibits two waves at potentials of 1.20 and 1.58 V, which is close to the oxidation potentials of free ligand **L3** (Table 3).

The reduction of complex **4** is an irreversible two-electron process (probably, to Ni^{0}), and oxidation is an irreversible multielectron process. The reduction of complex **5** occurs at potentials by 440 mV less cathodic than those for reduction of **4**, and oxidation occurs at potentials by 760 mV less anodic than those for the oxidation of complex **4**. Reduction can most likely be attributed to the cleavage of the Ni—Cl bond, which is indicated by the presence of the anode peak at 0.91 V corresponding to the oxidation of Cl$^-$.

The reduction of the quinolinethiolate complex **6** proceeds in two steps. The first step is quasi-reversible, and

Table 3. Electrochemical potentials of complexes **1—6** and some free ligands at the glassy-carbon electrode

Compound	Reduction				Oxidation E_p/V
	$-E_p^1$/V	i_{pa}/i_{pc}[a]	$-E_p^2$/V	i_{pa}/i_{pc}[a]	
1	1.58[b]				0.42[b]; 1.16[b]
2	0.18/0.10[c]	1	1.10/1.00	1	1.10[b]
3[d]	1.32 (2)[b]				1.20[b,e]; 1.58[b]
4	1.66 (2)[b,f]				1.24 (> 4)[b]
5	1.22 (1)[b]		1.70 (1)[b]		0.91[g]
6[h]	0.99/0.89	0.5	1.98 (1)[b]		0.55 (1)[b]; 1.00 (> 3)[b]
L1	1.40 (> 1)		1.88 (> 1)		0.80 (> 1); 1.54 (> 1)
L3	3.10[b]				1.16[b,i]; 1.57[b]
L5	1.60 (2)[b,j]				1.16[b,i]; 1.58[b]

Note. The number of transferred electrons is indicated in parentheses. The electrochemical potentials were measured in DMF, 0.05 *M* solution of Bu_4NBF_4, *vs.* Ag/AgCl/KCl (sat.).

[a] The ratio of currents of the inverse anode and direct cathode peaks.

[b] Irreversible peak.

[c] At the inverse anode scan, a peak appears at 0.12 V caused, probably, by the oxidation of Ni^0 that formed at −1.32 V.

[d] In the presence of a 0.05 *M* solution of Bu_4NClO_4.

[e] The high peak corresponding to the transfer of approximately four electrons.

[f] At the inverse anode scan, a peak appears at −0.12 V.

[g] The small peak, whose height increases by several times, if the potential is scanned to the anodic region after the cathodic potential achieved −2 V.

[h] In the presence of a 0.05 *M* solution of Bu_4NPF_6.

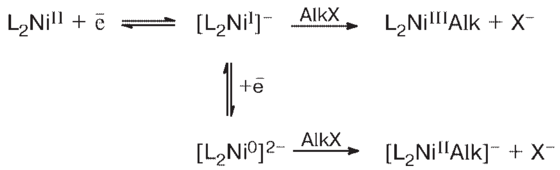
[i] Multielectron wave.

[j] At the inverse anode scan, a peak appears at −0.17 V.

the second step is completely irreversible. The same complex is oxidized in two irreversible steps (see Table 3).

Reactions of complexes 1—6 and their reduced forms with Bu^nI and Bu^nBr. The voltammetric method for detection of fast alkylation of chelate transition metal complexes is based on the electrochemical activation of the complex by one- or two-electron reduction. The reduced complex becomes active in S_N2 or radical reactions with alkylating agents. Criteria of the occurrence of the reactions are the appearance of a new wave in the cathode region corresponding to the alkylation product, a strong decrease in the reversibility of reduction of the initial complex, and the appearance of the oxidation waves of I^- or Br^- (for the alkylating agents Bu^nI and Bu^nBr, respectively).

The one-electron reduction of the Ni^{II} complexes results in anions in which Ni exists in a formal oxidation state of +1, and two-electron reduction results in the Ni^0 complexes. The Ni^I complexes in reactions with alkyl halides form Ni^{III} compounds, and the Ni^0 complexes form compounds with the alkyl—Ni^{II} bond.



$$\begin{tikzcd}
L_2Ni^{II} + \bar{e} \arrow[r, shift left] & \left[L_2Ni^{I}\right]^- \arrow[l, shift left] \arrow[r, "AlkX"] \arrow[d, shift left, "+\bar{e}"] & L_2Ni^{III}Alk + X^- \\
 & \left[L_2Ni^{0}\right]^{2-} \arrow[u, shift left] \arrow[r, "AlkX"] & \left[L_2Ni^{II}Alk\right]^- + X^-
\end{tikzcd}$$

To accomplish these reactions, it is necessary that both reduction steps or at least the addition of the first electron would be electrochemically reversible or quasi-reversible. For this reason, of the studied compounds, only complex **6** is appropriate for alkylation because the first step of electrochemical reduction is quasi-reversible.

The addition of Bu^nI or Bu^nBr results in the following changes in the CVA curve of a solution of **6**: a new wave appears at −1.34 V, which corresponds to the alkylation product; the reversibility of the first wave of reduction of complex **6** decreases strongly, and the oxidation waves of I^- or Br^- appear in the anode region of the CVA curve.

