

# Synthesis and electrochemical characterization of Co<sup>II</sup>, Ni<sup>II</sup>, and Cu<sup>II</sup> complexes with organic N<sub>2</sub>S<sub>2</sub>-type ligands derived from 2-thio-substituted benzaldehydes and aromatic amines

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Transition metal complexes (Ni<sup>II</sup>, Co<sup>II</sup>, and Cu<sup>II</sup>) with tetradentate N<sub>2</sub>S<sub>2</sub>-type ligands (L), which are reaction products of 2-thio-substituted benzaldehydes with aromatic amines (3-aminopyridine or 2-aminothiophenol), were synthesized for the first time. The complexes have the composition L·MX<sub>2</sub> or L·2MX<sub>2</sub> (X = Cl or ClO<sub>4</sub>). The electrochemical behavior of the ligands and complexes was studied by cyclic voltammetry and rotating disk electrode voltammetry. Depending on the structure of the complexes, the metal atom in the latter is initially reduced in a one- or two-electron process.

**Key words:** nickel(II) complexes, cobalt(II) complexes, copper(II) complexes, imines, sulfides, N<sub>2</sub>S<sub>2</sub> ligands, electrochemistry.

Transition metal complexes, in particular nickel(II),<sup>1</sup> cobalt(II),<sup>2</sup> and copper(II) complexes,<sup>3</sup> with organic S,N-containing ligands have attracted attention as models of metalloenzymes and electroactive catalysts. Thio-substituted imines are among promising types of organic ligands. Earlier, we have synthesized a series of acyclic and macrocyclic *S,S*-alkylidene-thiosalicylimines<sup>4</sup> and bis[2-(pyridylmethylideneamino)phenylthio]ethanes<sup>5</sup> and studied their electrochemical behavior. Such complexes were demonstrated to be reversibly reduced and serve as potential catalysts for electrochemically induced alkylation reactions.

In continuation of our studies on transition metal complexes with organic N<sub>2</sub>S<sub>2</sub>-type ligands, we synthesized and electrochemically characterized bis-sulfide and disulfide ligands, which are the reaction products of 2,2'-di-

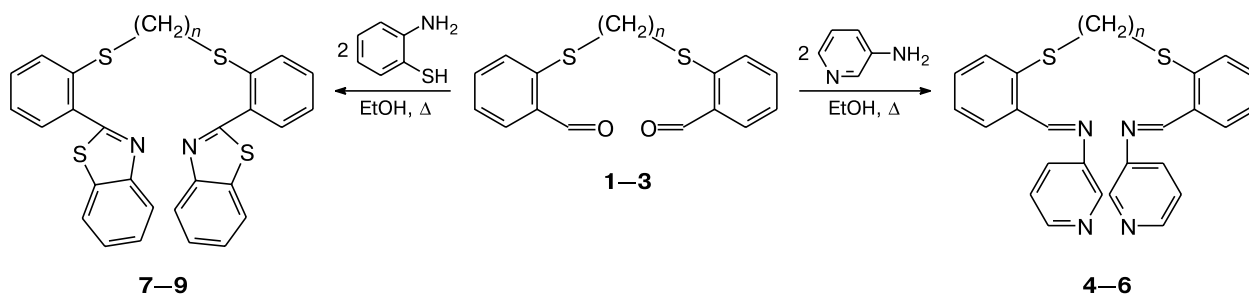
thiobenzaldehyde (**1**), 1,2-bis(2-formylphenylthio)ethane (**2**), or 1,3-bis(2-formylphenylthio)propane (**3**) with aromatic amines (3-aminopyridine or 2-aminothiophenol), and their complexes with Ni<sup>II</sup>, Co<sup>II</sup>, and Cu<sup>II</sup>.

## Results and Discussion

**Synthesis of ligands and complexes.** N<sub>2</sub>S<sub>2</sub>-Type imino-sulfide and iminodisulfide ligands **4–9** were synthesized by the reactions of bis-thio-substituted benzaldehydes **1–3** with 3-aminopyridine or 2-aminothiophenol under reflux in EtOH (Scheme 1).

The structure of ligand **7** was confirmed by X-ray diffraction. Crystallographic data and the X-ray data collection and refinement statistics for compound **7** are given in Table 1. Selected bond lengths and bond angles are listed

Scheme 1



$n = 0$  (**1**, **4**, **7**),  $2$  (**2**, **5**, **8**),  $3$  (**3**, **6**, **9**)

**Table 1.** Crystallographic data and the X-ray data collection and refinement statistics for compound 7

Parameter	Characteristics
Molecular formula	C <sub>26</sub> H <sub>16</sub> N <sub>2</sub> S <sub>4</sub>
Molecular weight	484.65
<i>T</i> /K	120(2)
$\lambda$ /Å	0.71073
Color, crystal shape	Red prisms
Crystal dimensions/mm	0.25×0.25×0.20
Crystal system	Monoclinic
Space group	<i>P</i> 2 <sub>1</sub> / <i>n</i>
<i>a</i> /Å	7.6422(4)
<i>b</i> /Å	7.7283(4)
<i>c</i> /Å	36.558(2)
$\alpha$ /deg	90.00
$\beta$ /deg	91.336(5)
$\gamma$ /deg	90.00
<i>V</i> /Å <sup>3</sup>	2158.58(19)
<i>Z</i>	4
<i>d</i> <sub>calc</sub> /g cm <sup>-3</sup>	1.491
$\mu$ /mm <sup>-1</sup>	0.459
<i>F</i> (000)	1000
$\theta$ Scan range/deg	3.0–30.0
Ranges of indices	$-10 \leq h \leq 10, -10 \leq k \leq 10,$ $-48 \leq l \leq 47$
Number of measured /independent reflections	5194/3880 ( <i>R</i> <sub>int</sub> = 0.0489)
Number of variables in the refinement	289
Goodness-of-fit on <i>F</i> <sup>2</sup>	1.000
<i>R</i> factors ( <i>I</i> > 2 $\sigma$ ( <i>I</i> ))	<i>R</i> <sub>1</sub> = 0.0465, <i>wR</i> <sub>2</sub> = 0.1079
<i>R</i> factors based on all reflections	<i>R</i> <sub>1</sub> = 0.0619, <i>wR</i> <sub>2</sub> = 0.1182

