Tetradentate diamido-bis-sulfide ligands on the base of *o*-aminobenzenethiol and their complexation with Ni^{II}, Co^{II}, Cu^{II} chlorides in DMF solution and on the gold electrode surface

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A series of cyclic and acyclic diamido-bis-sulfide ligands were synthesized by N-acylation of 1,2-bis(2-aminophenylthio)ethane and 1,4-bis(2-aminophenylthio)butane with acetic, malonic, and 3,3'-dithiodipropionic acid chlorides or esters. The complexation of obtained ligands with Cu^{II}, Ni^{II}, and Co^{II} salts in solution and on the gold electrode surface was studied. The formation of complexes of these ligands with copper(II) chloride in DMF is irreversible and accompanied by deprotonation of the amide nitrogen atoms.

Key words: copper(II) complexes, amides, sulfides, N₂S₂ ligands, electrochemistry.

Transition metal complexes, such as Ni^{II}, Cu^{II}, and Co^{II} complexes, with organic N.S-containing ligands are extensively studied as electroactive catalysts and models of metalloenzymes.¹⁻³ Low-molecular-weight nickel, cobalt, and copper copmlexes are used as catalysts of various organic reactions, including asymmetric synthesis, alkene epoxidation,⁴⁻⁶ cyclopropanation,⁷ aziridination,⁸ sulfide oxidation,^{9,10} the Diels-Alder reactions,¹¹ C-H bond activation,^{12–14} epoxide ring opening.^{15–19} Such complexes were studied²⁰ as catalysts for electrochemical reduction of organic halides. In recent years, the problem of Freon utilization²¹ attracts considerable attention and, therefore, the possibility of using nickel complexes with organic N₂S₂-ligands for electrocatalytic reduction of polyfluorochloroalkanes is of interest.²² Thus, the synthesis of novel N,S-containing organic ligands and their complexes with transition metals, as well as studies of their redox properties seem to be a topical problem.

Results and Discussion

Acylation of diamines 1 and 2 with acid chlorides and esters of carboxylic and dicarboxylic acids affords diamidobis-sulfide ligands 3-6 (Schemes 1-3).

Resinification occurs in the synthesis of macrocyclic ligand **4** by acylation with malonyl dichloride. Therefore, an alternative procedure was used, *viz*., the reaction of diamine **1** with dimethyl malonate in diphenyl ether (see Scheme 2).



Macrocyclic diamido-bis-sulfides 5 and 6 containing a disulfide fragment were prepared from 3,3'-dithiodi(propionyl chloride) 7 and diamines 1 and 2 (see Scheme 3).

Additional disulfide groups were introduced into compounds 5, 6 in order to ensure their chemisorption and of their complexes on the surface of metal with high thiophilicity (*e.g.*, on the gold electrode surface). As a result, a self-assembled monolayer of an organic compound forms on the surface.^{23,24}

Compounds 3-6 do not form crystalline complexes when Ni^{II}, Co^{II}, and Cu^{II} chlorides are mixed with solu-

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n = 1 (1, 5), 3 (2, 6)

tions of ligands (or boiled) in DMF, MeCN, or EtOH. However, the complex formation is evidenced by the gradual color change during addition of the metal salt to the ligand solution, as well as by comparing the electronic absorption spectra and the results of electrochemical studies for ligands **3–6** and their mixtures with Ni^{II}, Co^{II}, and Cu^{II} salts in the ratio of 1 : 1 in DMF.

In the electronic absorption spectra of the equimolar mixtures of 3-6 with CuCl₂·6H₂O (10⁻³ mol L⁻¹, DMF solutions), the absorption bands of the initial inorganic salt completely disappeared 30 min after mixing. In the case of NiCl₂·6H₂O and CoCl₂·6H₂O, the complexation reaction in DMF is likely reversible. Even several hours after mixing the reactants, the absorption bands of the initial salts were still observed in the electronic absorption

spectra in addition to new peaks corresponding to the complex compounds. For all the complexes obtained, one band of the d-d transition at 440-445 nm ($\epsilon = 680-780 \text{ L mol}^{-1} \text{ cm}^{-1}$) is recorded in the visible spectral region.

