Synthesis and properties of nickel(II) diiminodithiolate and diiminodisulfide N_2S_2-type complexes. New complexes with non-innocent ligands

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The following two groups of nickel(II) diiminodithiolate and diiminodisulfide N_2S_2-complexes were synthesized for the first time: (1) complexes with complete π conjugation between all four donor centers, *viz.*, compounds with non-innocent ligands, and (2) complexes containing a short conjugation system involving only two imino groups of the ligand. The complexes were studied by ^{1}H NMR, ESR, and UV spectroscopy, mass spectrometry, and electrochemistry. Solutions of glyoxal bis(2-mercaptoanil)nickel(II) in DMF showed an ESR signal, which decreased with time, the processes being accompanied by an analogous change in the intensity of the absorption band at 931 nm. The electrochemical properties of this complex also change with time. The results of studies demonstrated that compounds with non-innocent ligands of this type were initially generated as classical diiminodithiolate structures, which were transformed into the *ortho*-iminothiosemiquinonate biradicals and then into oligomeric complexes both in solution (fast transformation) and in the solid state (slow transformation). Oligomeric structures of these compounds are stable for a long period of time.

Key words: nickel, diiminodithiolate and diiminodisulfide complexes, non-innocent ligands, synthesis, ^{1}H NMR, ESR, and UV spectroscopy, mass spectrometry, electrochemistry, 9,10-phenanthrenequinonebis(2-mercaptovinylimino)nickel(II), glyoxal bis(2-mercaptoanil)nickel(II), variability of the ligand with time.

Redox enzymes whose active centers contain one or two nickel atoms are known.[1,2] In these enzymes, the nickel center often has a square-planar configuration and is coordinated by four sulfur atoms (S_4 type), four nitrogen atoms (N_4 type), or two nitrogen atoms and two sulfur atoms (N_2S_2 type).

In the catalytic cycle, the metal centers in Ni^{II}-containing CODH/MeCOS-CoA synthases (CODH is carbon monoxide dehydrogenase) and MeS-CoM reductases are reduced to Ni^{I} followed by methylation at the nickel atom to form organometallic compounds with the Ni^{III}—Me bond.[2—8] Stability of the latter compounds depends on the nature of the polydentate ligands coordinated to the metal atom.[3,9—12] Poorly stable compounds with the Ni^{III}—C bond as well as complexes containing Ni^{IV}, Ni^{I}, or Ni^{0} are most convenient to generate by electrochemical methods, which allow one to identify such species in solutions if their lifetimes are comparable to the characteristic time of the method used.[13,14]

Earlier,[14] we have reported the results of electrochemical study of nickel complexes with N_2S_2 aromatic ligands, *viz.*, benzene or quinoline derivatives. We have also found that the reduced Ni^{I}-containing species can be subjected to alkylation. In the present study, we examined another type of the nickel N_2S_2 complexes containing tetradentate ligands with diimine nitrogen centers. Most of the compounds investigated in the present study were synthesized for the first time.

Results and Discussion

We studied nine Ni^{II} complexes, whose hypothetical structures (according to the results of elemental analysis and ^{1}H NMR spectroscopy) are given below. The true structures of some of these complexes are discussed in the present study.

These complexes can be divided into two groups: (1) compounds with complete π-conjugation between all four donor centers of the tetradentate ligand (**1—5**) and (2) compounds containing a short conjugation system involving only two imino groups of the ligand (**6—9**).

There is a substantial difference between these two groups. The electronic structures of compounds **6—9** are virtually unambiguously described by the above-given formulas. Meanwhile, neutral molecule **1** possessing an extensive delocalized π-system can alternatively be repre-

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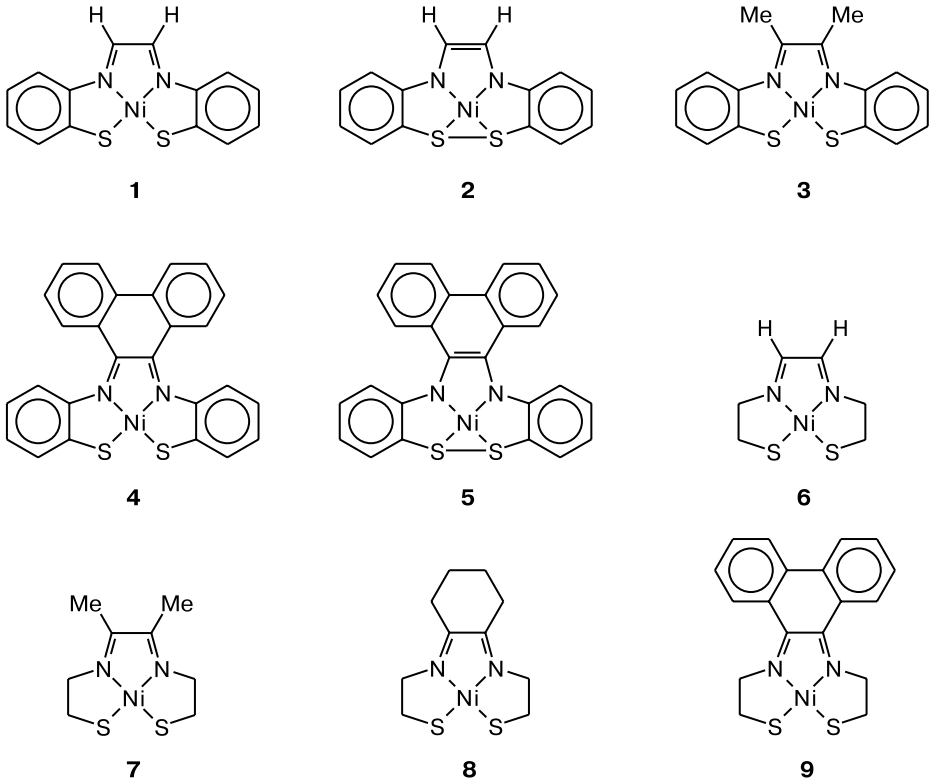
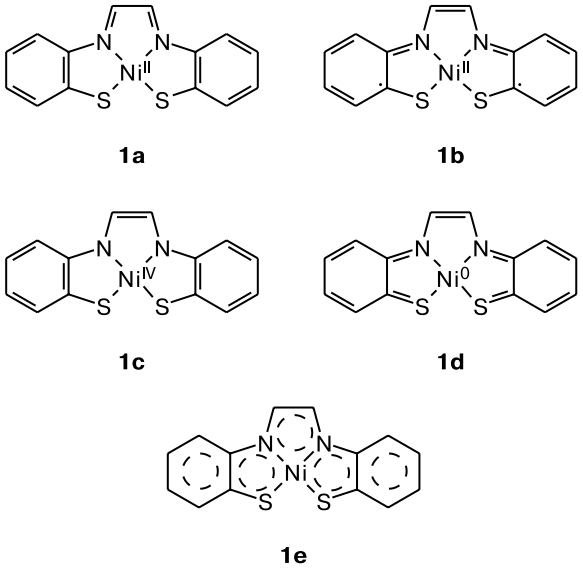


Note. Possible structures of the complexes under study; the true structures are discussed in the text.

sented as a 16-electron Ni^{II} complex with either diiminodithiolate (**1a**) or di(iminothiosemiquinone) (**1b**), as a 14-electron Ni^{IV} complex (**1c**), or as an 18-electron Ni^0 complex (**1d**).



Consequently, neither the oxidation state of the central metal atom nor the charges on the donor atoms of the ligand can *a priori* be precisely specified, and such complexes are often described by delocalized structures (**1e**).

To bring the metal atoms in the structures to a single oxidation state (Ni^{II}), it is necessary to add two electrons to the Ni atom in structure **1c** and to subtract two electrons from the Ni atom in structure **1d**. If the divalent state of nickel is retained, the ligand should have structure **1c** in the dianion and structure **1d** in the dication of complex **1**. Therefore, if only the ligand rather than the metal atom is involved in reduction (oxidation), the ligand under consideration can have different structures in different redox states of the complex.

Ligands of this type were given the name "non-innocent ligands"* because their structures in the complexes cannot be unambiguously described by formulas reasonable for the free ligand (in the example under consideration, this is the formula of the glyoxal bis(2-thiolatoanil) dianion). The ligands undergo changes upon coordination to metal. For example, the free ligand is irreversibly reduced and/or oxidized, whereas the redox transitions in the complexes become reversible.

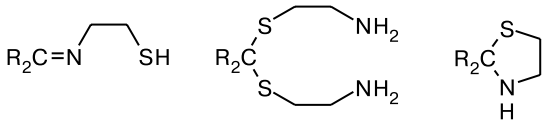
The characteristic feature of complexes with non-innocent ligands is that the ligands are involved in chemical

* See, for example, M. D. Ward and J. A. McCleverty, "Non-innocent behaviour of mononuclear and polynuclear complexes: consequences for redox and electronic spectroscopic properties," (*J. Chem. Soc., Dalton Trans.*, 2002, 275) and Refs. 15 and 16 (and references cited therein).

and physical transformations, whereas the metal atom is only weakly involved, if at all, in these processes.

o-Diaminophenylenes, catecholates, *o*-aminophenoxides, and *o*-aminothiophenoxides are prototypes of non-innocent ligands.[15,16] These ligands are redox-active and can exist in different oxidation and protonation states such as (1) aromatic mono- and dianions with a closed shell; (2) neutral *o*-quinone-type compounds; or (3) *o*-benzosemiquinonates, *i.e.*, radicals with an open electronic shell.