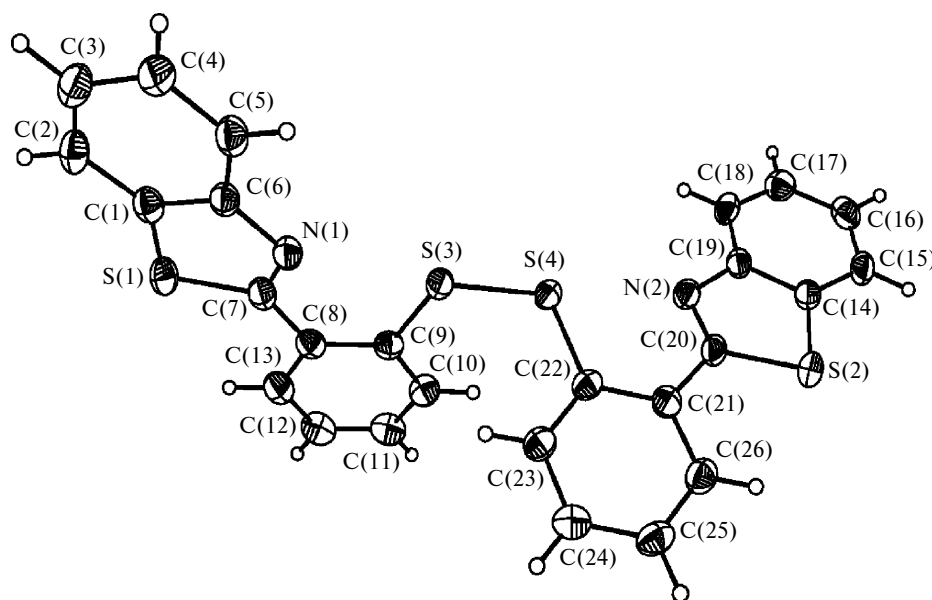
**Table 2.** Selected interatomic distances (*d*), bond angles ( $\omega$ ), and dihedral angles ( $\phi$ ) for compound 7

Parameter	Value
Bond	<i>d</i> /Å
S(3)—C(9)	1.795(2)
S(3)—S(4)	2.0599(8)
S(2)—C(14)	1.738(3)
S(2)—C(20)	1.761(2)
S(1)—C(1)	1.734(2)
S(1)—C(7)	1.762(2)
C(7)—N(1)	1.296(3)
C(6)—N(1)	1.387(3)
N(2)—C(20)	1.294(3)
N(2)—C(19)	1.392(3)
Angle	$\omega$ /deg
C(9)—S(3)—S(4)	104.35(8)
C(22)—S(4)—S(3)	103.74(8)
C(14)—S(2)—C(20)	88.84(11)
C(1)—S(1)—C(7)	89.29(11)
N(1)—C(7)—S(1)	115.12(17)
Angle	$\phi$ /deg
C(9)—S(3)—S(4)—C(22)	88.02(10)
C(7)—S(1)—C(1)—C(2)	179.5(2)
C(7)—S(1)—C(1)—C(6)	0.35(16)
S(1)—C(7)—C(8)—C(13)	11.9(3)
S(3)—S(4)—C(22)—C(23)	13.9(2)
S(4)—S(3)—C(9)—C(10)	8.6(2)

in Table 2. The molecular structure of compound 7 is shown in Fig. 1. The donor atoms of the N<sub>2</sub>S<sub>2</sub> system are not in a single plane; the C—S—S—C dihedral angle

is ~88°. Both benzothiazole fragments are planar. These fragments are noncoplanar with the adjacent benzene rings. The angle between the planes of the benzene and benzothiazole fragments is ~12°.

The complexes with metal chlorides were synthesized by two methods: by refluxing the ligand and the corresponding metal salt in EtOH (method *A*) and by the slow

**Fig. 1.** Molecular structure of compound 7. The displacement ellipsoids are drawn at the 50% probability level.



are characteristic of coordination compounds containing the central  $M^{2+}$  ion in the tetrahedral ligand environment.<sup>8,9</sup> The structures of copper-containing complexes **15**, **17**, and **18** cannot be unambiguously assigned based on the electronic spectroscopic data.

Complexes with  $N_2S_2$ -type disulfide ligands, such as ligands **4** and **7**, in which the same metal atom is coordinated by both sulfur atoms of the disulfide fragment, are unknown. The characterized complexes with these ligands can be divided according to their structures into three types: 1) complexes, in which disulfide is coordinated to the metal atom as a tridentate ligand, *i.e.*, through two nitrogen atoms and one sulfur atom (see, for example, Ref. 10); 2) dinuclear bis-disulfide complexes, in which the adjacent sulfur atoms of disulfide are involved in the coordination to two different metal atoms (see, for example, Refs 11 and 12); 3) complexes, in which the disulfide ligand is coordinated through the nitrogen atoms (the sulfur atom is not involved in the coordination).<sup>13,14</sup>

The known tetradentate  $N_2S_2$ -type ligands, which can give complexes with the metal : ligand compositions of both 1 : 1 and 2 : 1, generally form a coordination bond with the first metal cation through four donor atoms of the tetradentate system and with the second metal cation through two additional donor atoms (see, for example, Ref. 15).

Ligands containing the benzothiazole fragment are usually coordinated to transition metal ions through the nitrogen atom of the five-membered ring (see Ref. 16 and references therein).

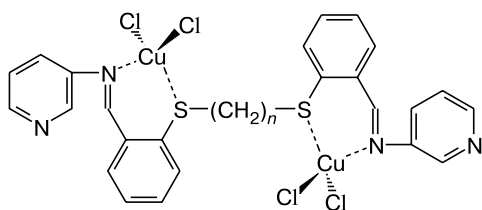
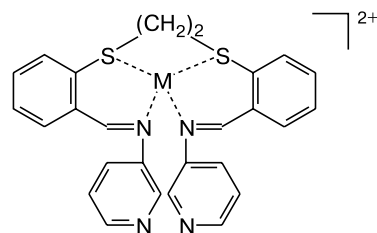
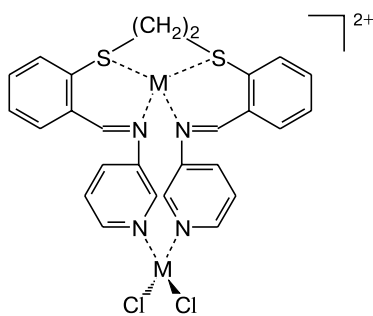
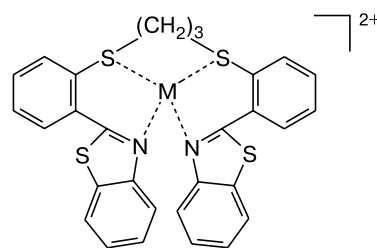
Based on the spectroscopic data, the data published in the literature, and the results of electrochemical studies

(see below), the following structures of the resulting complexes can be suggested:

**Electrochemical study.** Ligands **4–8** and complexes **10–18** were studied by cyclic voltammetry (CV) and rotating disk electrode (RDE) voltammetry at glassy-carbon (GC), Pt, and Au electrodes in anhydrous DMF in the presence of  $Bu_4NClO_4$  ( $0.05 \text{ mol L}^{-1}$ ) in DMF. The electrochemical oxidation and reduction potentials measured relative to  $Ag/AgCl/KCl(\text{satur.})$  are given in Table 5. The cyclic voltammograms (CV curves) are shown in Fig. 2.

The oxidation of compounds **4–6** is a one-step process. The oxidation of compounds **7** and **8** proceeds in two steps. The reduction proceeds in three steps, the first step being a two-electron process (see Fig. 2, *a* and Table 5). The first step of electrochemical reduction of compounds **4** and **7** proceeds at less negative potentials compared to that of compounds **5**, **6**, and **8** containing the sulfide fragments instead of the disulfide fragment.