These changes show that the alkylation of the anionic complex $\mathbf{6}^-$ is rather fast in the CVA time scale and results in the Bu^nNi^{III} complex, which is rather stable at the same time scale. Compounds **3**, **4**, and **5** are reduced irreversibly (see Table 3) to decompose the complex and, therefore, the electrochemical activation of alkylation is inappropriate for them. Blue complex **2** is reduced in two reversible steps first to the Ni^{III} anion and then to the Ni^{II} dianion. The alkylation of the latter should result in the formation of the alkylnickel(IV) anion, which is likely unstable. If both processes proceed at the ligand, alkylation at Ni should afford the $[L_2Ni^0—Alk]^-$ anion, which is probably also unstable. For these reasons, the addition of Bu^nBr or Bu^nI to a solution of the doubly reduced form $\mathbf{2}^{2-}$ does not give new cathode peaks. At the same time, the anode branch of the CVA curve contains oxidation peaks of Br^- or I^-. It can be assumed that in the considered case and, perhaps, in the case of other complexes, mono- or dialkylation at the ligand occurs without decomposition of the complex. Such reactions are known,**[19,26]** and they occur rather slowly without electric current.

Thus, stability of the complexes with Ni in the low-valence states (*i.e.*, reduction at the metal) and stabilization of the alkylnickel(III) complexes by chelating ligands are important factors affecting the possibility of electrochemical alkylation at the Ni atom.

Experimental

ortho-Aminothiophenol (**L1**) and *ortho*-methylthioaniline (**L3**) were used as received (both from Lankaster) for synthesis of the complexes. 2,2´-Diaminodiphenyl sulfide (**L5**) was synthesized by the treatment of *ortho*-aminothiophenol with aqueous H_2O_2 according to a known procedure.**[23]** Complex **1** was prepared according to a previously described procedure**[18,25]** from $NiCl_2 \cdot 6H_2O$ and *ortho*-aminothiophenol in EtOH under argon. Complex **1** was prepared by the treatment of the latter with aqueous NaOH in air.**[25]**

Dimethylformamide (reagent grade) was purified by successive refluxing and distillation *in vacuo* above anhydrous $CuSO_4$ and P_2O_5.

The X-ray diffraction study of complex **3** was conducted on a Bruker SMART diffractometer with a coordinate detector at 110 K (graphite monochromator, λ(Mo-Kα) 0.71073 Å, ω scan with an increment of 0.3°). Absorption was accounted by measurement of intensities of equivalent reflections (T_{min}/T_{max} = 0.6517/0.7996). The structure was solved by the direct method (SHELXS-97**[36]**) and refined in the full-matrix anisotropic least-squares method by F^2 for all nonhydrogen atoms (SHELXL-97**[37]**). All hydrogen atoms were objectively localized and refined in the isotropic approximation. The crystallographic data, details of experiment, and refinements of the structure for complex **3** are presented in Table 1.

A PI 50-1.1 potentiostat was used for electrochemical studies. A glassy-carbon (diameter 1.8 mm) or a platinum (diameter 3.5 mm) disks served as the working electrode, the supporting electrolyte was a solution of Bu_4NBF_4 or Bu_4NClO_4 in DMF, and Ag/AgCl/KCl(sat.) was the reference electrolyte. All measurements were carried out in an argon atmosphere.

ESR spectra of electrochemically generated paramagnetic species were recorded on a Bruker EMX spectrometer using an unique electrochemical cell, which represents a glass ampule 5 mm in diameter with a crane for evacuation and argon supply. It contained a helix-like working electrode of a platinum wire, an auxiliary electrode of a platinum wire, and a silver wire reference electrode. Control was performed using a potentiostat designed by the authors. A 0.01 *M* solution of the studied compound in DMF was placed in the cell (a 0.1 *M* solution of Bu_4NBF_4 was used as the supporting electrolyte), the solution was deaerated, and ESR spectra were recorded in the potentiostatic regime of work of the cell at several potentials within the interval from 0 to −1 V.

$[1,2\text{-}C_6H_4(SMe)NH_2]_2Ni(ClO_4)_2 \cdot 2MeCN$ (3). A solution of $Ni(ClO_4)_2 \cdot 6H_2O$ (0.356 g, 1 mmol) in MeCN (3 mL) was carefully added to a solution of *ortho*-methylthioaniline (0.28 g, 2 mmol) in EtOH (3 mL). Lilac crystals of compound **3** appropriate for X-ray study were formed in the dark-blue solution during slow evaporation at 20 °C. The crystals were filtered off, washed with MeCN and EtOH, and dried in air. The yield was 0.27 g (42%). Found (%): C, 32.89; H, 3.99; N, 9.15. $C_{16}H_{24}Cl_2N_4NiO_8S_2$. Calculated (%): C, 32.35; H, 4.07; N, 9.43.

(*o*-(NH)-C_6H_4-SS-C_6H_4-(NH)-*o*)Ni (4). NaH (0.064 g, 2 equiv.) was added to a suspension of complex **5** (0.374 g, 1 mmol) in anhydrous C_6H_6 (10 mL), and the resulting mixture was boiled for 3 h. After cooling to ~20 °C, the solution was filtered from the precipitated NaCl, the precipitate was washed with absolute C_6H_6, and combined benzene solutions were concentrated *in vacuo*. Compound **4** was obtained as a black-blue powder in 89% yield (0.27 g). Found (%): C, 47.93; H, 3.89; N, 8.71. $C_{12}H_{10}N_2NiS_2$. Calculated (%): C, 47.37; H, 3.32; N, 9.21. IR spectrum (Nujol), ν/cm^{-1}: 3010 (NH).

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