Oxidation of ligands 3-6 (a glassy carbon electrode) proceeds in one two-electron step (Table 1). Compounds 3 and 4 are reduced in one step (Fig. 1, *a*, dashed line), whereas compounds 5 and 6 are reduced in two steps (Fig. 1, *b*, solid line). The semi-empirical quantum chemical calculations that we have performed by the PM3 method²⁵ showed that both HOMO and LUMO of ligands 3 and 4 are predominantly localized on the sulfur atom and consequently the redox processes should involve the sulfide fragments. Indeed, the values of reduction and oxidation potentials fall in the range of redox potentials which are typical of alkyl aryl sulfides.^{26a}

Compounds 5 and 6 with a disulfide group differ from ligands 3 and 4 in the values of redox potentials (see Table 1). The values of both oxidation and reduction potentials are more typical of dialkyl disulfides.^{26b} This is in agreement with the fact that, according to the computational data,

Table 1. Oxidation (E^{Ox}) and reduction potentials (E^{Red}) of ligands **3**—**6** and their complexes formed in solution (glassy carbon electrode, *A*) and on the Au electrode surface (relative to Ag|AgCl|KCl sat., DMF, 0.1 *M* Bu₄NClO₄, *B*)^{*a*}

Compound (type of experiment)	$E_{\rm p}^{{\rm Red}b}$	$E_{1/2}^{\operatorname{Red} c}$	$E_{\rm p}^{\rm Ox}$	$E_{1/2}^{Ox c}$
	V			
3 (A)	-2.48	-2.41(2)	1.47	1.46 (2)
4 (A)	-2.68	-2.60		1.52 (2)
5 (A)	-2.09	-2.14 (2)	1.40	1.41 (2)
	-2.62	-2.66		
6 (A)	-2.04	-2.10(2)	1.40	1.40 (2)
	-2.63	-2.66		
5 (<i>B</i>)	-1.83/0.32			
6 (<i>B</i>)	-1.81/0.35			
$3 + CuCl_2$	$0.36/0.45^{d}$	$0.48(1)^d$	1.33	1.32 (2)
(A)	-2.46	-2.23 (2)		
$4 + CuCl_2$	$0.40/0.56^{d}$	$0.52(1)^d$	1.33	1.25 (2)
(A)	-2.46	-2.55 (1.9)		
$6 + \mathrm{CuCl}_2$	0.40/0.56	_	1.26	_
(A)	-2.00			
	-2.70			
$5(B) + CuCl_2$	-0.84			
-	-1.93			
6 (<i>B</i>) + CuCl ₂	-0.88			
	-1.97			

^{*a*} Presented in parentheses is the number of electrons as determined by comparison with the height of the one-electone oxidation wave of ferrocene.

 ${}^{b}E_{p}^{\text{Red}}$ is the cathodic peak potential (200 mV s⁻¹)/the reverse peak potential.

^c The half-wave potentials measured by RDE (2800 rpm).

^d The initial potential is 0.7 V.



Fig. 1. Cyclic voltammograms (glassy carbon electrode, DMF, 0.1 *M* Bu₄NClO₄): (*a*) ligand **3** (dashed line) and the complex of **3** with Cu²⁺ formed in solution (solid line) at the concentration 10^{-3} mol L⁻¹; (*b*) ligand **6** on a Au- and glassy carbon electrodes (dashed and solid lines, respectively) at the concentration $5 \cdot 10^{-4}$ mol L⁻¹; (*c*) monolayers of ligand **6** on a Au electrode (dashed line) and of the complex of ligand **6** with Cu²⁺ (solid line).

both HOMO and LUMO of macrocycles **5** and **6** are localized on the sulfur atoms of the disulfide fragment. For these ligands, the abnormally strong influence of the electrode nature on the reduction potential is observed (see Table 1, Fig. 1, *b*). It was for disulfides that a similar fact has been noted previously,^{26c} it has been rationalized by specific interaction of the disulfide group with the electrode surface. Thus, one can infer that the reduction of molecules **5** and **6** proceeds initially at the difulside fragment.