The semiempirical calculations by the PM3 method showed that the orbitals of the imine fragments make the major contribution to LUMO of ligands **5**, **6**, **8**, and **9**, and HOMO are located primarily on the sulfur atoms. By contrast, both HOMO and LUMO are located on the sulfur atoms of the disulfide fragment in ligands **4** and **7** (Fig. 3). The calculations demonstrated that the second electron should bind to the disulfide fragment in ligands **4** and **7** and to the imine fragment in ligands **5**, **6**, and **8**. In addition, according to the calculated data, the electroreduction of disulfide ligands **4** and **7** should proceed more readily than that of bis-sulfide ligands **5** and **8**, which is consistent with the experimental data. There-

**10, 16****11, 13–15****12****17, 18**

**Table 5.** Electrochemical reduction potentials ( $E^{\text{Red}}$ ) and oxidation potentials ( $E^{\text{Ox}}$ ) of compounds **4–18** measured by the CV method ( $E_p$  is the peak potential) and the RDE method ( $E_{1/2}$  is the half-wave potential) at a glassy carbon electrode (DMF, 0.05 M Bu<sub>4</sub>NClO<sub>4</sub> solution) relative to Ag/AgCl/KCl(satur.)

Compound	$E_p^{\text{Red}}$	$E_{1/2}^{\text{Red}}$	$E_p^{\text{Ox}}$	$E_{1/2}^{\text{Ox}}$
	V			
<b>4</b>	-1.10, -1.63, <sup>a</sup> -2.16	-1.06 (2), -1.78, -2.30 (2)	1.08, 1.33	1.13 (2), 1.40
<b>5</b>	-1.64, -2.12, -2.45	-1.62 (2), -2.20, -2.76	1.35, 1.54	1.20 (2), 1.48 (2)
<b>6</b>	-1.63, -2.01, -2.58	-1.59 (2), -2.07 (2), -2.63	1.34, 1.45	1.20 (2), 1.50 (2)
<b>7</b>	-1.09/0.06, -1.70, <sup>a</sup> -2.50	-1.07 (2), -2.52	1.39, 1.52	1.43 (2)
<b>8</b>	-1.82, -2.37/-0.16, -2.56	-1.81 (2), -2.54 (4)	1.47	1.61 (2)
<b>10</b>	0.42/0.52, <sup>b</sup> -0.52, <sup>c</sup> -1.25, -1.70, <sup>a</sup> -1.90, -2.13, -2.51	0.46 (2), <sup>b</sup> -0.36 (1), -1.07 (2), -1.43, -1.96 (2), -2.22	1.16	1.40 (2)
<b>11</b>	-1.34/0.47, -1.63, -2.50	-1.35, <sup>d</sup> -1.73	1.13	1.10 (2)
<b>12</b>	-1.34/-0.06, -2.28	—	1.24 1.42	—
<b>13</b>	-1.25/-0.02, -1.61, -2.43	-1.17 (2), -2.27 (2)	1.13	1.12 (2)
<b>14</b>	-1.23, -1.60, -2.48	-1.23, -1.70, -2.39	1.12, 1.46, <sup>a</sup> -2.39	1.15 (2), 1.68 (2)
<b>15</b>	0.08/0.30, <sup>b</sup> -0.92/0.07, -1.66	0.10 (1), <sup>b</sup> -0.65 (1), -1.83 <sup>d</sup>	1.12, 1.32	1.10 (2), 1.32 (2)
<b>16</b>	0.38/0.56, <sup>b</sup> 0.04, -0.41, <sup>c</sup> -1.62, -2.07, <sup>a</sup> -2.68	0.32 (1), <sup>b</sup> 0.07 (1), -0.80, -1.62	1.22	1.18 (2), 1.48
<b>17</b>	0.44/0.56, <sup>b</sup> -1.83, -2.31/-1.07	0.58 (1), <sup>b</sup> -0.66 (1), -1.83 <sup>d</sup>	1.04, 1.32	1.14 (2), 1.46 (2)
<b>18</b>	0.11/0.40, <sup>b</sup> -1.41, <sup>a</sup> -1.93	0.12 (1), <sup>b</sup> -0.68 (1), -1.86 <sup>d</sup>	1.04, 1.26,	1.05(2)

*Note.* The peak potentials on the reverse scan of the CV curves are given after the slash; the number of electrons transferred in this step is given in parentheses.

<sup>a</sup> The low-intensity peak.

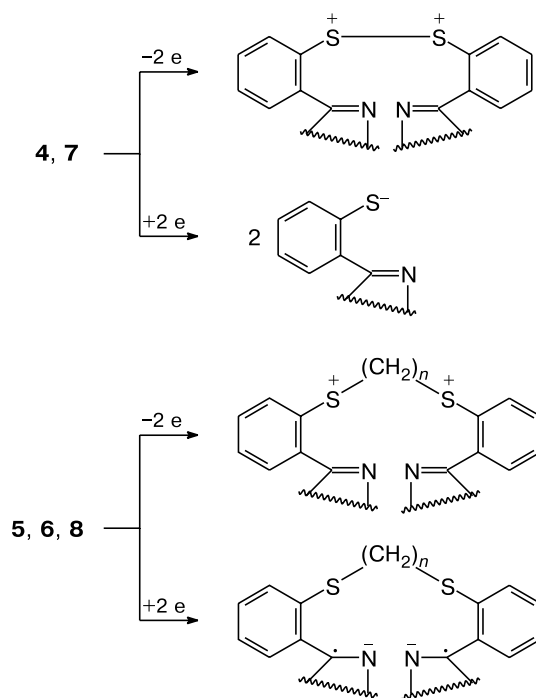
<sup>b</sup> The initial scan potential was 0.7 V.

<sup>c</sup> The peak is weakly pronounced and is not always reproducible.

<sup>d</sup> In the RDE experiments, the electrode processes are complicated by the adsorption of the starting complex, resulting in the surface modification, which is manifested in a decrease in the current. Because of this, it was impossible to determine the number of transferred electrons.

fore, the following mechanism of electrooxidation and electroreduction of ligands **4–9** can be suggested (Scheme 3).

