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Nickel(II) Complexes with Amino- and Iminocyclohexylsulfides: Synthesis and Electrochemical Study

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Abstract—Nickel(II) complexes with aminosulfide and iminosulfide ligands have been synthesized on the basis of phenyl- and ethynyl-(2-aminocyclohexyl)sulfides, glyoxal hydrate, and $Ni(ClO_4)_2 \cdot 6H_2O$. Electrochemical measurements were carried out using cyclic voltammetry (CVA) and a rotating disk electrode (RDE). The following has been shown: (1) the reduced species of iminosulfide complexes are more stable than the reduced species of aminosulfide complexes, and (2) the complexes containing a C≡C fragment in their organic ligand are polymerized during reduction.

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A method for preparing (2-aminocyclohexyl)phenylsulfide (compound **1**) from (2-chlorocyclohexyl)phenylsulfide by the Gabriel reaction was described and the possibility of complexing the resulting aminosulfide with nickel(II) and copper(II) salts was studied in [1].

Here, we report the synthesis of nickel(II) complexes with (2-aminocyclohexyl)phenylethynylsulfide (compound **2**) and glyoxalbis(2-thiocyclohexyl)imines. We also report the electrochemical study of these complexes by cyclic voltammetry (CVA) and with a rotating disk electrode (RDE).

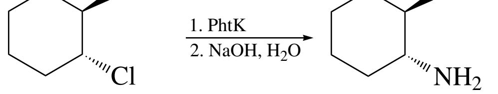
Aminosulfides **1** and **2** were synthesized by reacting chlorocyclohexylsulfides, which were prepared by reacting cyclohexene with sulfenamide in the presence of phosphorus oxochloride [2, 3], with potassium phthalimide (Scheme 1).

Compounds **1** and **2** contain N and S donor atoms; they are potential ligands capable of forming five-membered chelate rings with metal ions. We have studied the reaction of these aminosulfides with nickel(II) perchlorate. When hot solutions of compound **1** or **2** and an inorganic salt are mixed, their color changes rapidly, proving that the ligand is coordinated to the metal ion. Upon cooling, the products crystallize from the solution in colored powdered compounds with mp > 300°C; these powders are well soluble in DMA and DMSO and poorly soluble in most of the other organic solvents and water. The compositions of the complexes were derived from elemental analysis. Their structure was verified by electronic and IR spectra (Scheme 2).

The available data do not allow us to decide whether the ligand moieties in complexes **3** and **4** have a *cis* or *trans* configuration. However, from the results of subsequent reactions with glyoxal (see below), the *cis* configuration seems more probable.

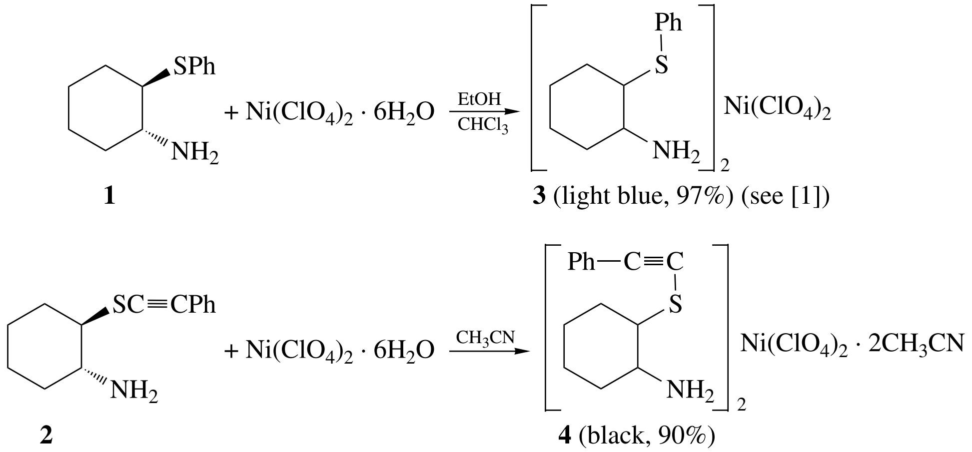
Two nickel(II) complexes of another structure type (complexes **5** and **6**) were synthesized on the basis of 2-aminocyclohexylsulfides. Complexes **5** and **6** contain a chelating organic N,S-ligand, but they also contain an imine donor moiety instead of the amine moiety. Complex **5** was synthesized by reacting complex **3** with glyoxal hydrate in ethanol. Complex **6** was prepared by two routes: (1) by the reaction with glyoxal hydrate, as used to prepare complex **5**, or (2) by three-component condensation of aminosulfide **2**, glyoxal hydrate, and nickel perchlorate (Scheme 3).