The investigation of ligands **5** and **6** on an Au electrode revealed an additional, as compared with a glassy carbon and Pt electrodes, cathodic peak at $E_{\rm pc} \approx -0.9$ V, which corresponds to the reduction of the fragment Au—S (Au–S–R + e⁻ \rightarrow Au⁰ + R–S⁻)^{27–29} and suggests chemisorption of a ligand on the electrode surface to form gold thiolate (Fig. 1, *c*, dashed line).

The CV curves obtained in a pure solvent (*i.e.*, ligandfree) with an Au electrode that has been immersed into a solution of a ligand (5 or 6) for 30 min and then rinsed multiply with DMF reveal the same peaks as those observed in the CV curves obtained for ligand solutions. This fact also confirms the ligand chemisorption on the Au electrode surface to form the Au—S bond (see Table 1, Fig. 1, *c*).

In a study of interaction of ligands 3-6 with CuCl₂·6H₂O, NiCl₂·6H₂O, and CoCl₂·6H₂O in DMF in an electrochemical cell, the irreversible complexation was observed only for copper(II) chloride. The completion of complex formation (~30 min, the ligand and salt concentrations are each 10^{-3} mol L⁻¹) is evidenced by the change in the solution color and the disappearance of the peaks of the initial inorganic salt in the voltammogram. At the same time, according to the electrochemical data (see discussion below), it its the metal that is initially reduced in the complexes with the composition Cu(L - 2 H)₂ (L = 3, 4, 5, or 6), which have been formed in solution. In the first step, single-electron quasireversible reduction at the copper atom occurs at $E_{pc} \approx 0.4$ V (Scheme 4).

Scheme 4

$$Cu^{II}(L-2H)_2 = e^{-} [Cu^{I}(L-2H)_2]$$

L=3-6

The intermediate $[Cu(L - 2 H)_2]$ formed upon reduction on a glassy carbon electrode is stable in the CVA time scale. The peak of oxidative desorption of the copper metal from the electrode on the reverse scan of the CV curve is absent even after achieving the potential $E_{pc} = -2.0$ V (see Table 1, Fig. 1, *a*). At the same time, on the metal electrodes (on Pt to a lesser degree and on Au to a greater degree), an intermediate resulting from complex reduction undergoes disproportionation into a Cu^{II} compound and a complex containing Cu⁰. The latter is decomposed releasing the copper metal and, additionally, it is visually observed that copper is deposited on the electrode surface



L=**3**—6

as a black powder (see Refs 30, 31). We have noted³² such a phenomenon for copper(II) salts and coordination compounds; in particular, the reduction product of copper(II) chloride is not disproportionated on a glass carbon electrode in DMF, but it is disproportionated upon reduction on a Pt- and Au-electrodes to release copper metal.

The second cathodic peak in the CV curve (see Fig. 1, *a*, solid line) corresponds to reduction of the ligand fragment of the complex.

It is known that two types of compounds can be produced upon complexation of the amide-type ligands with the transition metal salts: the complexes with the metal ion coordinated by the neutral amide ligand^{33–35} or complexes with the covalent nitrogen—metal bond that is formed upon deprotonation of the amide nitrogen atom.^{36,37} In the case of the studied ligands, complexes of type I or II must be produced, respectively (Scheme 5).

The results of the electrochemical study of the copper(II) complexes with ligands 3-6 in DMF and on the Au electrode surface allow one to assume that the studied ligands are deprotonated during the complex formation and thereby the coordination compounds with the composition Cu(L - 2 H) are formed (see Scheme 5, type II).

For the preparation of monolayers of the Cu^{2+} complexes with ligands **5** and **6** (Scheme 6), the Au electrode with ligand adsorbed on its surface (*vide supra*) was immersed into a solution of $CuCl_2 \cdot 6H_2O$ for 1 h and then washed with solvent to remove the excess of the inorganic salt. When the voltammograms were recorded in the saltfree solution, only the peaks of copper-containing complex were observed in CV. The ligand deprotonation during the formation of the coordination compounds follows from the absence of the oxidation peaks of the chloride ions in the CV curves of the adsorbed complexes with ligands 5 and 6 (see Table 1, Fig. 1, c).