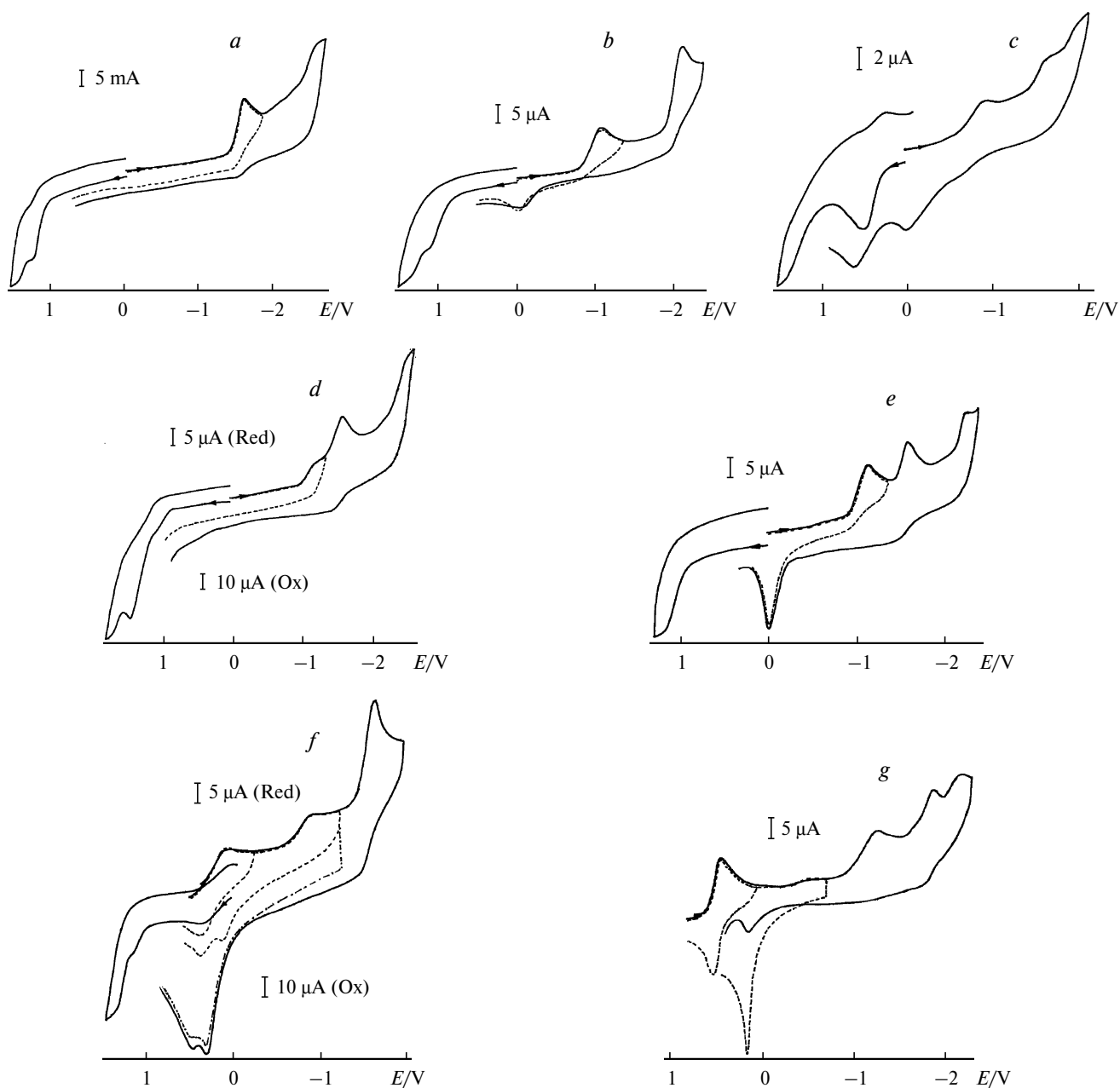
**Scheme 3**



Reoxidation peaks are observed on the reverse scan of the CV curves of ligands **4** and **7** in solution after the first cathodic peaks at nearly zero potentials (see Table 5 and Fig. 2, b). This corresponds to the oxidation potentials of the thiolate ion. This fact additionally confirms the proposed mechanism of two-electron electroreduction, the first step of which proceeds, apparently, at the sulfur atoms.

The further reduction of ligands **4** and **7** at the imine fragment proceeds at more negative potentials compared to the first cathodic potentials of ligands **5**, **6**, and **8** (based on our earlier data,<sup>5</sup> these ligands should be initially reduced at the imine fragment). The shift of the electroreduction potentials to the cathodic region can be attributed to the fact that the first step affords thiolate ions, in which the negatively charged sulfur atoms are conjugated with the imine fragments hindering the reduction.

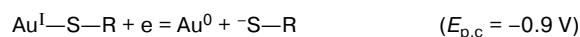
In the case of ligands **5**, **6**, and **8**, the dianion that is formed as a result of the addition of two electrons to two imine fragments, apparently, undergoes protonation with the solvent to form a product containing the amino group. The formation of amine is confirmed by the appearance of the anodic peak at +1.12 V on the reverse scan of the voltammograms after the first cathodic peak of electroreduction of the ligands.<sup>5</sup>