Synthesis of complexes. Since sulfur-containing Schiff's bases belong to an important class of polydentate ligands, methods for their preparation have been developed in sufficient detail. Mercapto-substituted imines cannot be directly synthesized by the reactions of *o*-aminothiophenol of β-aminoethanethiol with carbonyl compounds[17,18] because the amino and thio groups in these compounds act as competing nucleophiles and react with aldehydes or ketones to form products of three types, *viz.*, the expected imine **10**, mercaptal **11**, and thiazolidine (or benzothiazoline) **12**.



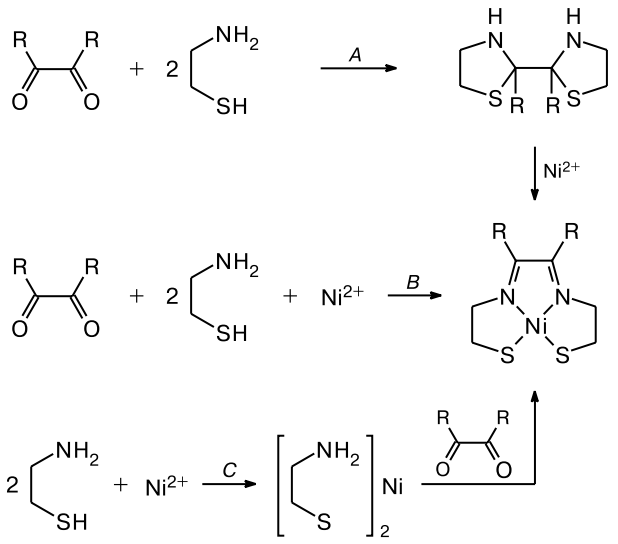
10 **11** **12**

The reactions afford thiazolidine as the major product, whereas the total yield of mercaptal and imine is generally at most 10%.

This problem, which has first been mentioned by Schiff as early as 1869,[17] can be solved by performing condensation of an α-dicarbonyl compound with aminothiol in the presence of metal ions (Ni, Zn, Cd, Hg)[16,18—21] to form the corresponding metal complexes with α-diketone bis-iminothiol.[19] An alternative approach to the synthesis of complexes with such structures involves the preliminary preparation of thiazolidine **12**, which then undergoes the quantitative ring opening by Lewis acid (metal salt) to give the target compound.[16,18]

Complexes of 2,2′-dimercapto-substituted diimines **1**, **3**, **4**, and **6—9** were prepared according to three procedures. These procedures differ in the order in which the starting reagents are introduced in the reaction (Scheme 1). It should be noted that compounds **1**, **7**, and **8** have been described earlier,[16,19] whereas compounds **3**, **4**, **6**, and **9** (first two complexes contain non-innocent ligands) were synthesized for the first time. Two procedures for the synthesis of these complexes have been described earlier. One procedure involves the reaction of a 1,2-dicarbonyl compound with aminothiol to form dithiazolidine (dithiazoline) followed by its reaction with $NiCl_2$ to give the corresponding complex (path *A*). Another procedure is based on template condensation of an α-dicarbonyl compound with aminothiol in the presence of $NiCl_2$ (path *B*). In the present study, we developed the third approach to the synthesis of nickel dimercaptodiimine complexes by the reaction of the complex $Ni(aet)_2$ (aet is β-aminoethanethiol), which is readily generated from Ni^{II} salts and β-aminoethanethiol,[22] with the corresponding 1,2-dicarbonyl compound (path *C*).

Scheme 1



All the compounds synthesized are intensely colored powders. Solid complexes based on phenanthrenequinone are bright-green. The color of the remaining complexes varies from dark-cherry to almost black. The compositions of the complexes were determined by elemental analysis. The structures were established by ^1H NMR spectroscopy. In some cases, the structures were determined by mass spectrometry (Table 1).

The complexes with diamino disulfides, which are arbitrarily described by formulas **2** and **5**, were prepared by template condensation of 2,2′-diamino diphenyl disulfide with the corresponding dicarbonyl compounds in the presence of $Ni(ClO_4)_2 \cdot 6H_2O$.

A series of Ni^{II} complexes with nitrogen-containing disulfides, which are potential N_2S_2-type ligands, were described in the literature. These complexes can be divided into the following three classes: I, complexes in which the disulfide ligand is coordinated to the metal atom in a tridentate fashion through two N atoms and one S atom;[23,24] II, binuclear bis-disulfide complexes in which the adjacent S atoms of disulfide are involved in coordination with two different Ni atoms;[25,26] III, complexes in which the disulfide ligand is coordinated through the N atom (S atom is not involved in coordination).[27,28] To our knowledge, Ni complexes in which a single metal atom is coordinated through both S atoms of the disulfide

Table 1. Properties of complexes **1—9** [a]

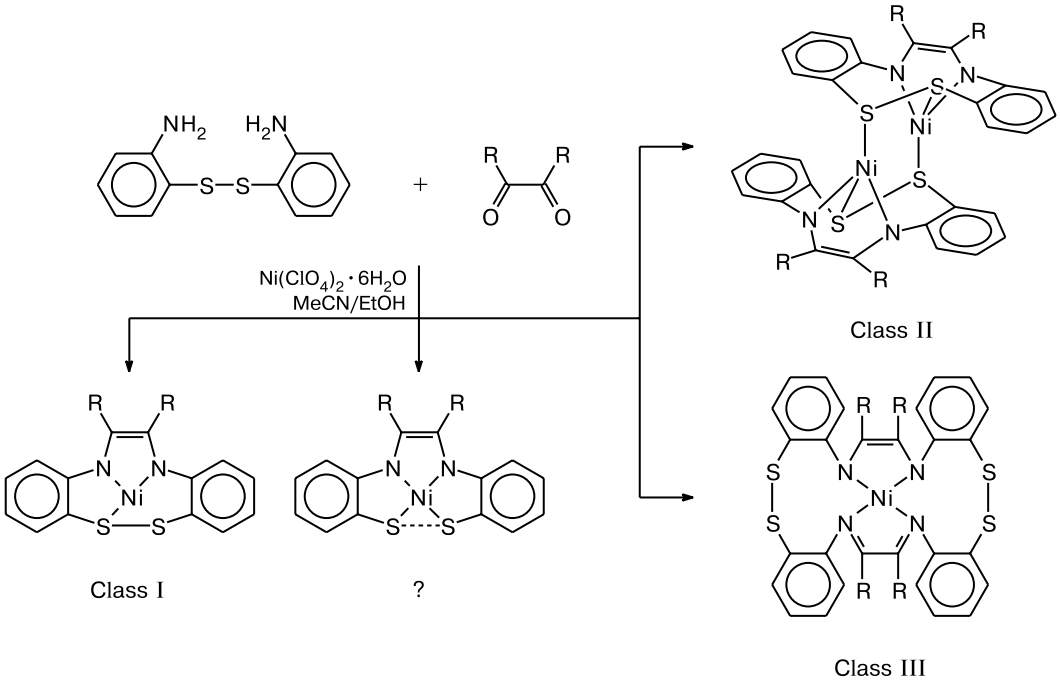
Compound	Method of synthesis	Yield (%)	M.p./°C	Found / Calculated (%)			^{1}H NMR, δ (*J*/Hz) [solvent]
				C	H	N	
Glyoxal bis(2-mercapto-anil)nickel(II) (**1**)[16]	*A*	71	>300 (fresh), 230 (old)	50.96 [b]	3.09 [b]	8.82 [b]	7.60, 7.67 (both t, 2 H each, *J* = 8.8); 8.18, 8.40 (both d, 2 H each, *J* = 8.8); 6.55 [c] (t, 2 H, *J* = 8.8); 7.00 [c] (d, 2 H, *J* = 8.8); 7.15 [c] (t, 2 H, *J* = 8.8); 7.20 [c] (d, 2 H, *J* = 8.8); 8.99 [c] (s) [DMF-d_7]
	B	95		51.10	3.06	8.51	
(1,13-Dithia-5,8-diaza-dibenzo[*a*,*g*]cyclo-decene)nickel(II) (**2**)	—	96	265	51.10	3.22	8.99	5.49 (s); 7.48, 7.55 (both t, 2 H each, *J* = 8.8); 7.99, 8.16 (both d, 2 H each, *J* = 8.8) [$CDCl_3$]
				51.10	3.06	8.51	
Diacetyl bis(2-mercapto-anil)nickel(II) (**3**)	*A*[d]	37	>330	53.28	3.48	7.38	2.91 (s, 6 H); 7.40, 7.49 (both t, 2 H each, *J* = 8.8); 7.84, 8.00 (both d, 2 H each, *J* = 8.8) [$CDCl_3$]
	B	39	(from AcOEt)	53.81	3.95	7.84	
9,10-Phenanthrene-quinone-bis(2-mercapto-vinylimino)nickel(II)	*B*	42	133—134	64.65	3.56	5.72	6.58 (t, 2 H, *J* = 8.8); 6.70, 7.14 (both d, 2 H each, *J* = 8.8); 7.22, 7.47, 7.72 (all t, 2 H each, *J* = 8.8); 8.01, 8.19 (both d, 2 H each, *J* = 8.8) [$CDCl_3$]
				65.16	3.36	5.85	
[6,7-(2,2′-Diphenyleno)-13,14-dithia-5,8-diaza-dibenzo[*a*,*g*]cyclo-decene]nickel(II) (**5**)	—	45	189—190	65.39	3.57	5.86	6.61 (t, 2 H, *J* = 8.8); 6.70, 7.17 (both d, 2 H each, *J* = 8.8); 7.21, 7.48, 7.55 (all t, 2 H each, *J* = 8.8); 7.98, 8.15 (both d, 2 H each, *J* = 8.8) [$CDCl_3$]
				65.16	3.36	5.85	
Glyoxal bis(2-mercapto-ethylimino)nickel(II) (**6**)	*A*	56	~250	30.45	4.21	11.90	—[e]
	B	50	(decom.)	30.93	4.33	12.02	
Diacetyl bis(2-mercapto-ethylimino)nickel(II) (**7**)[19]	*B*	48	>300	36.75	5.35	10.68	2.00 [f] (s, 6 H); 2.80 [f], 3.20 [f] (both m, 4 H each) [DMSO-d_6]
				36.81	5.41	10.73	
1,2-Cyclohexanedione-bis(2-mercaptoethyl-imino)nickel(II) (**8**)[19]	*A*	71	>280	41.38	5.68	9.49	1.51 [f], 2.35 [f], 2.55 [f], 2.82 [f] (all m, 2 H each); 2.99 [f], 3.25 [f] (both t, 4 H each, *J* = 6.5) [$CDCl_3$]
	C	83		41.84	5.62	9.76	
9,10-Phenanthrene-quinone-bis(2-mercapto-ethylimino)nickel(II) (**9**)	*B*	42	>280	56.83	4.90	6.92	2.97, 3.33 (both t, 4 H each, *J* = 6.7); 7.40 (t, 2 H, *J* = 8.7); 7.64 (dt, 2 H, J_1 = 8.7, J_2 = 1.2); 7.96 (d, 2 H, *J* = 8.7); 8.13 (dd, 2 H, J_1 = 8.7, J_2 = 1.2) [$CDCl_3$]
	C	37		56.43	4.21	7.31	