Scheme 6



For the copper(II) chloride complexes with ligands **3** and **4** that have been synthesized in DMF solution the observed CV curves are similar to those of the complexes with ligands **5** and **6**, which were obtained on the surface. For this reason, one can conclude that the copper(II) coordination compounds formed in solution and on the electrode surface have similar structures. In the CV curves, after completion of the complexation, no oxidation peaks of the chloride ions of the initial salt are observed in solution in the region of ~1.1–1.2 V.³⁸

In the anodic potential region, the oxidation wave at 1.26-1.46 V is also recorded for the complexes of ligands **3–6**. At the same time, in the preparation of complexes in the solutions containing ligand and copper(II) chloride in a ratio of 1:2 and 1:3, an additional peak at 1.18 V remains in the anodic potential region, which corresponds to the oxidation reaction $Cl^- \rightarrow 0.5$ Cl_2 .

In the reaction of ligands **3**–**6** with NiCl₂·6H₂O and CoCl₂·6H₂O in DMF, the complex compounds are also formed, but, in contrast to CuCl₂·6H₂O, the complexation reaction is apparantely reversible. Even several hours after mixing the reactants, the peaks of the initial salt and ligand are still observed in CV in addition to the new peaks related to the coordination compounds formed. The following data are in favor of complex formation: (1) the peak of desorption of the zerovalent nickel or cobalt observed in the reverse scan after the first two-electron cathodic peak ($E_{\rm pc} = -1.25$ V) is less intensive than that of the corresponding salts; (2) the values of reduction potentials related to Ni^{II} \rightarrow Ni⁰ and Co^{II} \rightarrow Co⁰ transitions are somewhat (by ~0.10–0.15 V) different from the values of the reduction potentials of the initial salts.

Thus, we have synthesized a series of novel cyclic and acyclic diamido-bis-sulfide ligands by N-acylation reaction of α, ω -bis(2-aminophenylthio)alkanes. The results of the electrochemical studies support deprotonation of the amide ligands during the formation of their complexes with copper(11) chloride.

Experimental

¹H NMR spectra were recorded on a Bruker Avance 400 instrument (400 MHz). IR spectra were recorded on a UR-20 instrument in Nujol.

A PI-50-1.1 potentiostat connected to a PR-8 programmer was used for electrochemical study. The working electrodes were a glassy carbon (d = 2 mm), a platinum disk (d = 3 mm), and a gold disk (d = 2 mm). The supproting electrolyte was a 0.1 M Bu₄NClO₄ solution in DMF, the reference electrode was Ag/AgCl/KCl(sat.), and the auxiliary electrode was a platinum plate. The surface of the working electrodes was polished with alumina powder having a particle size less than 10 µm (Sigma-Aldrich). The potential sweep rate in the CV and RDE studies were 200 and 20 mV s⁻¹, respectively. The potentials are given with allowance for the iR compensation. The number of electrons transferred in redox processes was determined by comparing the limiting wave current in the RDE experiments with the current of one-electron oxidation of ferrocene at the concentration equal to that of the compound under study. All measurements were carried out under dry argon. The samples were dissolved in the pre-deareated solvent. DMF (pure grade) was purified by stirring with freshly calcined K_2CO_3 for 4 days followed by successive vacuum distillation over P_2O_5 and anhydrous $CuSO_4$.