The compositions of complexes **5** and **6** were derived from elemental analysis; their structures were determined from electronic and IR spectra. For complex **5**, the electronic spectrum shows medium-intensity absorption bands at 252, 257, 263, and 307 nm. The absorption in this spectral range is intrinsic to the organic ligand. The band at 257 nm is the only band observed in the electronic spectrum of complex **6**. Complexes **5** and **6** do not have noticeable absorption intensities in the visible, which proves the octahedral surrounding of the nickel atom in them. The existence of a coordinated water molecule in the complexes is confirmed by elemental analysis and IR spectra (a broad band at 3200–3500 cm^{-1}).

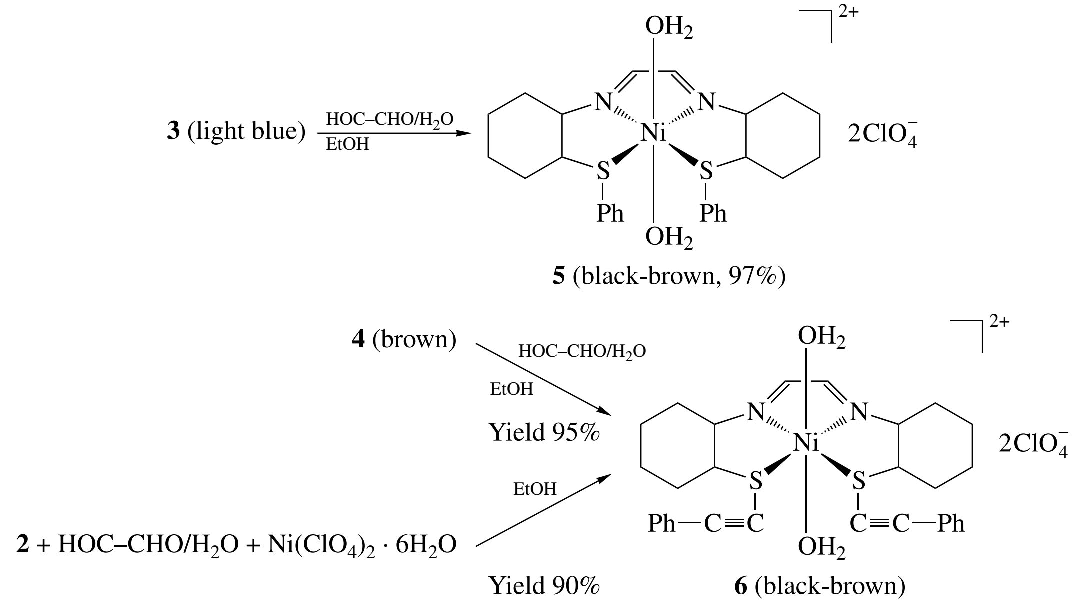


1. R = Ph, 65% (see [1]);
2. R = C≡C–Ph, 65%.

Scheme 1.



Scheme 2.



Scheme 3.

The formation of complexes **5** and **6** from complexes **3** and **4** provides an argument in favor of the *cis* configuration of the latter or at least of the existence of equilibrium between the *cis*- and *trans*-species in solution.

With the goal of studying the redox ability of our prepared metal complexes and of ascertaining a potential catalytic activity of these compounds as alkyl-group carriers, we studied the electrochemical behavior of compounds **1** and **3**–**6**.

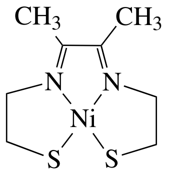
The one-electron reduction of nickel(II) complexes yields anions in which nickel has the formal oxidation number +1; their two-electron reduction yields dianions of complexes containing nickel(0). Nickel(I) complexes in their reactions with AlkX produce nickel(III) compounds; nickel(0) complexes produce compounds with alkyl–nickel(II) bonds. Such alkylnickel compounds can further transfer alkyl groups to various substrates [4] (Scheme 4).

In order for the aforementioned conversions to occur, it is necessary that both reduction stages or at least addition of the first electron be electrochemically reversible or quasireversible. The voltammetric indica-

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

Scheme 4.