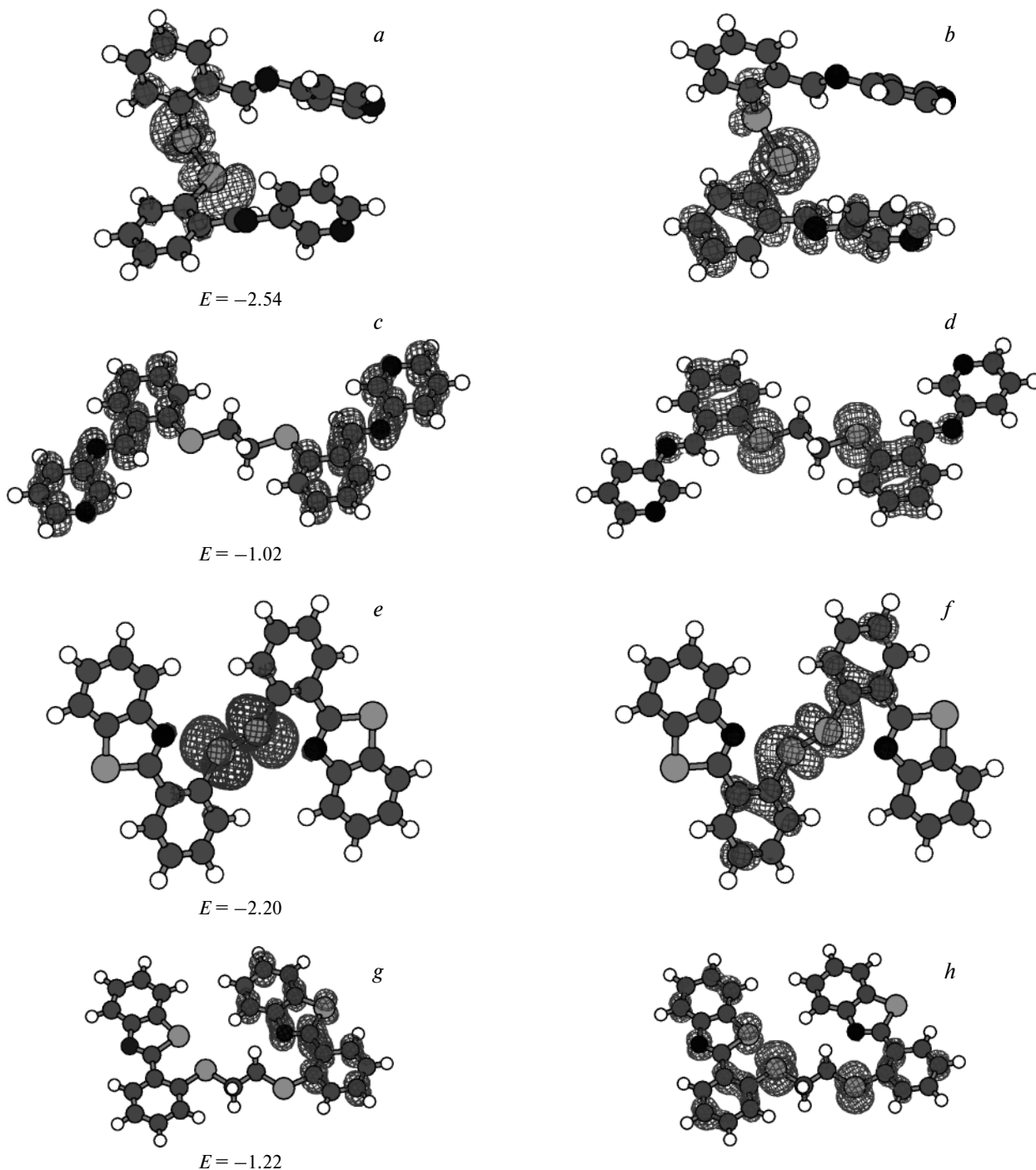


**Fig. 2.** Cyclic voltammograms of compounds **6** (a), **4** (b, c), **14** (d), **13** (e), **15** (f), and **10** (g) at a glassy-carbon electrode (a, b, d–g) and an Au electrode (c) (DMF,  $C = 10^{-3} \text{ mol L}^{-1}$ ,  $0.1 \text{ M Bu}_4\text{NClO}_4$  solution).

As compared to the processes at glassy-carbon and Pt electrodes, the redox processes at an Au electrode for ligands **4** and **7** are characterized by the appearance of an additional cathodic peak already on the first scan at  $E_{p,c} \approx -0.9 \text{ V}$ , which corresponds to the reduction of the Au<sup>I</sup>–S bond that is formed as a result of chemisorption of the disulfide groups of the substrates on the electrode surface.<sup>17–19</sup> To confirm this fact, the Au electrode was kept in a solution of ligand **4** or **7** ( $C = 10^{-3} \text{ mol L}^{-1}$ ) for 20 h, washed with acetone, and dried. After this treatment, the electrode was placed in the pure supporting electrolyte.

For ligands **4** and **7**, the electroreduction peak of the Au<sup>I</sup>–S bond ( $E_{p,c} \approx -0.9 \text{ V}$ ) was observed on the CV curves, whereas the reduction peak of the disulfide bond ( $E_{p,c} \approx 1.10 \text{ V}$ ) was completely absent. During the reverse potential scan, the reoxidation peak of the thiolate anion at  $E_{p,a} = -0.03 \text{ V}$  was observed after the reduction peak of the Au<sup>I</sup>–S bond (see Table 5 and Fig. 2, c).





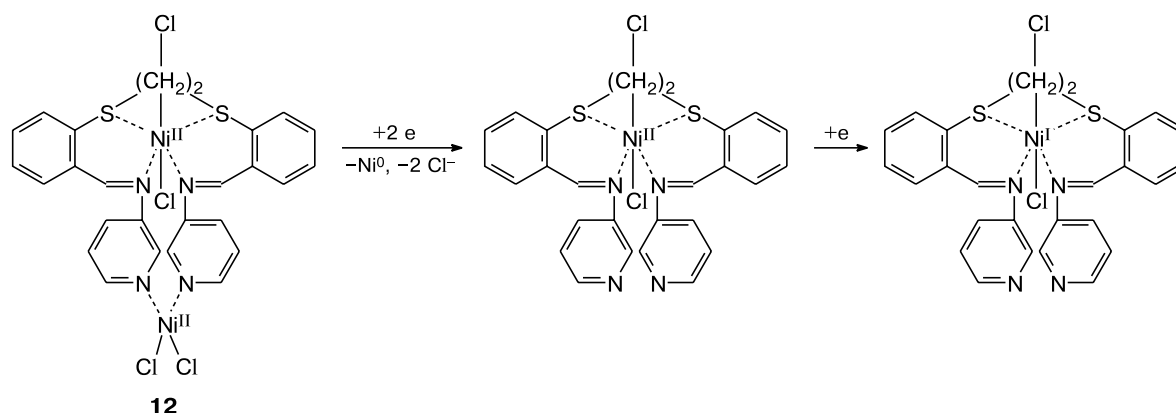
**Fig. 3.** Frontier orbitals of compounds **4** (*a, b*), **5** (*c, d*), **7** (*e, f*), and **8** (*g, h*) calculated by the PM3 method: LUMO (*a, c, e, g*) and HOMO (*b, d, f, h*). The figure also gives the energies of LUMO/eV.

The absence of the peak at  $\sim 1.10$  V on the voltammogram, and the presence of this peak in the case of reduction of ligands **4** and **7** in solution confirm that this peak corresponds to the reduction of the S—S bond.

As compared to the electroreduction of the free ligand, the CV curve of a solution of cobalt-containing complex **14** shows an additional peak in the cathodic region at

$E_p^{\text{Red}} = -1.23$  V (see Table 5 and Fig. 2, *d*). This peak, apparently, corresponds to the  $M^{\text{II}} \rightarrow M^{\text{I}}$  transition. On the reverse scan of the voltammogram for this chlorine-containing complex, a peak of oxidative desorption of cobalt metal from the electrode surface was not observed even after performing the electrolysis for 1 min. Reduced  $\text{Co}^{\text{I}}$  is evidently held by the tetradentate ligand, as

Scheme 4



was described for cyclam,<sup>20</sup> pyridyl-substituted benzo-thiazoles,<sup>16</sup> and iminosulfide<sup>5</sup> complexes.

In mononuclear Ni<sup>II</sup> (**11**) and Co<sup>II</sup> (**13**) complexes containing perchlorate ions, the metal atom is also, apparently, reduced; however, as opposed to complex **14**, the redox reaction of these complexes is a two-electron process, resulting in the decomposition of the complexes to form zero-valent metal (this is confirmed by the appearance of the peak of oxidative desorption of metal from the electrode surface on the CV curve during the reverse potential scan; see Table 5 and Fig. 2, *e*). Two subsequent cathodic peaks on the CV curves are associated with the reduction of the ligands.

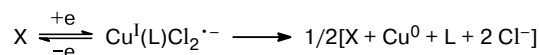
The cathodic branch of the CV curve of dinuclear complex **12** in solution has, in addition to peaks corresponding to the reduction of the ligand, two closely spaced cathodic peaks belonging, apparently, to the reduction of two nickel atoms. On the reverse scan of the CV curve, an intense peak of oxidative desorption of Ni<sup>0</sup> was observed after the first of these peaks; however, after the potential of the second peak, the intensity of the desorption peak unexpectedly sharply decreased and remained low even after performing the electrolysis for 1 min. This fact confirms the suggestion that two nickel atoms in complex **12** are in the different ligand environment. Apparently, the electroreduction of complex **12** involves the two-electron reduction of the nickel ion coordinated by the pyridine nitrogen atoms followed by elimination of nickel. On the contrary, the electroreduction of another nickel ion coordinated to four donor atoms of the ligand occurs without a loss of metal by analogy with compound **14** (Scheme 4).

The electroreduction of the copper ion in copper-containing mononuclear complexes **15**, **17**, and **18** proceeds in two successive one-electron steps: Cu<sup>II</sup> → Cu<sup>I</sup> → Cu<sup>0</sup> (see Table 5 and Fig. 2, *f*). The desorption peak indicative of the decomposition of the complex is observed only after the second redox transition Cu<sup>I</sup> → Cu<sup>0</sup>. It should be noted that mononuclear copper complexes containing

chloride ions as counterions are reduced ~300 mV easier than their perchlorate-containing analogs.