[a] The literature references are given for the compounds, which have been described earlier but have not been characterized by ^{1}H NMR spectroscopy or have been synthesized according to alternative procedures.
[b] For a freshly prepared sample.
[c] The signals were present only in the spectrum of a freshly prepared sample and disappeared upon storage of the solution for one day.
[d] Before cooling, the reaction mixture was filtered to remove $Ni(abt)_2$ (abt is *o*-aminothiophenoxide) formed in a large amount. To isolate the target complex, the filtrate was concentrated *in vacuo* and the oily residue was crystallized from AcOEt.
[e] The compound is poorly soluble in all the solvents used.
[f] The low-intensity signals because the compound is poorly soluble.

fragment have not been reported in the literature. In the $NiCl_2$ complex with 2,2′-diamino diphenyl disulfide, the disulfide ligand is coordinated to the metal atom in a tridentate fashion[23] through two N atoms and one S atom. The octahedral structure with the bridging Cl atoms was assigned to this complex based on the spectroscopic data and the non-conductivity of solutions. Complexes of nickel(II) and other transition metals with another nitrogen-containing disulfide, *viz.*, 2,2′-dipyridyl disulfide, have also been synthesized. The latter ligand was described as a bidentate ligand coordinated to the metal atom exclusively through the N atoms (S atom is not involved in coordination at all). This conclusion was made based on analysis of the IR spectra.[27,28] The possible structures of complexes **2** and **5** are shown in Scheme 2.

The compositions of the complexes synthesized were determined based on the elemental analysis data (see Table 1), which correspond to structures of classes I or II

Scheme 2



R = H (**2**); RR = 2,2′-biphenyl-2,2′-diyl (**5**)

in Scheme 2 but not to structures of class III. To elucidate the structures of these complexes in more detail, we used the data from ^{1}H NMR spectroscopy, electronic spectroscopy, mass spectrometry, and electrochemistry. The ^{1}H NMR spectra of compounds **2** and **5** (see below) have only one set of signals for the aromatic protons of the *o*-aminophenylthiolate fragment, which is indicative of either symmetrical structures of the disulfide complexes (like in Scheme 2) or the occurrence of the fast equilibrium involving alternatively one of the two S atoms of the disulfide ligand in coordination. As demonstrated above, it is unlikely that complexes **2** and **5** contain a strained three-membered ring because the lone electron pairs of the S atoms in these complexes point away from the ligand.

^{1}H NMR spectra. The ^{1}H NMR spectra of thiolate complexes **7—9**, which do not contain a conjugation chain between the N and S atoms, have two triplets with the spin-spin coupling constant of ~6.5 Hz at δ 2.80—3.35 (see Table 1; compound **6** was not studied because of its low solubility). These signals can be assigned to the protons of the SCH_2CH_2N fragment. In addition, these spectra show signals for the protons of the imine fragment R(R′)C=N. Therefore, the structures of complexes **7—9** (and, apparently, of complex **6**) are consistent with the above formulas. It should be emphasized that the NMR spectra remained unchanged upon storage of the complexes in solutions.

The fundamental distinguishing feature of compound **1** containing a large conjugation system is the temporary appearance of signals of two compounds in the spectrum. The spectrum of freshly prepared complex **1** measured immediately after its dissolution in DMF-d_7 has signals of two compounds in a ratio of ~1 : 1 at δ 7.60 (t), 7.67 (t), 8.18 (d), 8.40 (d) (compound **A**) and 6.55 (t), 7.00 (d), 7.15 (t), 7.20 (d) (compound **B**). After one day, the spectrum of the same sample has only signals for the C—H protons of compound **A**. Besides, the signal at δ 8.99, which was observed in the spectrum of a freshly prepared solution and which can be assigned to the proton of the imino group HC=N, disappears (for compound **A**, the signal for the protons of the imino group is not observed).

Complex **3** and new complex **4** with non-innocent ligands also belong to this structural type of compounds with a long conjugation chain. However, the ^{1}H NMR spectra of these two compounds recorded within a few minutes after the preparation of solutions have only one set of signals. The spectrum of compound **4** has four signals for the protons assigned to the phenanthrene fragment (δ 7.47, 7.49, 8.01, and 8.19; the chemical shifts of these signals are similar to those observed in the spectrum of complex **9**, which also contains the phenanthrene fragment) along with low-field signals of the *o*-substituted benzene ring. The chemical shifts of the latter signals are similar to those observed for form **B** of complex **1**, which was present only immediately after its dissolution in DMF.

By contrast, the ^1H NMR spectrum of compound **3** has signals, whose chemical shifts are similar to those observed in the spectrum of the final product of the transformation of complex **1** in solution (form **A**).

It is also noteworthy that there is a large difference in the chemical shifts of the protons of the Me group in the spectra of compounds **3** and **7**. In the spectrum of complex **3**, the signal of the Me group is shifted downfield by almost 1 ppm compared to the analogous signal in the spectrum of complex **7** (δ 2.91 and 2.00, respectively). This shift is indicative of a substantial difference in the electronic characteristics of the structural fragment adjacent to the Me group in compounds **3** and **7**. It can be assumed that this fragment in complex **7** has a structure similar to N=C—C=N, whereas this fragment in complex **3** has a structure similar to N^-—C=C—N^-.

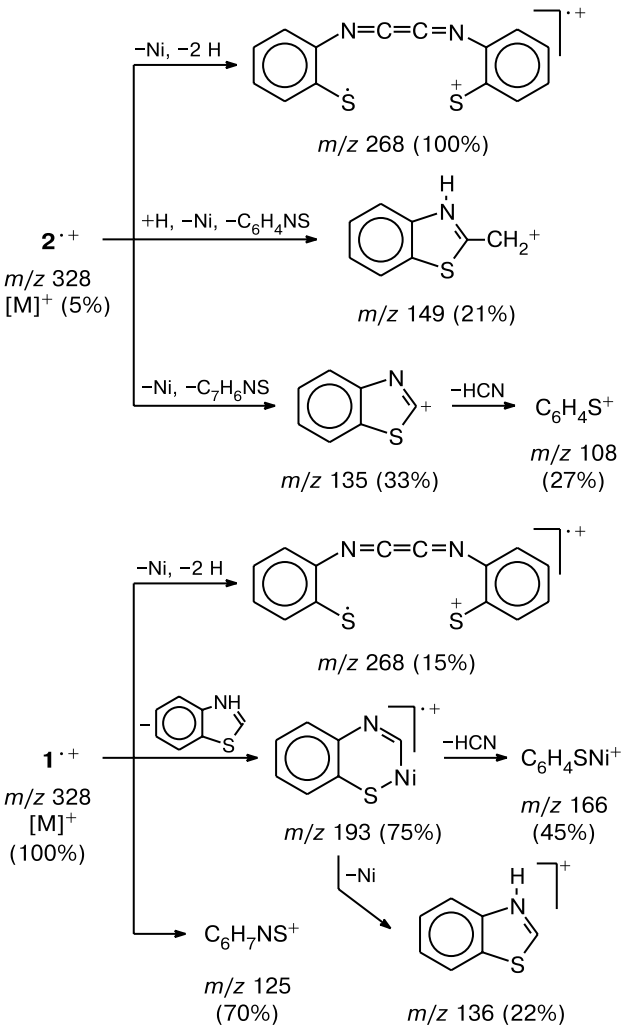
The ^1H NMR spectra of complexes **2** and **5** are similar to the spectra of related complexes **1** and **4**, respectively. The chemical shifts for complex **2** are very similar to the corresponding values for the final transformation product of compound **1** in solution (form **A**). The spectrum of complex **2**, which was synthesized from disulfide, also has a singlet at δ 5.49 (in the region characteristic of the protons of the HC=C group containing electron-releasing substituents at the double bond), which can presumably be assigned to the N^-—C=C—N^- fragment.