Electrochemical potentials for compounds **1** and **3–6** (concentration, 10^{-3} mol/L) measured in DMF on SU, Pt, or Au electrodes in the presence of 0.05 M Bu_4NClO_4 with reference to Ag|AgCl|KCl (sat) at room temperature (after a slash, reverse peak potentials are indicated; in parentheses, the number of transferred electrons determined on an RDE with reference to the one-electron ferrocene oxidation wave)

Compound	$-E_p^{Red}$, V	$-E_{1/2}^{Red}$, V	E_p^{Ox}, V	$E_{1/2}^{Ox}$, V
2	(SU) peaks are unobserved		0.94^{a}	
	(Pt) peaks are unobserved		1.10^{a}	
3	(SU) 0.65^{b}; 1.23/0.06; 1.93; 2.63	0.65^{b} (1/4); 1.30 (1/2); 1.76 (1/8)	1.00; 1.42	1.20 (1.2)
	(Pt) 0.44; $0.85/0.37^{a}$; 1.62	0.46 (0.5); 0.76 (0.33); 1.56 (0.13)	1.06	1.25 (2.5)
	(Au) 0.77^{b}; 1.47	0.60 (0.7)	0.49; 1.06; 1.39	0.90 (1.1); 1.44 (0.85)
4	(SU) 0.70^{b}; $1.42/0.05^{c}$	0.72^{b} (0.1); 1.50 (0.5)	0.98^{a}	1.10 (0.33)
	(Pt) 0.72^{a}; $1.00/0.14^{c}$; 1.31	0.66^{b} (0.1); 1.42 (0.5)	0.99^{a}	1.15 (0.33)
	(Au) 0.73^{b}; 1.17/+0.08	0.62^{b} (0.13); 1.32 (1)	0.46^{b}; 0.99^{a}	0.72 (0.1); 0.97 (1/6)
5^{d}	(SU) 0.74^{b}; 1.75; 1.93; 2.36	0.70 (2.4); 1.35 (5.4)	0.95; 1.25	0.96 (1.3); 1.24 (10.4)
	(Pt) 0.46^{b}; 0.90/0.20; 1.67	0.76 (34); 1.45 (8)	0.56; 0.88	1.22 (95)
	(Au) 0.58; 1.07; 1.60	0.62 (1.4); 1.06 (1.4); 1.80 (1.2)	1.42	0.82 (2.5); 1.28 (3.2)
6	(SU) 1.49/0.04; 1.89; 2.21	1.32 (0.8); 1.50 (0.4)	0.88^{a}	–
	(Pt) 0.86/0.16; 1.30^{a}; 1.70	1.19 (0.66); 1.62 (0.25)	–	0.89 (0.14)
	(Au) 1.14/+0.08	1.23 (1.2); 1.82 (0.3)	1.65	1.17 (0.2)
 **7** (see [6])	(Pt) 1.18/0.24	0.76 (0.1); 1.12 (1)		1.16 (2)

Notes: [a] A low-intensity peak; [b] an adsorption prewave (see discussion in the text); [c] the intensity of the reverse peak of nickel metal desorption from the electrode surface increases with time during electrolysis at the potential of the first reduction wave; [d] for complex **5** (concentration, $<10^{-3}$ mol/L), *E* is followed by the parenthesized current ratio on an RDE.

tion of the fast alkylation reactions of transition-metal chelates is based on the electrochemical activation of the complex via one- or two-electron reduction; as a result, the complex becomes active in S_N2 or radical reactions with alkylating agents. The criteria of the occurrence of such reactions are as follows: (1) the appearance of a new cathodic peak associated with the reduction of the alkylation product, (2) a noticeable decrease in the reversibility of the reduction of the starting complexes, and (3) the appearance of peaks due to the oxidation of I^- or Br^- (when alkyl iodides or alkyl bromides are used as alkylating agents) [5]. The results of the potential measurements are listed in the table.

All peaks observed for the test complexes have very low intensities in both the reduction and the oxidation regions, especially in the oxidation region.

In the reduction of complexes **3**, **4**, and **5** on Pt or CG electrodes, low-intensity peaks are observed in the range from –0.7 to –0.9 V; the appearance of these peaks indicates the adsorption of the starting complex on the electrode [7]. The subsequent reduction peaks in the range from –1.00 to –1.75 V should correspond to the reduction of the complex at the nickel atom.

