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5-[2-(Methylthio)ethyl]-3-phenyl-2-thioxoimidazolidin-4-one and its complexes with transition metals (Co^{II}, Ni^{II}, and Cu^{II}). Synthesis and electrochemical investigation

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The reaction of 5-[2-(methylthio)ethyl]-3-phenyl-2-thioxoimidazolidin-4-one (LH) with salts $MCl_2 \cdot xH_2O$ (M = Co, Ni, Cu; x = 2, 6) afforded the $[M(L)Cl]_n$ complexes of Ni^{II}, Co^{II}, and Cu^{II}. The electrochemical behavior of the LH ligand and its complexes was studied using the cyclic voltammetry and rotating disk electrode techniques. The structures of the synthesized compounds were determined by the data of UV—Vis and IR spectroscopy, mass spectrometry, and electrochemical characteristics.

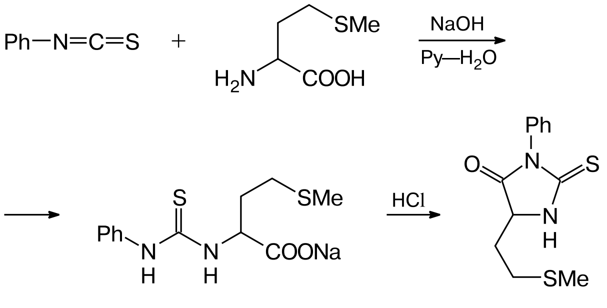
Key words: 2-thioxoimidazolidin-4-one, 2-thiohydantoine, nickel(II) complexes, cobalt(II) complexes, copper(II) complexes, cyclic voltammetry, rotating disk electrode technique.

Complexes of transition metals, in particular, nickel(II),[1] cobalt(II),[2] and copper(II),[3] with organic S,N-containing ligands attrack attention as models of metal enzymes and electroactive catalysts. Among promising organic ligands are, *e.g.*, thio-substituted imidazolones. We have earlier[4—7] synthesized the Co^{II}, Ni^{II}, and Cu^{II} complexes with a series of 5-(pyridylmethylidene)-substituted 2-thioxoimidazolidin-4-ones (2-thiohydantoines). Particular representatives of these compounds are able to reversibly electrochemically reduce[5] and catalyze alkene epoxidation.[6,7] In the present work, we synthesized a series of the complexes of 5-[2-(methylthio)ethyl]-substituted 2-thiohydantoine and determined their structures.

Results and Discussion

Synthesis of 5-[2-(methylthio)ethyl]-3-phenyl-2-thioxoimidazolidin-4-one (1) and its complexes with the Co^{II}, Ni^{II}, and Cu^{II} salts. The most convenient method for the synthesis of 2-thiohydantoines are the reactions of amino acids with aryl or alkyl isothiocyanates.[8] Ligand **1** (hereinafter LH) was synthesized by the reaction of phenyl isothiocyanate with methionine in a pyridine—water mixture in the presence of sodium hydroxide, affording substituted thiourea, whose ring closure with target product formation was carried out by the treatment with hydrochloric acid (Scheme 1).

Scheme 1



1 (85%)

No changes occur upon reflux of ligand **1** with metal chloride hydrates in EtOH; however, a precipitate of complexes **2—4** is formed upon the addition of an equivalent amount of triethylamine (Scheme 2).

Scheme 2

$$\underset{\mathbf{1}}{\mathrm{LH}} + \mathrm{MCl_2 \cdot}x\mathrm{H_2O} \xrightarrow[\mathrm{EtOH},\ \Delta]{\mathrm{Et_3N}} \underset{\mathbf{2-4}}{[\mathrm{M(L)Cl}]_n}$$

x = 2 (M = Cu), 6 (M = Co, Ni); M = Co (**2**), Ni (**3**), Cu (**4**)

According to elemental analysis data, the composition of the synthesized compounds corresponds to the simplest molecular formula M(L)Cl. Nevertheless, a monomeric structure for them seems improbable because of geometric concepts. This elemental composition is possible for dimeric coordination compounds with bridging