Based on the ^1H NMR spectroscopic data, it can be concluded that compounds **1** and **4** in freshly prepared solutions occur as two species (**A** and **B**), which differ in the electronic characteristics of the NCCN fragment, which can have either a diimine (species **B**) or diamidoethylene (species **A**) structure. It should be noted that species **B** in solutions of complex **1** is rather rapidly transformed into species **A**. The compounds synthesized from disulfides (**2** and **5**) are, apparently, similar to species **A**.

Mass spectrometry. The mass spectra of compounds **1**, **2**, and **5** differ substantially from each other (Scheme 3). The mass spectrum of complex **2** has a low-intensity parent ion peak (*m/z* 328, I_{rel} = 5%) and fragmentation ion peaks at *m/z* 268 ($[M - Ni - 2\ H]^+$), 149 ($[M + H - Ni - C_6H_4NS]^+$), 135 ($[M - Ni - C_7H_5NS]^+$), and 108 ($[C_6H_4S]^+$). In the mass spectrum of compound **5**, a parent ion peak (*m/z* 478) is not observed, but this spectrum has fragmentation peaks analogous to those reported for compound **2** (*m/z* 418 ($[M - Ni - 2\ H]^+$, I_{rel} = 12%); *m/z* 299 ($[418 - C_6H_4NS]^+$, I_{rel} = 8%); *m/z* 108 ($[C_6H_4S]^+$, I_{rel} = 29%)).

The differential thermogram of complex **1**, which was recorded within 10 days after the synthesis, has four peaks (at 300, 310, 330, and 350 °C). The mass spectra, which were measured for samples corresponding to each of these peaks, are virtually identical to each other and have a high-intensity molecular ion peak (*m/z* 328, I_{rel} = 100%) and the ion peak $[M - Ni - 2\ H]^+$ (*m/z* 268) along with a set of peaks corresponding to the nickel-containing fragmentation ions $[M - C_7H_5NS]^+$ (*m/z* 193) and $[C_6H_5SNi]^+$ (*m/z* 166) as well as peaks of the ions $[C_7H_6NS]^+$ (*m/z* 136), $[C_6H_7NS]^+$ (*m/z* 125), and $[C_6H_7S]^+$ (*m/z* 108). The intensity ratio of isotope peaks in the multiplets correspond to the assignment made. Taking into account the character of the thermogram of complex **1** and its difference from the thermograms of disulfide complexes **2** and **5**, in which only one delay of the temperature change is observed, we hypotheized that solid complex **1** ($C_{14}H_{10}N_2S_2Ni$) was transformed into a mixture of the $(C_{14}H_{10}N_2S_2Ni)_n$ oligomers upon storage.

Scheme 3



Electronic spectroscopy. Upon dissolution in deaerated DMF, complex **1** underwent fast changes. The initially dark-cherry solution turned first brown and then yellow-green during one minute. Analogously, dissolution of compound **4** gave first a green solution, whose color very rapidly changed first to brown and then to pale-brown. For compounds **7—9**, analogous changes in the color were not observed.

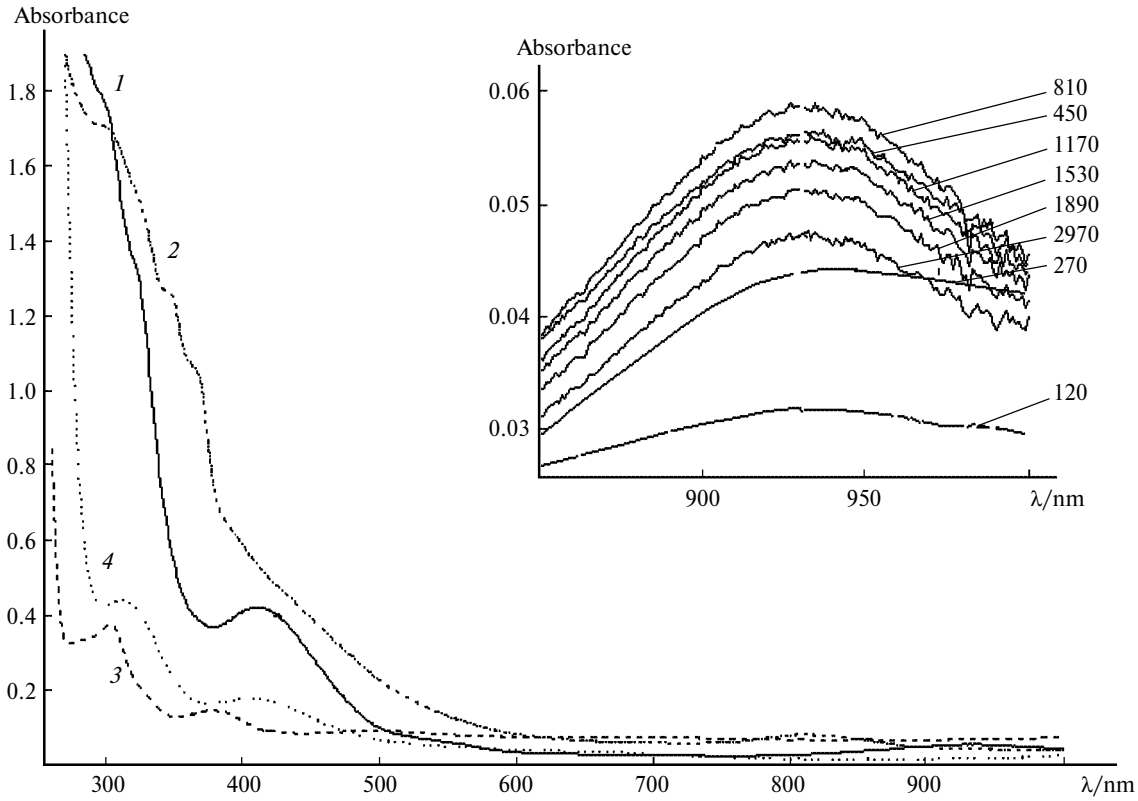


Fig. 1. Electronic spectra of complexes **1** (*1*), **2** (*2*), **7** (*3*) ($1 \cdot 10^{-3}$ mol L^{-1}), and **9** (*4*) ($2.6 \cdot 10^{-3}$ mol L^{-1}) in DMF. For complex **1**, the spectrum of a freshly prepared solution is presented. A change in the intensity of the long-wavelength absorption band at λ_{max} = 931 nm with time in the spectrum of complex **1** (the times in seconds are indicated) is shown in the inset.

The UV spectrum of freshly synthesized compound **1**, which was recorded immediately after dissolution in DMF (Fig. 1), has the overlapping π—π*-transition and charge-transfer bands at λ < 350 nm, which are characteristic of nickel(II) square-planar low-spin complexes,[29] and a medium-intensity band with a maximum at 413 nm. The intensities of these bands begin to decrease immediately after the preparation of solutions of a fresh sample, and a low-intensity broad absorption band with a maximum at 931 nm simultaneously appears. The intensity of the latter band increases during several tens of minutes and then also decreases, after which the long-wavelength band completely disappears during one day. After several days, the spectrum contains no absorption bands at λ > 350 nm.

In the study of the intermediates generated upon nanosecond laser flash photolysis of solutions of *N*-hydroxy-4-pyridinethione in argon-saturated THF,[30] the formation of a compound with λ_{max} = 420 nm was observed. Based on the fact that photolysis of di-4-pyridyl disulfide also afforded a compound with λ_{max} = 420 nm, the structure of the 4-pyridylthiyl radical was assigned[30] to the above-mentioned intermediate. Other aryl- (ArS$^{\bullet}$) and hetarylthiyl radicals (HetS$^{\bullet}$) are also characterized by low-intensity absorption bands in the region of 380—600 nm, whose positions depend substantially on the nature of the aryl group and the solvent.[31] Taking into account these data, it can be assumed that the structure of the ligand in complex **1** is very similar to the structure of the thiyl radical, for example, to structure **1b** (see above) in which the unpaired electron is located on the antibonding π orbital.

It was necessary to elucidate whether the low-intensity absorption band with λ_{max} = 931 nm and the band at 413 nm belong to one and the same compound or the former band belongs, for example, to an unstable intermediate. In the study,[15] the electronic spectra of Ni^{II}, Pd^{II}, and Pt^{II} complexes with the substituted *o*-iminothionobenzosemiquinone radical were investigated, and an absorption band with a similar shape in the region of 800—1000 nm was assigned to the coordinated *o*-iminothionobenzosemiquinone radical. It can be hypothesized that the changes in the spectra with time are associated with radical structures of complex **1**, for example, of type **1b**, to which both bands (at 931 and 413 nm) can be assigned. However, it is not improbable that complex **1** reacts with oxygen upon storage in air.

It is known that thiolate complexes of transition metals (particularly, of late transition metals) are sensitive to atmospheric oxygen. This is associated with the character of their highest occupied MO, which is localized prima-

rily on the S atom and is antibonding (see the review on nickel complexes[32]). Oxidation with oxygen can afford metal disulfides and oxides, *i.e.*, lead to undesirable degradation of the catalytic centers in enzymes. Another oxidation pathway involves the oxygen capture by the S atom with retention of the M—S bond, *i.e.*, the modification of the complex resulting in a substantial change in its redox potential. This pathway has been studied in most detail using Ni^{II} complexes with N_2S_2 saturated ligands,[32–34] which are of particular interest as models of the active centers of Ni-containing enzymes, as examples. Depending on the conditions, a broad series of oxidized complexes, *viz.*, monosulfenate, disulfenate, monosulfinate, disulfinate, mixed sulfinate-sulfenate, and disulfonate complexes, can be isolated. Recently, it has been demonstrated[35] that analogous products were generated upon oxidation of Ni^{II} and Pd^{II} 1,2-benzenedithiolate complexes as well.