The electrochemical reduction of Cu<sup>II</sup> in these complexes at Pt and Au electrodes also involves two steps, but the second cathodic peak is less intense compared to the first peak. This fact can be attributed to the faster disproportionation of Cu<sup>I</sup> in the complex that is formed in the first step of electroreduction at metal electrodes compared to the process at a glassy-carbon electrode. The disproportionation of Cu<sup>I</sup> at Pt and Au electrodes is confirmed by the presence of a desorption peak on the reverse scan of the voltammogram after the potential of the first cathodic peak.<sup>5</sup> Apparently, the Cu<sup>I</sup> compound that is formed in the first step of electroreduction is stable under experimental conditions at a glassy-carbon electrode, whereas this compound is decomposed in experiments at metal electrodes to give copper metal (Scheme 5).

Scheme 5



X = **15**, **17**, **18**; L = **6**, **9**

The CV curves of dinuclear copper complexes **10** and **16** in solution show only one quasireversible transition at ~0.4 V corresponding to the Cu<sup>II</sup> → Cu<sup>I</sup> transition. The observed two-electron transfer in this step suggests the simultaneous one-electron reduction of both metal centers. The resulting intermediate containing two Cu<sup>I</sup> ions is, apparently, poorly soluble, due to which the intensity of its reduction peak is low; however, the desorption peak of Cu<sup>0</sup> is observed on the reverse scan after the potential of this peak (see Table 5 and Fig. 2, *g*). Evidently, these complexes have a symmetrical structure and contain copper ions in the identical ligand environment, such that interactions between the copper ions are impossible because of the absence of conjugation between two coordi-



nating NS-type fragments. As a result, the redox processes proceed independently and simultaneously with the involvement of two copper atoms at the same potential.

From all the aforesaid, it can be concluded that in the first step, the mononuclear  $\text{Co}^{\text{II}}$  and  $\text{Ni}^{\text{II}}$  complexes with chloride ions undergo one-electron reduction to give stable  $\text{M}^{\text{I}}$ -containing intermediates. Analogous complexes with perchlorate ions undergo two-electron reduction accompanied by decomposition of the complexes to give free ligands and metal. This difference in the electrochemical behavior of complexes with  $\text{Cl}^-$  and  $\text{ClO}_4^-$  ions can be attributed to the difference in the structure of the complexes. The nucleophilic chloride anion is, apparently, coordinated to the metal ions, thus stabilizing the initial electroreduction product, whereas the non-nucleophilic perchlorate anion is not coordinated directly to the metal ion and the resulting initial reduction product is unstable and immediately undergoes further reduction. Dinuclear chloride-containing complex **12** with two non-identical  $\text{Ni}^{\text{II}}$  ions undergoes two-electron reduction accompanied by elimination of one of the nickel atoms as  $\text{Ni}^0$ . The further reduction proceeds analogously to that of the corresponding mononuclear complexes (**11**, **13**, and **14**). All mononuclear copper-containing complexes (**15**, **17**, and **18**) are successively reduced in two one-electron steps. After the second redox transition, the complexes are decomposed to give  $\text{Cu}^0$  and the free ligand. In dinuclear copper-containing complexes **10** and **16**, the electroreduction of two metal centers proceeds independently at the same potential.

The further reduction of all complexes proceeds at the ligand fragment.

Therefore, of all the compounds under consideration, complexes **11**, **13**, and **14** containing  $\text{Co}^{\text{II}}$  or  $\text{Ni}^{\text{II}}$  ions and chloride anions are most promising for further investigations as catalysts for electrochemically induced alkylation reactions. These compounds undergo one-electron reduction to give  $\text{M}^{\text{I}}$ -containing stable intermediates, which can react with  $\text{AlkX}$  to give  $\text{M}^{\text{III}}$  compounds followed by the transfer of the alkyl groups to different types of substrates.<sup>21</sup>

## Experimental

The  $^1\text{H}$  NMR spectra were recorded on a Varian-XR-400 instrument (400 MHz) in  $\text{CDCl}_3$ . The IR spectra were measured on an UR-20 instrument in films or Nujol mulls. The EI mass spectra were obtained on a JMS-D300 mass spectrometer (direct inlet, the ion source temperature was 150 °C, the ionizing electron energy was 70 eV, the accelerating voltage was 3 kV).

Quantum chemical calculations were carried out by the semiempirical SCF PM3 method,<sup>22</sup> which was extended by including the parameters for all first-row transition metals and selected second- and third-row metals. The geometry optimiza-

tion of the molecules was performed with a specified convergence gradient of at most  $10 \text{ kcal } \text{Å}^{-1} \text{ mol}^{-1}$ .

Electrochemical studies were carried out on a PI-50-1.1 potentiostat equipped with a PR-8 programmer. Glassy-carbon ( $d = 2 \text{ mm}$ ), platinum ( $d = 3 \text{ mm}$ ), or gold ( $d = 2 \text{ mm}$ ) disks were used as the working electrodes; a 0.05 M  $\text{Bu}_4\text{NClO}_4$  solution in DMF served as the supporting electrolyte;  $\text{Ag}/\text{AgCl}/\text{KCl}(\text{satur.})$  was used as the reference electrode; a Pt plate was used as an auxiliary electrode. The potentials are given taking into account the  $iR$  compensation. The potential scan rates were 200 (CV method) and  $20 \text{ mV s}^{-1}$  (RDE method). The numbers of electrons transferred in redox processes were determined by comparing the limiting wave current in experiments at an RDE with the current of one-electron oxidation of ferrocene at an equal concentration.

All measurements were carried out under dry argon. The samples were dissolved in a pre-deaerated solvent. Dimethylformamide (high-purity grade) was purified by stirring over freshly calcined  $\text{K}_2\text{CO}_3$  for four days followed by vacuum distillation successively over  $\text{P}_2\text{O}_5$  and  $\text{CuSO}_4$ .

**2,2'-Dithiobenzaldehyde (1).** *o*-(*tert*-Butylthio)benzaldehyde (which was synthesized according to a known procedure<sup>23</sup>) (7.26 g, 37 mmol), glacial acetic acid (20 mL), and concentrated HBr (20 mL) were placed in a round-bottom flask. Then DMSO (2.63 mL, 2.89 g, 37 mmol) was added dropwise with stirring, the reaction mixture was stirred for 5 h, and cold water (50 mL) was added. The precipitate that formed was filtered off and recrystallized from MeOH. Compound **1** was obtained in a yield of 3.55 g (70%) as pale-yellow crystals, m.p. 148 °C (*cf.* lit. data<sup>24</sup>: m.p. 145 °C).  $^1\text{H}$  NMR ( $\text{CDCl}_3$ ),  $\delta$ : 10.24 (s, 2 H); 7.89 (d, 2 H,  $J = 6.6 \text{ Hz}$ ); 7.79 (d, 2 H,  $J = 8.1 \text{ Hz}$ ); 7.51 (t, 2 H,  $J = 7.1 \text{ Hz}$ ); 7.40 (t, 2 H,  $J = 7.3 \text{ Hz}$ ).