Regarding their electrochemical behavior, nickel complexes are grouped as follows. One group includes

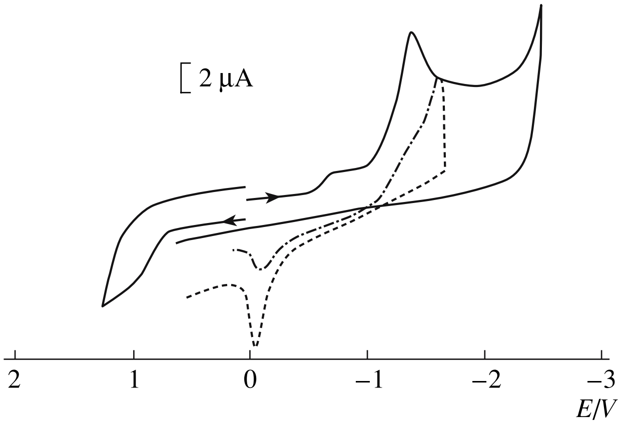


Fig. 1. CVAs for complex **3** (DMF, 0.05 M Bu_4NClO_4, 10^{-3} mol/L) on a CGelectrode (the dashed line shows CVAs obtained during electrolysis at the potential of the first reduction wave for ~10 min).

complexes that are reduced stagewise through a nickel(I) intermediate, which converts to nickel(0) at far higher cathodic potentials [4–6]. Such complexes are nickel(II) complexes with cyclames, dimethylglyoxime, and others. The other group includes complexes that are electrochemically reduced to zero-valence species immediately, in one two-electron stage. Such complexes are nickel(II) complexes of 2,2'-bipyridyls, 1,10-phenanthrolines, PPh_3, or 1,2-bis(diphenylphosphino)ethane.

When the reduction proceeds to nickel(0), the resulting complex is stable only when it contains a nitrogen-containing macrocyclic ligand [8]. Otherwise, the complex as a rule degrades to metal nickel and the free ligand.

The reduction of complex **3** occurs as a two-electron reaction at –1.42 V. We can state that the electron is transferred to the nickel(II) atom: for uncomplexed ligand **1**, no peaks are observed in the reduction region until the potential reaches –2.20 V (table). It is especially noteworthy that, although complex **3** contains bidentate N,S-ligands, and not macrocyclic ligands, the product of the two-electron reduction to nickel(0) is stable only to a certain degree. Nickel elimination on the electrode (the characteristic triangular peak due to nickel desorption is observed at –0.05 V) occurs only upon electrolysis at the potential of the first reduction wave. Without accumulation, the peak associated with oxidative nickel desorption virtually does not appear (table, Fig. 1).

We obtained similar data for complexes **4** and **6**. Both complexes are reduced irreversibly with metal nickel elimination, at the first stage of the two-electron reduction. However, the reduced species of complexes **4** and **6** are more stable than those of complex **3**. At the same time, iminosulfide complex **5** is reduced at the first stage without eliminating metallic nickel. We should note that the oxidation and reduction mechanism of the complexes depends on the nature of the electrode (table; Figs. 2, 3). For compound **6**, for example, reduction on a CGelectrode occurs at –1.41 V and on a Pt electrode at –0.86 V. In both cases, reduction is irreversible and results in elimination of metallic nickel. At the same time, reduction on an Au electrode occurs at *E* = –1.14 V, and nickel elimination is not observed. This can be due to the different adsorption mechanisms of the test compounds on different electrodes. The fact of adsorption is verified by the appearance of adsorption prepeaks at about –0.7 V for the test complexes (table). The different oxidation mechanisms agree with data obtained in [7].

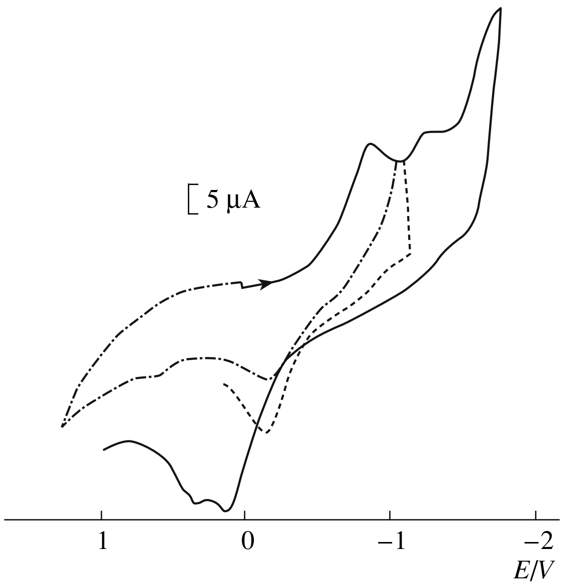


Fig. 2. CVAs for complex **6** (DMF, 0.05 M Bu_4NPF_6, 10^{-3} mol/L) on a Pt electrode.