Apparently, the oxygen capture by the S atoms of the thiolate complexes involves coordination of the O_2 molecule in the ground state to the sulfur or metal atom or simultaneously to both these centers.[32,35] It is known[36] that free alkylthiyl radicals can reversibly add the O_2 molecule to form the thiyl peroxyl radicals AlkS—O—O$^{\bullet}$, *viz.*, weakly bound adducts with a bond energy of 48.6 kJ mol^{-1} in the gas phase.

$$MeS^{\bullet} + {}^3O_2 \rightleftharpoons MeSOO^{\bullet}$$

The spectra of the AlkSOO$^{\bullet}$ radicals (Alk = Pr^n, Pr^i, or Bu^t) in a methanol matrix have a low-intensity broad band at ~900 nm (see Ref. 37, Fig. 1; the theoretical analysis of the spectrum of the methylthiyl peroxyl radical was carried out in the study[38]). Therefore, it cannot be ruled out that the absorption maximum at 931 nm is associated with the formation of thiyl peroxyl radicals. It is also possible that complex **1** binds molecular dioxygen, which accounts for a change in the results of elemental analysis upon storage of the complex in the solid state in air. A freshly prepared sample precisely corresponds to the molecular formula $C_{14}H_{10}N_2S_2Ni$, whereas the percentages of C, H, and N gradually decrease in the course of storage.

The electronic spectra of the final products of the transformations of complexes **1** and **2** in solutions are very similar to each other (Table 2).

No changes are observed in the electronic spectra of solutions of complexes **7—9** and the near-IR region has no bands, which is in complete agreement with visual observations.

The electronic spectra of complexes **4** and **5** (Fig. 2), like the spectra of compounds **1** and **2**, substantially differ from each other. Dithiolate compound **4**, like complex **1**, is characterized by a broad low-intensity peak in the near-IR region.

Table 2. Electronic spectra of complexes **1—5**, **7**, and **9** in DMF

Complex	λ/nm (ε · 10^{-4}/L mol^{-1} cm^{-1})
1	350*, 413*, 931*; 291**, 304**
2	300*, 346*, 366*; 291**, 304**
3	317*, 514*, 551*; 346.5**
4	355 (1.95), 818
5	318 (3.67), 412, 561
7	303 (0.25), 379 (0.97)
9	312 (0.53), 411 (0.22)

* A freshly prepared sample.
** After storage in DMF for one day.

ESR spectroscopy. Complex **1** becomes paramagnetic upon storage in the solid state at ~20 °C for several days. The ESR spectrum of a glassy solution of a freshly prepared sample of **1** in DMF at 77 K is shown in Fig. 3. The spectral pattern is characteristic of a paramagnetic species with three different principal values of the Zeeman tensor. One can say with a fair degree of assurance that a

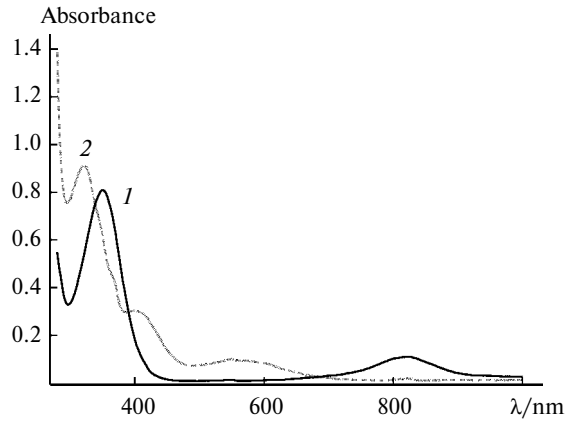


Fig. 2. Electronic spectra of complexes **4** (*1*) and **5** (*2*) in DMF ($0.84 \cdot 10^{-3}$ mol L^{-1}).

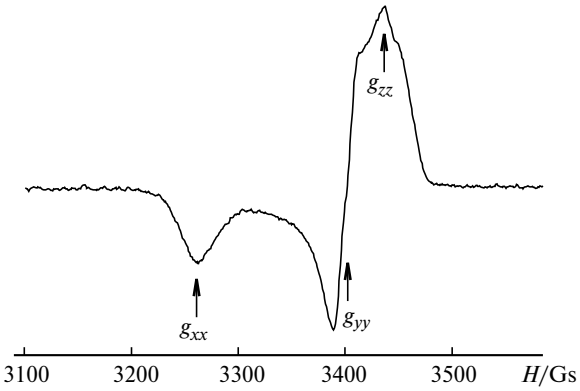


Fig. 3. ESR spectrum of compound **1** ($1 \cdot 10^{-2}$ *M* solution in DMF) at 77 K.

Table 3. Values and anisotropy of the *g* factors of complex **1** and the related compounds in DMF ($1 \cdot 10^{-2}$ mol L^{-1})

Complex	g_x	g_y	g_z	g_{iso}	Reference
1	2.011	2.027	2.120	2.053	—[a]
$[Ni(1,2\text{-}S(NH)C_6H_4)_2]^{\bullet -}$	2.005	2.028	2.126	2.053	16
$[Ni(1,2\text{-}S(NH)\text{-}2,4\text{-}Bu^t{}_2C_6H_2)_2]^{\bullet -}$	2.0055	2.0282	2.1147	2.067	15
$\mathbf{1}^{\bullet -}$ [b]	1.978	2.003	2.005	2.026	16
$\mathbf{1}^{\bullet -}$ [c]	1.978	2.004	2.006	2.028	16
$[Ni(1,2\text{-}S(NH)\text{-}2,4\text{-}Bu^t{}_2C_6H_2)_2]^{+}$	1.9901	1.9970	2.0127	2.0014	15
$CysSOO^{\bullet}$	2.002	2.008	2.035	—	37
$GSOO^{\bullet}$	2.002	2.009	2.035	—	37
$PenSOO^{\bullet}$	2.002	2.009	2.037	—	37

Note. Cys is $HOOCCH(NH_3^+)CH_2$—, G is glutathione, Pen is $HOOCCH(NH_3^+)C(Me)$—.
[a] The results of the present study.
[b] After reduction with Na/Hg.
[c] After electrochemical reduction.

hyperfine structure is absent. In Table 3, the *g*-tensor components are compared with the data published in the literature. These components are substantially larger than the *g* factor for the free electron (2.0023), which is indicative of an interaction between the unpaired electron and the heteroatom possessing a rather large spin-orbital coupling constant and a zero nuclear spin. Most likely, the S atom serves as such an atom in the system under consideration. It should be noted that the *g*-tensor components are very similar to those observed earlier for single-charged cationic and anionic complexes produced upon oxidation or reduction of nickel complexes with the *o*-iminothiosemiquinone radicals. The observed spectrum is most similar to the spectrum of the bis(2,4-di-*tert*-butyl-*o*-iminothiosemiquinonate)nickel(II) monoanion, which provides evidence that these compounds are structurally similar. By contrast, the ESR spectrum of the product, which was generated by reduction of complex **1** with sodium amalgam or electrochemical reduction, recorded earlier[16] differs substantially from the spectrum measured in the present study (see Table 3). For the cationic complex, the *g* factor is closer to the *g* factor of the free electron (2.0023), which indicates that interaction between the unpaired electron and the S atom is weaker.

The ESR spectrum recorded immediately after dissolution of a fresh sample of **1** in DMF has a very weak signal. Then the intensity of the signal substantially increases, reaches a maximum after ~1000 s, and begins to slowly decrease (Fig. 4). After one day, the ESR signal virtually disappears. The intensity of the ESR signal in the spectrum of the dissolved compound changes with time in parallel with a change in the intensity of the absorption band at $\lambda = 931$ nm in the electronic spectrum (see Fig. 4). According to our estimates (with respect to the total concentration of complex **1**), at most 15% of the molecules of the mononuclear complexes have unpaired spins when the ESR signal reaches a maximum.

Based on the data from ESR and electronic spectroscopy, it can be assumed that freshly prepared complex **1** is described by formula **1a** (see above). Complex **1a** is gradually transformed into complex **1b** with the *o*-iminothiosemiquinonate-type biradical both in solutions (fast transformation) and in the solid state (slow transformation). This chelating biradical in structure **1b** is responsible for absorption at 931 nm, but it is inactive in the ESR spectrum because this biradical is a singlet species, as evidenced by a close analogy with the Ni^{II} complexes containing the *o*-iminothiosemiquinonate radicals.[15] Subsequently, complex **1b** can undergo dimerization, which can give rise to an ESR signal, because the spins of the C atoms can become independent since these atoms in the dimer are not linked by a system of conjugated π bonds. Then, further transformations afford dimers, trimers, *etc.*