**1,2-Bis(2-formylphenylthio)ethane (2).** *o*-Nitrobenzaldehyde (9.06 g, 60 mmol) and ethane-1,2-dithiol (2.51 mL, 2.82 g, 30 mmol) were dissolved with stirring in DMF (75 mL). Finely dispersed potassium carbonate (9 g) was added, and the reaction mixture was stirred at 60 °C for 27 h. The hot solution was filtered and cooled. Then EtOH (60 mL) was added. The precipitate that formed was filtered off and recrystallized from EtOH. Compound **2** was obtained in a yield of 5.83 g (64%), m.p. 134 °C (*cf.* lit. data<sup>25</sup>: m.p. 133 °C).  $^1\text{H}$  NMR ( $\text{CDCl}_3$ ),  $\delta$ : 10.40 (s, 2 H); 7.87 (d, 2 H,  $J = 7.8 \text{ Hz}$ ); 7.53 (t, 2 H,  $J = 7.6 \text{ Hz}$ ); 7.37 (m, 4 H,  $J = 5.1 \text{ Hz}$ ); 3.21 (s, 4 H).

**1,3-Bis(2-formylphenylthio)propane (3).** *o*-Nitrobenzaldehyde (12.08 g, 80 mmol) and propane-1,3-dithiol (4.04 mL, 4.32 g, 40 mmol) were dissolved with stirring in DMF (100 mL). Finely dispersed potassium carbonate (12 g) was added, and the reaction mixture was stirred at 60 °C for 27 h. The hot solution was filtered and cooled. Then EtOH (60 mL) was added. The precipitate that formed was filtered off and recrystallized from EtOH. Compound **3** was obtained in a yield of 9.19 g (73%), m.p. 51–53 °C (*cf.* lit. data<sup>26</sup>: m.p. 54–56 °C).  $^1\text{H}$  NMR ( $\text{CDCl}_3$ ),  $\delta$ : 10.38 (s, 2 H); 7.86 (d, 2 H,  $J = 7.6 \text{ Hz}$ ); 7.53 (dt, 2 H,  $J = 7.2 \text{ Hz}$ ,  $J = 7.5 \text{ Hz}$ ); 7.43 (d, 2 H,  $J = 7.8 \text{ Hz}$ ); 7.34 (t, 2 H,  $J = 7.4 \text{ Hz}$ ); 3.15 (t, 4 H,  $J = 7.0 \text{ Hz}$ ); 2.12 (q, 2 H,  $J = 7.0 \text{ Hz}$ ).

**Bis[2-(3-pyridyliminomethyl)phenyl] disulfide (4).** 2,2'-Dithiobenzaldehyde (**1**) (274 mg, 1 mmol) and 3-aminopyridine (188 mg, 2 mmol) were dissolved in EtOH (15 mL). The reaction mixture was refluxed for 15 h and filtered. The solvent was distilled off. A brown oil was obtained in a yield of 347 mg (81%).

$^1\text{H}$  NMR ( $\text{CDCl}_3$ ),  $\delta$ : 8.77 (s, 2 H); 8.47 (m, 4 H); 7.92 (d, 2 H,  $J = 7.3$  Hz); 7.78 (d, 2 H,  $J = 7.6$  Hz); 7.50 (d, 2 H,  $J = 8.1$  Hz); 7.35 (m, 6 H).

**2,2'-[Ethane-1,2-diylbis(thio)]bis[*N*-(3-pyridyl)benzaldimine] (5).** Compound **2** (906 mg, 3 mmol) and 3-aminopyridine (564 mg, 6 mmol) were dissolved in EtOH (15 mL). The reaction mixture was refluxed for 15 h and filtered. The solvent was distilled off. A brown oil was obtained in a yield of 1 g (73%).  $^1\text{H}$  NMR ( $\text{CDCl}_3$ ),  $\delta$ : 8.99 and 9.00 (both s, 2 H); 8.46 (m, 4 H); 8.12 (d, 2 H,  $J = 7.7$  Hz); 7.47 (d, 2 H,  $J = 7.9$  Hz); 7.30 (m, 8 H); 3.07 and 3.03 (both d, 4 H,  $J = 2.5$  Hz).

**2,2'-[Propane-1,3-diylbis(thio)]bis[*N*-(3-pyridyl)benzaldimine] (6).** Compound **3** (948 mg, 3 mmol) and 3-aminopyridine (564 mg, 6 mmol) were dissolved in EtOH (15 mL). The reaction mixture was refluxed for 15 h and filtered. The solvent was distilled off. A brown oil was obtained in a yield of 980 mg (70%).  $^1\text{H}$  NMR ( $\text{CDCl}_3$ ),  $\delta$ : 9.02 and 9.01 (both s, 2 H); 8.49 (m, 4 H); 8.12 and 7.50 (both m, 2 H each); 7.34 (m, 8 H); 3.03 and 3.02 (both t, 4 H,  $J = 7.0$  Hz); 1.93 (m, 2 H). MS,  $m/z$  ( $I_{\text{rel}}$  (%)): 467 [ $\text{M} - \text{H}$ ] $^+$  (2.5), 161 (57.0), 149 (43.0), 137 (100.0), 109 (79.7).

**Bis[2-(2-benzothiazolyl)phenyl] disulfide (7).** A mixture of 2,2'-dithiobenzaldehyde (**1**) (274 mg, 1 mmol) and 2-aminothiophenol (0.216 mL, 250 mg, 2 mmol) was refluxed in EtOH (15 mL) in the presence of glacial acetic acid (0.5 mL) for 15 h. The precipitate that formed was filtered off and dried in air. A pale-yellow powder was obtained in a yield of 404 mg (84%), m.p. 202 °C. Found (%): C, 64.55; H, 3.35; N, 5.70.  $\text{C}_{26}\text{H}_{16}\text{N}_2\text{S}_4$ . Calculated (%): C, 64.46; H, 3.31; N, 5.79.  $^1\text{H}$  NMR ( $\text{CDCl}_3$ ),  $\delta$ : 8.17 and 7.97 (both d, 2 H each,  $J = 7.9$  Hz); 7.93 (dd, 2 H,  $J_1 = 0.9$  Hz,  $J_2 = 7.9$  Hz); 7.87 (dd, 2 H,  $J_1 = 1.3$  Hz,  $J_2 = 7.7$  Hz); 7.55 (dt, 2 H,  $J_1 = 1.1$  Hz,  $J_2 = 7.6$  Hz); 7.46 (dt, 2 H,  $J_1 = 1.1$  Hz,  $J_2 = 7.5$  Hz); 7.39 (dt, 2 H,  $J_1 = 1.5$  Hz,  $J_2 = 7.2$  Hz); 7.33 (dt, 2 H,  $J_1 = 1.3$  Hz,  $J_2 = 7.5$  Hz).