For complexes containing a C≡C fragment in their organic ligands, the further reduction peaks at potentials higher than –1.42 V have substantially decreased intensities; visually, the electrode surface is coated with a reaction-product film. Apparently, the test compound is polymerized at its acetylene fragment. This is proven by the low intensity of the reduction peaks, associated with the formation of a low-conducting polymer layer on the electrode [12]. Transition-metal (copper [14], cobalt [15], and nickel [15]) complexes can catalyze the electrochemically activated reactions of acetylene polymerization. According to [14], the radical anion produced at the first reduction stage adds to the C≡C bond, initiating acetylene polymerization. Thus, the complexes we synthesized can catalyze electrochemically induced alkyne polymerization.

The oxidation and reduction mechanisms for imine complex **5**, as for complex **4**, are different on SU, Pt, and Au electrodes.

The electrochemical behavior of imine complexes **5** and **6** is in general characterized by a higher stability of

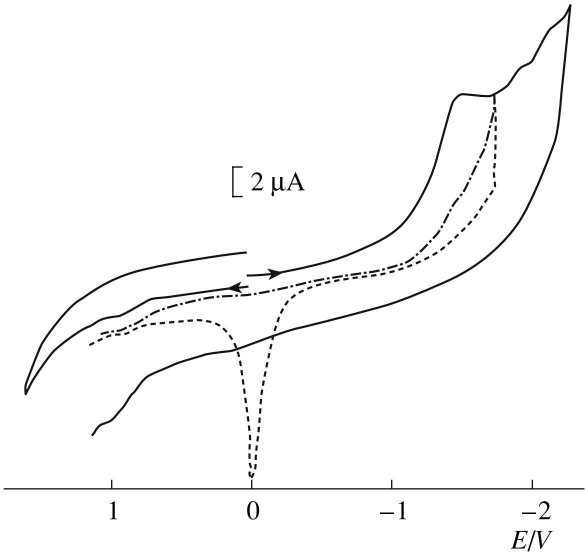


Fig. 3. CVAs for imine complex **6** (DMF, 0.05 M Bu_4NClO_4, 10^{-3} mol/L) on a CG electrode.

the product of the first reduction stage compared to amine complexes **3** and **4** (cf. Figs. 3, 2, table). Complex **6** on an Au electrode and complex **5** on CG and Au electrodes are reduced without eliminating metallic nickel. The reduction of complex **6** on a CG electrode produces an insignificant peak due to nickel(0) desorption; this peaks becomes intense only upon accumulation.

An electrochemical study of iminothiolate complex **7** on a Pt electrode was previously carried out in our laboratory (see [6] and table). We compared the results of [6] with the results of the electrochemical study of iminosulfide complexes **5** and **6** obtained in this work. Complex **7** is reduced on a Pt electrode in one two-electron stage with E_p = –1.18/–0.24 V with nickel(0) desorption. These results are similar to the reduction of complex **5** (E_p = –0.90/–0.20 V) and complex **6** (E_p = –0.86/–0.16 V). Therefore, we can suggest that the possibility or impossibility of covalent bonding between the nickel ion and sulfur atom is not decisive for the ability of the complex to stabilize low oxidation states of nickel. For both types of complexes, the product of the two-electron reduction is unstable and eliminates metallic nickel. The easier reduction of sulfide complexes compared to the thiolate complex is easily interpreted in view of the fact that a dication is reduced in the former and a neutral species is in the latter.

The oxidation potentials of the iminothiolate complex and the iminosulfide complex are practically identical (1.22 and 1.16 V for complexes **5** and **7**, respectively), proving that the oxidation occurs at the imine moiety of the molecule.

As a result of the electrochemical study of our synthesized complexes, the following preliminary conclusions can be drawn:

(1) The reduced species of iminosulfide complexes **5** and **6** are more stable than those of aminosulfide complexes **3** and **4**.