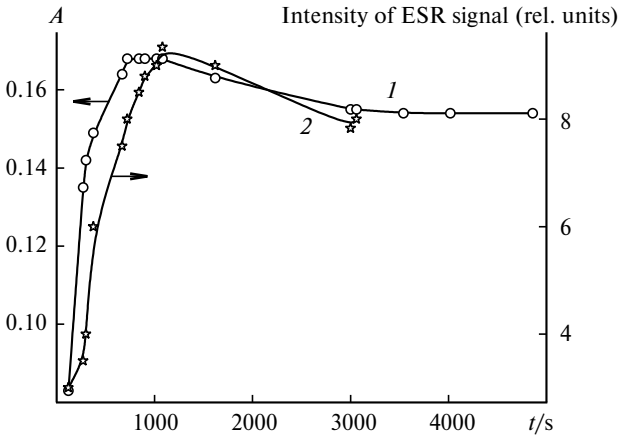
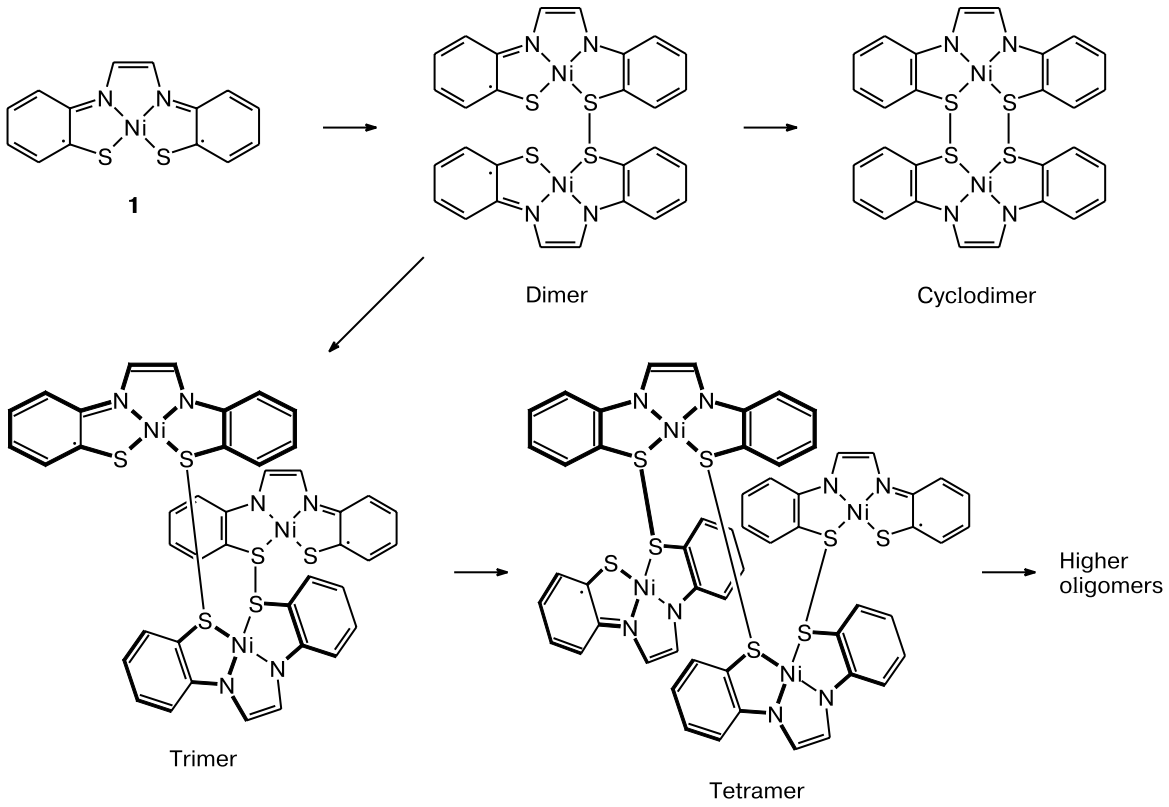


Fig. 4. Time dependence of the intensity of the peak at $\lambda_{max} =$ 931 nm in the electronic spectrum of a solution of compound **1** in DMF (~$1 \cdot 10^{-3}$ mol L^{-1}) (*1*) and the intensity of the signal in its ESR spectrum (*2*); the time was measured from the moment of dissolution (spectroscopic measurements were carried out within 0.5 h after the synthesis of the compound).

Scheme 4



(Scheme 4). These transformations are accompanied by a decrease in the intensity of the ESR signal (and a decrease in the intensity of absorption at 931 nm) because this signal is caused only by the terminal groups in oligomers. The formation of cyclic structures (see Scheme 4), which do not give an ESR signal at all, must not be ruled out as well.

An alternative description of the processes taking place in the system can be proposed. It is conceivable that a small amount of dissolved oxygen is present in the initial deaerated solution of complex **1**. This oxygen interacts with the thiyl-type radicals, and the observed ESR spectrum is associated with the appearance of the ArSOO$^{\bullet}$ radicals of the thiyl peroxyl type. The *g* factors for the AlkSOO$^{\bullet}$ radicals published in the literature[37] are given in Table 3. In the cited study, the electronic spectra of these radicals were also presented. These spectra have a weak absorption band at ~900 nm. Unfortunately, the published data on electronic and ESR spectra of the thiyl peroxyl radicals are scarce. We found no data on electronic spectra in the region of 900 nm even for the free arylthiyl peroxyl radicals, not to mention their metal complexes. However, the principal values of the *g* tensor for the radicals of the alkylthiyl peroxyl type differ substantially from those determined by us in that the differences in these values published in the literature are smaller (see

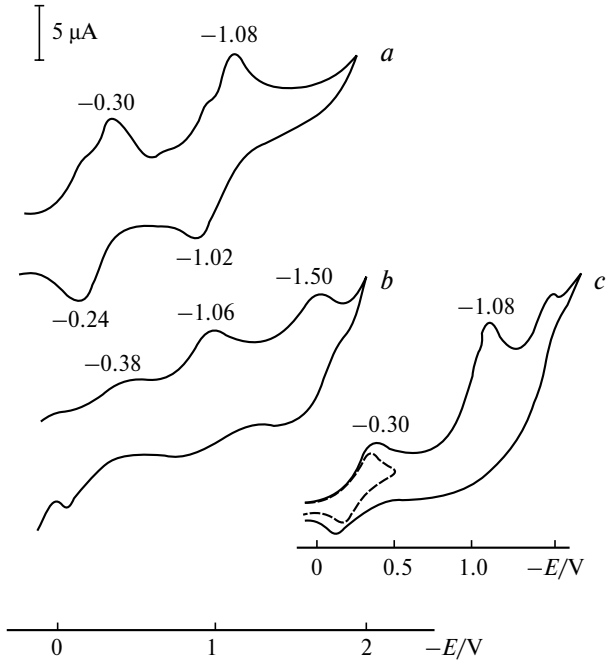


Fig. 5. Cyclic voltammograms of a $1 \cdot 10^{-3}$ *M* solution of compound **1** in DMF containing Bu_4NClO_4 (0.05 mol L^{-1}): a freshly prepared sample within 2 min after dissolution (*a*), the same solution after 5 h (*b*), a freshly prepared sample in the presence of Bu^nI ($5 \cdot 10^{-2}$ mol L^{-1}) (*c*).

Table 4. Electrochemical reduction potentials (E_p^{Red}) and oxidation potentials (E_p^{Ox}) of complexes **1—5** and **7—9** ($1 \cdot 10^{-3}$ mol L^{-1})*

Compound	$-E_p^{Red}$ [$-E_{1/2}^{Red}$]/V	E_p^{Ox} [$E_{1/2}^{Ox}$]/V	Note
1	0.30/0.24, 1.08/1.02, 1.80 (Pt)	0.65, 1.03	Sample was synthesized immediately before measurements performed within 30 s after dissolution in deaerated DMF
2	1.42/1.28 (Pt); 1.46, 2.12 (CG)	—	Freshly prepared sample. In the anodic regions, no pronounced waves were observed
3	0.37/0.28, 1.05/0.96, 1.93 (Pt); [0.36], [1.05]	1.20 (2 e), [1.12]	Ratio between the limiting currents of the first and second cathodic waves varies from 1 : 1.2 to 1 : 2 with increasing time of storage of the sample
4	0.36/0.26, 1.14, 1.61 (Pt); 0.36/0.28, 1.12, 1.70 (CG); [0.36] (1 e), [0.88] (2 e)	[1.05] (2 e), [1.24] (<2 e)**	Upon dissolution in DMF, the initially green solution turned brown in a few seconds
5	0.60/0.46, 1.43/1.28 (Pt); 0.61/0.51, 1.42 (CG); [0.58] (1 e); [1.14] (0.7 e)	1.10 (Pt); 1.18 (CG); [1.14]	Second reduction peak gradually shifts to more cathodic potentials in the course of repeated cyclic voltammetry measurements. Upon dissolution in DMF, the initially blue solution turned brown in a few seconds
7	1.18/0.24 (Pt); [0.76] (0.1 e), [1.12] (1 e)	1.16 (2e)	Freshly prepared sample
8	1.05/0.82, 1.64 (Pt); 1.36/1.12, 1.92 (CG); [0.92] (1 e), [1.36] (1 e)	1.38 (Pt); 1.25 (CG)	Compound is poorly soluble
9	0.39/0.32 (2 : 1), 1.39 (Pt); 0.41/0.36 (1 : 1); 1.36 (CG); [0.36] (1 e), [0.92] (2 e)	1.30 (Pt); 1.09 (CG); [1.30] (2—3 e)	—

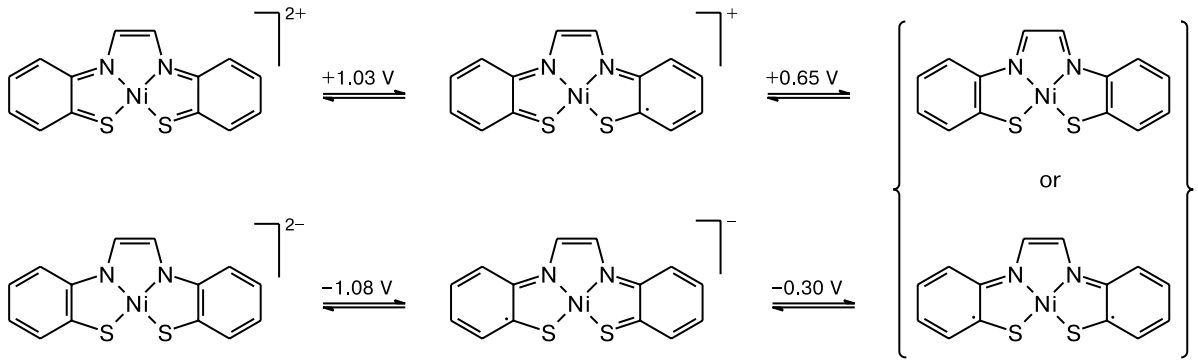
* The potentials were measured in DMF on a platinum or glassy-carbon (GC) electrode in the presence of a 0.05 *M* Bu_4NClO_4 solution as an indifferent electrolyte with respect to Ag/AgCl/KCl(sat.) at ~20 °C. The scan potential rates for the cyclic voltammetry on a stationary electrode and a rotating disk Pt electrode (2800 rpm) were 200 and 20 mV s^{-1}, respectively. For reversible and quasireversible peaks, the potentials of the reverse peaks are given after a slash.
** The wave with a sharp decrease on the plateau of the limiting current.