In the experiments for electrochemical study of complexation, a solution of ligands **3–6** in DMF ($5 \cdot 10^{-4} - 10^{-3} \text{ mol } \text{L}^{-1}$) was mixed in an electrochemical cell with solutions of NiCl₂·6H₂O, CoCl₂·6H₂O or CuCl₂·6H₂O in DMF at the same concentrations at the ratio of 1 : 1. The gold electrode with surface-adsorbed ligand was prepared by incubation of the electrode in a solution of ligand **5** or **6** ($10^{-3} \text{ mol } \text{L}^{-1}$) for 1 h. It was then washed with DMF, air dried, and placed into pure supporting electrolyte. In the experiments for studying complexation with the ligands adsorbed on the electrode surface, the gold electrode with the monolayer of ligand **5** or **6** prepared as described above was immersed into a solution of $CuCl_2 \cdot 6H_2O$ in DMF (10^{-2} mol L⁻¹) for 1 h and then washed once again with DMF and dried in air. Afterwards, the electrochemical curves were recorded in pure supporting electrolyte.

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Synthesis of α, ω -bis(2-aminophenylthio)alkanes (general procedure). In a 500 mL three-necked flask equipped with a reflux condenser, a dropping funnel, and a stirring bar, EtOH (100 mL) was placed and sodium metal was dissolved in EtOH. *o*-Aminobenzenethiol was added to the resulting solution. A solution of α, ω -dibromoalkane in EtOH (50 mL) was then added under reflux. The reaction mixture was stirred for 7 h under reflux, cooled and quenched with water (150 mL). The precipitate that formed was filtered off and recrystallized from EtOH.

1,2-Bis(2-aminophenylthio)ethane (1) was prepared from sodium (1.84 g, (80 mmol), *o*-aminobenzenethiol (8.51 mL, 10.0 g, 80 mmol), and 1,2-dibromoethane (3.46 mL, 7.52 g, 40 mmol). The yield was 8.12 g (74%), m.p. 76–78 °C (*cf.* Ref. 39: m.p. 76–78 °C). ¹H NMR (CDCl₃, δ): 7.35 (dd, 2 H, H(5), J_1 = 7.6 Hz, J_2 = 1.3 Hz); 7.15 (td, 2 H, H(2), J_1 = 7.4 Hz, J_2 = 1.6 Hz); 6.71 (m, 4 H, H(3), H(4)); 4.28 (br.s, 4 H, NH₂); 2.89 (s, 4 H, CH₂S). IR, v/cm⁻¹: 3330 (NH).

1,4-Bis(2-aminophenylthio)butane (2) was prepared analogously in the form of an oil from sodium (0.92 g, 0.04 mol), *o*-aminobenzenethiol (5.00 g, 0.04 mol) and 1,4-dibromobutane. The yield was 4.84 g (80%). ¹H NMR (CDCl₃, δ): 7.36 (dd, 2 H arom., J_1 = 7.7 Hz, J_2 = 1.5 Hz); 7.13 (ddd, 2 H arom., J_1 = 7.7 Hz, J_2 = 1.5 Hz); 6.74 (m, 2 H arom.), 6.70 (m, 2 H arom.), 4.31 (br.s, 4 H, 2 NH₂); 2.73 (m, 4 H, 2 CH₂S); 1.68 (m, 4 H, 2 SCH₂CH₂).

1,4-Bis(2-acetylamidophenylthio)ethane (3). In a beaker equipped with a stirring bar, compound **1** (1.00 g, 3.62 mmol) was dissolved in benzene (40 mL) and acetic anhydride (0.74 g, 7.20 mmol) was added. The reaction mixture was stirred for 30 min. The precipitate that formed was filtered off, twice washed with benzene, and dried in air. The yield was 1.147 g (88%), m.p. 204–206 °C. ¹H NMR (DMSO-d₆, δ): 9.33 (s, 2 H, NH); 7.56 (d, 2 H, H(3), J = 7.6 Hz); 7.34 (d, 2 H, H(6), J = 7.6 Hz); 7.25 (t, 2 H, H(5), J = 7.8 Hz); 7.14 (t, 2 H, H(4), J = 7.4 Hz); 3.00 (s, 4 H, CH₂S); 2.06 (s, 6 H, COCH₃). IR, v/cm⁻¹: 2940 (NH); 1620 (C=O). Found (%): C, 60.32; H, 5.77; N, 7.71; S, 17.71. C₁₈H₂₀N₂O₂S₂. Calculated (%): C, 60.00; H, 5.56; N, 7.78; S, 17.78.