(2) The adsorption of complexes **3** and **4** on electrodes is likely due to the amino groups in their organic moiety.

(3) Complexes **4** and **6**, which contain the C≡C fragment in their organic ligands, are polymerized upon reduction. The low intensity of their reduction peaks (at cathodic potentials higher than –1.42 V), associated with the formation of a poorly conducting polymer layer on the electrode, and the product film visually observed on the electrode surface prove the polymerization of complexes **4** and **6**.

Thus, it seems most pertinent to further study the potential of iminosulfide complexes for use as alkylation catalysts. Iminosulfide complexes containing the acetylene moiety also form stable reduction products; however, they are polymerized upon reduction, forming a poorly conducting layer on the electrode surface.

At the same time, the last fact means that the amino- and iminosulfide complexes we synthesized can further be studied as potential catalysts in acetylene polymerization reactions.

EXPERIMENTAL

IR spectra were recorded as thin films or Nujol mulls on a UR20 instrument. Electronic spectra were recorded on a Specord M40 instrument (200–900 nm) in quartz cells 0.1 cm thick at 20–22°C. For electrochemical experiments, a PI-50-1.1 potentiostat was used. All measurements were carried out under an argon atmosphere. Test samples were dissolved in the deaerated solvent. Dimethylformamide (pure grade) was purified by stirring over freshly calcined K_2CO_3 for 4 days, followed by vacuum distillation first from P_2O_5 and then from anhydrous $CuSO_4$. Aminosulfide **1** and complex **3** were prepared as described in [1], and aminosulfide **2**, as in [3].

Bis(2-phenylethynylsulfidocyclohexyl)nickel(II) bis(acetonitrile) diperchlorate (4). A solution of aminosulfide **2** (1 mmol) in EtOH (5–6 mL) was mixed with a solution of $Ni(ClO_4)_2 \cdot 6H_2O$ (0.5 mmol) in a minimal amount of EtOH, and the resulting solution was allowed to stand at 20°C until about two-thirds of the solvent were evaporated. To the residue, Et_2O (3 mL) was added. A powdered brown precipitate was filtered and vacuum dried. mp > 300°C.

For $C_{32}H_{40}N_4S_2NiCl_2O_8$ anal. calcd. (%): C, 47.90; H, 5.02; N, 6.98.

Found (%): C, 48.86; H, 5.73; N, 6.58.

Electronic spectrum (λ, nm): 250, 263, 310.

Glyoxalbis(2-phenylsulfidocyclohexyl)nickel(II) diaqua perchlorate (5). A solution of glyoxal hydrate (1 mmol) and complex **3** (1 mmol) in EtOH (10 mL) was refluxed for 15 min, then cooled to 0°C. The color of the solution changed from brown to black. A precipitate was filtered, rinsed with EtOH, and air dried. mp > 300°C.

For $C_{26}H_{36}N_2S_2NiCl_2O_{10}$ anal. calcd. (%): C, 42.76%; H, 4.97; N, 3.84%.

Found (%): C, 43.25; H, 4.39; N, 3.76.

IR spectrum (ν, cm^{-1}): 1620, 1650, 3200–3500 (H_2O).

Electronic spectrum (λ, nm): 252, 257, 263, 307.

Glyoxalbis(2-phenylethynylsulfidocyclohexyl) nickel(II)diaqua perchlorate (6).

Method A. A solution of glyoxal hydrate (1 mmol) and complex **4** (1 mmol) in EtOH (10 mL) was refluxed for 15 min, then cooled to 0°C. The color of the solution changed under reflux from light blue to black. The precipitate was filtered, rinsed with EtOH, and air dried.

Method B. A solution of glyoxal hydrate (1 mmol), $Ni(ClO_4)_2 \cdot 6H_2O$ (1 mmol), and 2-aminocyclohexyl-2-phenylethynylsulfide **2** (2 mmol) in EtOH (15 mL) was refluxed for 15 min, then cooled to 0°C. The precipitate was filtered, rinsed with EtOH, and air dried. mp > 300°C.

For $C_{30}H_{36}N_2S_2NiCl_2O_{10}$ anal. calcd. (%): C, 46.29; H, 4.66; N, 3.60.

Found (%): C, 46.32; H, 4.61; N, 3.89.

Electronic spectrum (λ, nm): 257.

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