Table 3), which counts in favor the former of the proposed mechanisms of the appearance of ESR signals.

Electrochemistry. Electrochemical measurements were carried out using cyclic voltammetry (CV) and the rotating disk electrode voltammetry in anhydrous DMF in the presence of a 0.05 *M* Bu_4NClO_4 solution as an indifferent electrolyte. The results of measurements of the potentials are given in Table 4.

The electrochemical patterns for solutions of complex **1** change with time. For a sample synthesized immediately before the experiment, two pronounced electrochemically reversible reduction stages with peak poten-

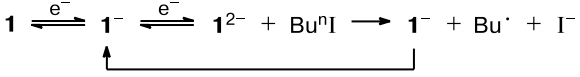
Scheme 5



tials of −0.30 and −1.08 V (Fig. 5, *a*) and two irreversible oxidation peaks at +0.65 and +1.03 V (see also Ref. 16) were observed. In the molecule of this compound (represented by formula **1a** or **1b**), the thiolate S atom is responsible for oxidation and the electron-withdrawing diimine system is responsible for reduction. Four redox transitions can be localized at the ligand with weak participation of the metal atom. These transitions can be represented by Scheme 5.

The polarization curve changes after storage of complex **1** in solution for 10 min. The amplitude of the peak at −0.30 V decreases and a new peak at −1.50 V appears. After 5 h, the cyclic voltammogram turns into an unclear curve (Fig. 5, *b*). This curve is very similar to the voltammogram of compound **2**, which was measured after its prolonged storage, and is slightly different from that of freshly prepared compound **2** (Fig. 6, *a*, *b*). Therefore, compounds **1** and **2** were finally transformed into the same product.

The addition of a large excess of Bu^nI ($5 \cdot 10^{-2}$ mol L^{-1}) to a $1 \cdot 10^{-3}$ *M* solution of the complex led to the following changes in the polarization pattern: the second reduction peak (at −1.08 V) becomes irreversible and its current substantially increases (Fig. 5, *c*). This indicates that dianion $\mathbf{1}^{2-}$ can reduce Bu^nI through a catalytic mechanism.



The reduced forms of complex **1** were not subjected to alkylation giving rise to a compound with the Ni^{III}—Bu bond, as in the case of a series of other Ni^{II} complexes studied earlier.[13,14] This fact is consistent with the above mechanism. According to this mechanism, the ligand

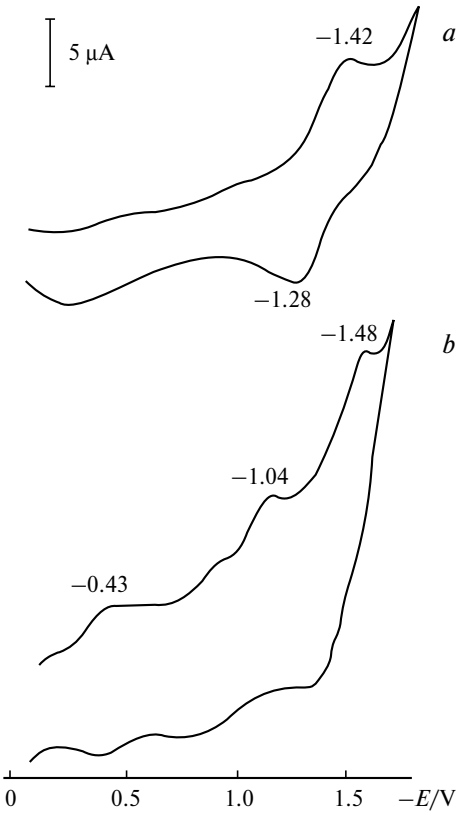


Fig. 6. Cyclic voltammograms of a $1 \cdot 10^{-3}$ *M* solution of compound **2** in DMF containing Bu_4NClO_4 (0.05 mol L^{-1}) measured on a Pt electrode: a freshly prepared sample within 2 min after dissolution (*a*), the same solution after 20 h (*b*).

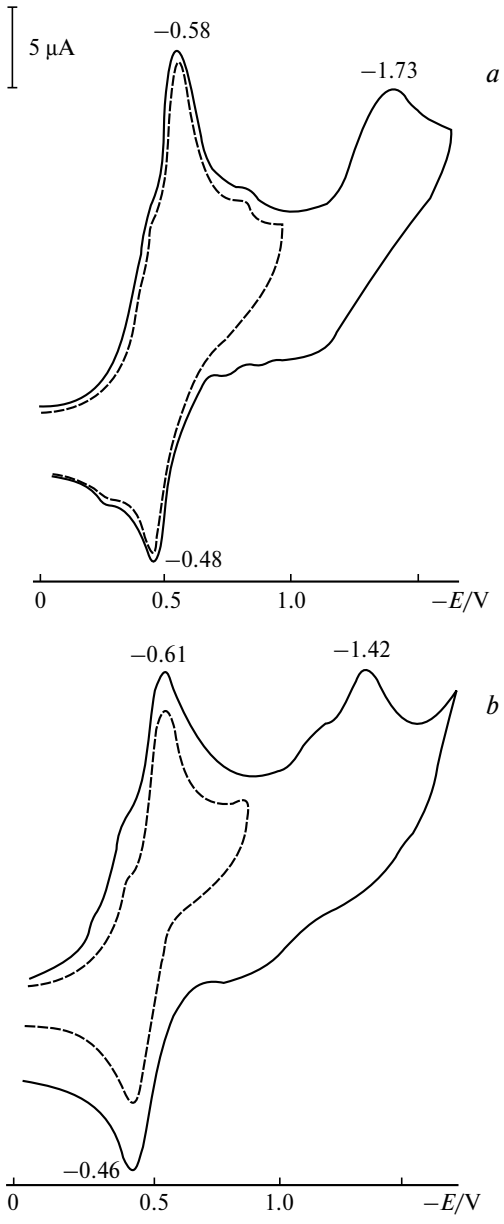


Fig. 7. Cyclic voltammograms of $1 \cdot 10^{-3}$ *M* solutions of the complexes in DMF containing Bu_4NClO_4 (0.05 mol L^{-1}) measured on a Pt electrode: freshly prepared compound **4** within 2 min after dissolution (*a*), freshly prepared compound **5** (*b*).

rather than the metal atom is involved in reduction (to give the supernucleophilic nickel anion).

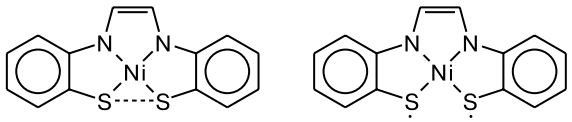
For complex **4**, we failed to obtain a curve analogous to that shown in Fig. 1, *a* characterized by two pronounced electrochemically reversible stages. The cyclic voltammogram for thiolate complex **4** is very similar to that for disulfide complex **5** (Fig. 7), which indicates that complex **4** either undergoes very rapid changes analogous to those observed for complex **1** or does not undergo changes at all. The former assumption is in agreement with the ^{1}H NMR spectroscopic data (see above). It can be hypothesized that complexes **4** and **5** have similar structures.

The data for other complexes under study and some comments are given in Table 4.

Our study of the Ni^{II} diiminodithiolate and diiminodisulfide complexes demonstrated that the structures of compounds **1—5** with the non-innocent ligands change with time both in the solid state and, particularly, in solutions. Thiolate complex **1** and the corresponding disulfide compound **2** were studied in most detail. Although the first studies of complex **1** were carried out about 40 years ago,[16] its properties remain unclear. In the present study, we demonstrated for the first time that this complex in solution shows the ESR activity during the first day with the simultaneous activation of the electron transition in the near-IR region. Subsequently, compound **1** is transformed into the final ESR-inactive structure, whose spectroscopic and electrochemical properties differ substantially from those of the starting form generated in the course of the synthesis of this compound. Complex **2** also undergoes changes both in solution and in the solid state, but these changes are much less pronounced.

We failed to prepare crystals of the complexes suitable for X-ray diffraction analysis. However, at the qualitative level, it can be stated that the dithiolate complex whose initial structure corresponds to formula **1a** or **1b** tends to be transformed into the disulfide structure similar to structure **2**.

For simplicity, the disulfide complex can be represented by formula **2a** with a weak S—S bond or by formula **2b** as a singlet biradical.