**2,2'-[Ethane-1,2-diylbis(thio-2,1-phenylene)]bis(1,3-benzothiazole) (8).** Compound **2** (604 mg, 2 mmol) and 2-aminothiophenol (0.431 mL, 500 mg, 4 mmol) were refluxed in EtOH (15 mL) in the presence of glacial acetic acid (0.5 mL) for 15 h. The precipitate that formed was filtered off and dried in air. A yellow powder was obtained in a yield of 715 mg (70%), m.p. 128 °C. Found (%): C, 65.50; H, 3.70; N, 5.40.  $\text{C}_{28}\text{H}_{20}\text{N}_2\text{S}_4$ . Calculated (%): C, 65.36; H, 3.91; N, 5.47.  $^1\text{H}$  NMR ( $\text{CDCl}_3$ ),  $\delta$ : 8.13 (d, 2 H,  $J = 8.0$  Hz); 7.99 (dd, 2 H,  $J_1 = 1.8$  Hz,  $J_2 = 8.1$  Hz); 7.93 (d, 2 H,  $J = 8.0$  Hz); 7.53 (t, 2 H,  $J = 7.4$  Hz); 7.40 (m, 8 H); 3.10 (s, 4 H).

**2,2'-[Propane-1,3-diylbis(thio-2,1-phenylene)]bis(1,3-benzothiazole) (9).** Compound **3** (316 mg, 1 mmol) and 2-aminothiophenol (0.216 mL, 250 mg, 2 mmol) were refluxed in EtOH (15 mL) in the presence of glacial acetic acid (0.5 mL) for 15 h. The reaction solution was passed through a silica gel filter column ( $h = 3$  cm), and the solvent was distilled off. A brown oil was obtained in a yield of 0.28 g (52%).  $^1\text{H}$  NMR ( $\text{CDCl}_3$ ),  $\delta$ : 8.13 (d, 2 H,  $J = 8.0$  Hz); 7.99 (dd, 2 H,  $J_1 = 1.8$  Hz,  $J_2 = 8.1$  Hz); 7.93 (d, 2 H,  $J = 8.0$  Hz); 7.53 (t, 2 H,  $J = 7.4$  Hz); 7.40 (m, 8 H); 3.10 (s, 4 H).

**Synthesis of the complexes (general procedure A).** A solution of the corresponding metal salt (0.02 mmol) in EtOH (1 mL) was added to a solution of ligand **4–9** (0.02 mmol) in EtOH (3–4 mL). The reaction mixture was refluxed for 15 h and then cooled to  $-18$  °C. The precipitate was filtered off, washed with  $\text{Et}_2\text{O}$ , and dried in air.

**General procedure B.** A solution of the corresponding metal salt (0.02 mmol) in EtOH (1 mL) was slowly added along the wall of the vessel to a solution of ligand **4–9** (0.02 mmol) in  $\text{CHCl}_3$  (1 mL) in such a way as to obtain a two-phase system. The vessel with the reaction mixture was tightly closed and kept until crystals formed. The precipitate was filtered off, washed with  $\text{Et}_2\text{O}$ , and dried in air.

**Tetrachloro[bis[2-(3-pyridyliminomethyl)phenyl]disulfide]dicopper(II) (10)** was synthesized according to the method **A**. The yield was 70%. Found (%): C, 42.57; H, 3.90; N, 8.20.  $\text{C}_{26}\text{H}_{24}\text{Cl}_4\text{Cu}_2\text{N}_4\text{OS}_2$ . Calculated (%): C, 42.11; H, 3.24; N, 7.56.

**{2,2'-[Ethane-1,2-diylbis(thio)]bis[*N*-(3-pyridyl)benzaldimine]}nickel(II) diperchlorate (11)** was synthesized according to the method **B**. The yield was 34%. Found (%): C, 39.30; H, 3.90; N, 7.05.  $\text{C}_{26}\text{H}_{30}\text{Cl}_2\text{N}_4\text{NiO}_{12}\text{S}_2$ . Calculated (%): C, 39.80; H, 3.83; N, 7.14.

**Dichloro{2,2'-[ethane-1,2-diylbis(thio)]bis[*N*-(3-pyridyl)benzaldimine]}dinickel(II) (12)** was synthesized according to the method **B**. The yield was 83%. Found (%): C, 43.73; H, 3.96; N, 7.81.  $\text{C}_{28}\text{H}_{28}\text{Cl}_4\text{N}_4\text{Ni}_2\text{OS}_2$ . Calculated (%): C, 44.21; H, 3.68; N, 7.37.

**{2,2'-[Ethane-1,2-diylbis(thio)]bis[*N*-(3-pyridyl)benzaldimine]}cobalt(II) diperchlorate (13)** was synthesized according to the method **B**. The yield was 65%. Found (%): C, 39.10; H, 3.35; N, 7.57.  $\text{C}_{26}\text{H}_{30}\text{Cl}_2\text{CoN}_4\text{O}_{12}\text{S}_2$ . Calculated (%): C, 39.80; H, 3.83; N, 7.14.

**Dichloro{2,2'-[ethane-1,2-diylbis(thio)]bis[*N*-(3-pyridyl)benzaldimine]}cobalt(II) (14)** was synthesized according to the method **B**. The yield was 65%. Found (%): C, 50.30; H, 3.84; N, 9.21.  $\text{C}_{26}\text{H}_{26}\text{Cl}_2\text{N}_4\text{NiO}_2\text{S}_2$ . Calculated (%): C, 50.32; H, 4.19; N, 9.03.

**{2,2'-[Propane-1,3-diylbis(thio)]bis[*N*-(3-pyridyl)benzaldimine]}copper(II) diperchlorate (15)** was synthesized according to the method **B**. The yield was 92%. Found (%): C, 44.48; H, 3.50; N, 7.81.  $\text{C}_{27}\text{H}_{24}\text{Cl}_2\text{CuN}_4\text{O}_8\text{S}_2$ . Calculated (%): C, 44.35; H, 3.29; N, 7.67.

**{2,2'-[Propane-1,3-diylbis(thio)]bis[*N*-(3-pyridyl)benzaldimine]}copper(II) diperchlorate (16)** was synthesized according to the method **B**. The yield was 56%. Found (%): C, 44.69; H, 3.53; N, 8.01.  $\text{C}_{29}\text{H}_{30}\text{Cl}_4\text{Cu}_2\text{N}_4\text{OS}_2$ . Calculated (%): C, 44.44; H, 3.83; N, 7.15.

**Dichloro{2,2'-[propane-1,3-diylbis(thio-2,1-phenylene)]bis(1,3-benzothiazole)}copper(II) (17)** was synthesized according to the method **A**. The yield was 85%. Found (%): C, 52.16; H, 3.92; N, 4.32.  $\text{C}_{29}\text{H}_{26}\text{Cl}_2\text{CuN}_2\text{S}_4$ . Calculated (%): C, 52.37; H, 3.91; N, 4.21.

**{2,2'-[Propane-1,3-diylbis(thio-2,1-phenylene)]bis(1,3-benzothiazole)}copper(II) diperchlorate (18) A.** The yield was 85%. Found (%): C, 43.99; H, 2.91; N, 3.72.  $\text{C}_{29}\text{H}_{26}\text{Cl}_2\text{CuN}_2\text{S}_4$ . Calculated (%): C, 43.88; H, 2.77; N, 3.79.

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