6,7,12,13-Dibenzo-1,5-diaza-8,11-dithiacyclotridecan-2,4dione (4). Compound **1** (0.30 g, 1.09 mmol), dimethyl malonate (0.143 g, 1.09 mmol), and diphenyl ether (5 mL) were placed into a 50 mL round-bottomed flask equipped with air condenser. The reaction mixture was refluxed for 5 h and then cooled. The precipitate that formed was filtered off and recrystallized from DMSO. The crystalline residue formed 4 h after cooling the solution to -15 °C. The yield was 0.238 g (64%). ¹H NMR (DMSO-d₆, δ): 10.18 (s, 2 H, 2 NH); 7.87 (d, 2 H arom., J = 7.6 Hz); 7.62 (d, 2 H arom., J = 7.6 Hz); 7.38 (t, 2 H arom., $J_1 = J_2 = 7.6$ Hz); 7.19 (t, 2 H arom., $J_1 = J_2 = 7.6$ Hz); 3.60 (s, 2 H, COCH₂CO); 2.98 (s, 4 H, 2 CH₂S). Found (%): C, 59.65; H, 4.09; N, 8.19.

Ligands 5–6 (general procedure). A. 3,3'-dithiodi(propionyl chloride). Powdered 3,3'-dithiodi(propionic acid) (5.00 g, 23.80 mmol) and SOCl₂ (11.33 g, 95.20 mmol) were placed into Ehrlemeyer's flask equipped with reflux condenser connected to a calcium chloride tube. The flask contents was stirred with heating on a water bath at 45–50 °C for 3 days. The reaction **B.** Preparation of macrocyclic ligands. A solution of pyridine in dry benzene (100 mL) was heated to 75 °C. At this temperature, a solutions of a diamine and 3,3'-dithiodipropionic acid (each in dry benzene (60 mL)) were added simultaneously dropwise for 6 h and stirred at this temperature for 3 h. Then the solvent was evaporated *in vacuo* and the residue was washed with 1 *M* HCl (100 mL), dried in air, and recrystallized from DMSO.

11,12,17,18-Dibenzo-1,10-diaza-5,6,13,16-tetracyclooctadecane-2,9-dione (5). Compound **5** was prepared from compound **1** (0.50 g, 1.81 mmol) and 3,3'-dithiodi(propionyl chloride) (0.45 g, 1.81 mmol) in the presence of pyridine (1.44 mL, 17.8 mmol) in a yield of 0.42 g (51%). M.p. 244–246 °C. ¹H NMR (DMSO-d₆, δ): 9.46 (s, 2 H, NH); 7.67 (d, 2 H arom., J = 7.4 Hz); 7.52 (d, 2 H arom., J = 7.5 Hz); 7.29 (t, 2 H arom., J = 7.6 Hz); 7.18 (t, 2 H arom., J = 6.9 Hz); 3.08 (m, 4 H, CH₂CO); 2.95 (m, 4 H, CH₂S–S); 2.85 (s, 4 H, CH₂S). Found (%): C, 50.25; H, 5.00; N, 5.60. C₂₀H₂₂N₂O₂S₄. Calculated (%): C, 53.33; H, 4.88; N, 6.22.

11,12,19,20-Dibenzo-1,10-diaza-5,6,13,18-tetracycloeicosan-2,9-dione (6) was prepared from compound **2** (0.50 g, 1.64 mmol) and 3,3'-dithiodi(propionyl chloride) (0.41 g, 1.64 mmol) in the presence of pyridine (1.44 mL, 17.8 mmol) in a yield of 0.57 g (73%). M.p. 264–266 °C. ¹H NMR (DMSO-d₆, δ): 9.45 (s, 2 H, NH); 7.59 (d, 2 H arom., J = 7.8 Hz); 7.47 (d, 2 H arom., J = 7.2 Hz); 7.25 (m., 2 H arom.); 7.16 (m, 2 H arom.); 3.03 (m, 4 H, CH₂CO); 2.81 (m, 8 H, CH₂SS + CH₂S), 1.55 (m, 4 H, CH₂CH₂).

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