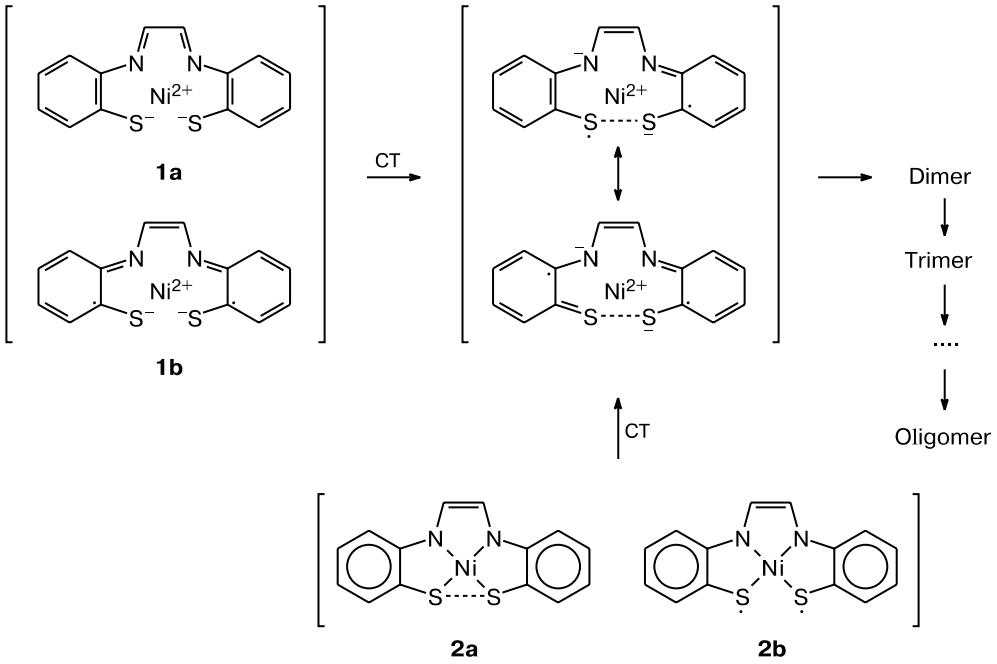


2a **2b**

Structures **2a** and **2b** cannot be related to formulas **1a** and **1b** for the dithiolate by resonance within the ligand molecule. Consequently, the transformation **1** → **2** corresponds to the true chemical reaction (Scheme 6).

This reaction involves the inner-sphere charge transfer and proceeds more readily from left to right than from right to left because the thiolate ion acts as a strong electron donor, whereas diimine serves as a strong electron acceptor. Consequently, the dithiolate-like ⟶ disulfide-like transformation rather than the reverse should be pref-

Scheme 6



CT is charge transfer

erable. We observed this phenomenon in all experiments. These reactions involving complexes **6—9** are much less probable because the negative charges on the N atoms are not stabilized due to the absence of the phenyl rings. As a result, the latter complexes are more stable.

Based on the results of our study, it can be assumed that freshly synthesized complex **1** is described by imine formula **1a** or **1b** (see above). The chelating biradical in structure **1b** is responsible for absorption at 931 nm, but it is inactive in the ESR spectrum. Subsequently, oligomerization takes place to give diamide structures containing the iminothioquinonate groups (see Scheme 4). Presumably, this process is preceded by charge transfer (see Scheme 5), *i.e.*, the intramolecular oxidation—reduction process involving no atmospheric oxygen. This process can be accompanied by the appearance of the ESR signal because the spins on the C atoms can become independent (in the dimer these atoms are not linked by a system of conjugated π bonds). Further transformations afford dimers, trimers, *etc.* The latter processes are accompanied by a decrease in the intensity of the ESR signal (and a simultaneous decrease in the intensity of absorption at 931 nm), because this signal is caused only by the terminal groups of oligomers.

It cannot also be ruled out that traces of oxygen present in the solvent are also involved in the above-considered processes. In this case the ESR activity and a band at 900 nm in the electronic spectrum can appear as a result of the formation of the arylthiyl peroxyl radicals.

The above processes involving complexes **4** and **5** are much faster due to which these compounds appear as stable compounds.

We believe that compounds **1**, **3**, and **4** with non-innocent ligands are synthesized as classical diiminodithiolate structures of type **1a**. However, the ligands in the solid state undergo further transformations into the *o*-iminothiosemiquinonate biradicals of type **1b** and then into oligomeric structures, which can be stored over a long period of time.

Experimental

Commercial *o*-aminothiophenol, β-mercaptoethylamine hydrochloride (β-aminoethanethiol (aet)), glyoxal hydrate, and diacetyl (Lankaster) were used without additional purification. β-Aminoethanethiol hydrochloride was transformed into free base by treating with an equivalent amount of an ethanolic solution of KOH immediately before the use in the synthesis. The resulting solution of β-aminoethanethiol was filtered from KCl that precipitated and then used in the reaction without additional purification. Dimethylformamide (high-purity grade) was purified by successive refluxing and vacuum distillation over anhydrous $CuSO_4$ and P_2O_5. The ^1H NMR spectra were recorded on a Varian-VXR-400 instrument operating at 400 MHz. The electronic spectra were measured on Specord-M40 (200—900 nm) and Helios-α Nicolet (200—1100 nm) instruments in a 0.1-cm quartz cell at 20—22 °C. The mass spectra (EI, 70 eV, direct inlet of the sample) were obtained on a Varian MAT-202 instrument. The ESR spectra were recorded on a Varian E-3 X-range radiospectrometer at 77 K under conditions precluding saturation and modulation broadening. The *g* factors of the complexes were determined with the use of the relative method by measuring the ESR spectra of copper ions simultaneously with the components of the hyperfine structure of Mn^{2+} ions in MgO. The scale of the *g* factors was calibrated by simultaneous measurements of the spectra of a diamagnetically diluted solid solution of Mn^{2+} ions in MgO (according to the data from the All-Russia Research Institute for Physicotechnical and Radiotechnical Measurements, the effective *g* factors of the third and fourth components and splitting between them are $g_3 = 2.0328\pm0.0001$ Gs, $g_4 = 1.9812\pm0.0001$ Gs, $\Delta_{3,4} = 86.76\pm0.05$ Gs, respectively).

The number of paramagnetic centers in the samples (N_x) was determined by the relative method according to the equation $N_x = N_{st}S_x/S_{st}$, where N_{st} is the number of paramagnetic centers in a $CuCl_2\cdot2H_2O$ single crystal used as the standard, S_{st} and S_x are the areas under the absorption curves of the standard and the sample under study, respectively, related to the standard conditions of measurements. The ESR spectra were recorded as the first derivative of the absorption line $dI(H)/dH$. The areas S were calculated using the homemade program package and an automated system for data collection. The steady-state conditions of measurements in a resonator of the ESR spectrometer were controlled by recording the spectrum of the sample under study simultaneously with a particular component of the spectrum of a ruby single crystal as the internal standard. The relative accuracy of measurements of the concentration of the paramagnetic Cu ions was ±10%.

Electrochemical studies were carried out using a PI-50-1.1 potentiostat. Glassy-carbon (d = 2.0 mm) or platinum (d = 2.8 mm) disks were used as working electrodes; a 0.05 *M* Bu_4NClO_4 solution in DMF served as the supporting electrolyte; Ag/AgCl/KCl(sat.) was used as the reference electrode. All measurements were carried out under argon. The samples were dissolved in the pre-deaerated solvent.

Kinetic measurements (general procedure). A weighed sample was placed in a 10-mL flask. Then the solvent was added. The samples were withdrawn and placed in a spectrophotometric cell. The time was measured from the moment of addition of the solvent. The first spectrum was recorded within 2—7 min after the addition of the solvent.

Diiminodithiol complexes (template synthesis).[3] Method *A*. A solution of a 1,2-dicarbonyl compound (1 mmol) and the corresponding aminothiol (2 mmol) in EtOH (10 mL) was heated to boiling and a hot solution of $NiCl_2\cdot6H_2O$ (1 mmol) in EtOH (5 mL) was added. The reaction mixture was refluxed for 3 h and cooled to 0 °C. The precipitate that formed was filtered off and then washed with EtOH or recrystallized from EtOH.

Method *B* (with isolation of thiazoline (thiazolidine)).[2] A solution of a 1,2-dicarbonyl compound (1 mmol) and the corresponding aminothiol (2 mmol) in MeCN or EtOH (10 mL) was refluxed for 15 min and then cooled to 0 °C. The precipitate of thiazoline (thiazolidine) that formed was filtered off and washed with EtOH. Thiazoline (thiazolidine) (1 mmol) was added to a solution of $NiCl_2\cdot6H_2O$ (1 mmol) in EtOH (15 mL) and the mixture was refluxed for 1 h, after which the resulting complex was isolated as described in the method *A*.

Method *C* (reaction of a 1,2-dicarbonyl compound with Ni(aet)$_2$). A 1,2-dicarbonyl compound (1 mmol) was added to a suspension of Ni(aet)$_2$ [7] (1 mmol) in EtOH (10 mL) and the suspension was refluxed for 4 h. A pale-green precipitate of Ni(aet)$_2$ was dissolved in the course of refluxing and the solution turned dark-cherry. After complete dissolution of Ni(aet)$_2$, the reaction mixture was cooled to 0 °C and the complex that formed was isolated as described in the method *A*.

Diiminodisulfide complexes. A solution of a 1,2-dicarbonyl compound (1 mmol) and 2,2´-diamino diphenyl disulfide (1 mmol) in EtOH (10 mL) was heated to boiling and a hot solution of Ni(ClO$_4$)$_2$·6H$_2$O (1 mmol) in MeCN (5 mL) was added. The solution immediately turned dark-cherry. The mixture was refluxed for 3 h and cooled to 0 °C. The precipitate that formed was filtered off, washed with EtOH, and dried in air.

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