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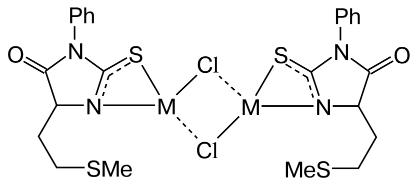
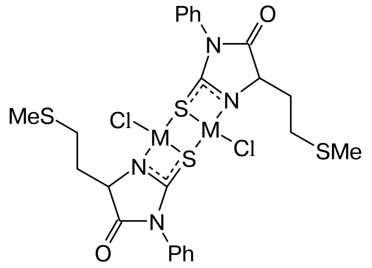
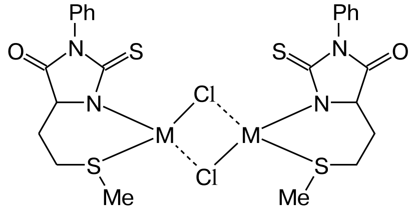


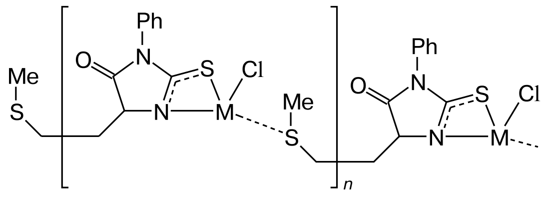
I



III



II



IV

chlorine atoms of types **I** and **II** (similar structures with four-membered metallacycles have been described earlier[9,10]), for dimeric structure **III** with the bridging thiolate sulfur atoms (see Refs 10 and 11), and for polymeric structures, *e.g.*, **IV**.

Unfortunately, we failed to synthesize complexes **2—4** as crystals appropriate for X-ray diffraction analysis. Therefore, the structures of complexes **2—4** were ascribed on the basis of the spectral and electrochemical data.

Electronic and IR spectroscopy. The results of studying ligand **1** and complexes **2—4** by electronic and IR spectroscopy are presented in Table 1.

In the IR spectra of the synthesized complexes, the absorption band of the C=S group is shifted to higher frequencies compared to an analogous band of the free ligand (see Table 1), which makes it possible to reject structure **II**, where the sulfur atom of the C=S group is not involved in coordination. The absorption band of the N—H group observed for the free ligand is absent in the IR spectra of the complexes. This confirms that the N(1) atom in the complex is deprotonated.

The electronic spectra of complexes **2—4** contain one or two bands in the UV region, which are similar to those in the UV spectrum of ligand **1** and correspond, most likely, to the π—π*- and n—π*-transitions in the organic fragment. The spectra of the complexes contain also lower-absorption bands in the visible spectral region. For cobalt complex **2**, the shape of the spectrum agrees with the tetrahedral or distorted tetrahedral coordination environment of the metal ion.[12,13] One should assume either planar-square geometry or a structure intermediate between planar square and tetrahedron of the coordination environment of Ni^{II} for nickel complex **3** (because absorption bands of noticeable intensity at 600—700 nm are absent).[13,14] The electronic spectrum of copper complex **4** contains a low-intensity band at 710—720 nm, which is also characteristic of tetrahedral complexes.[13,14] Therefore, based on the data of optical spectroscopy, we can ascribe structures with a distorted tetrahedral environ-

Table 1. Results of studying compounds **1—4** by IR and electronic spectroscopy

Compound	IR, ν/cm^{-1}					Electronic spectrum, λ/nm (logε)
	N—H	C=O	C=C (Ph)	C=S	Other bands	
1	3180	1745	1595, 1435, 1360	1150, 1170	755, 720, 705	296 (3.90), 323 (2.15)
2	—	1720	1595, 1485, 1455, 1375	1183	740, 710, 690	271 (3.95), 307 (3.54), 625 (2.0)
3	—	1720	1600, 1485, 1460, 1375	1183	740, 720, 690	268 (3.94), 403 (1.90)
4	—	1750	1600, 1510, 1520, 1465, 1380	1205	760, 705	287 (3.98), 323 (2.22), 714 (1.22)

ment of metal ions to the synthesized complexes of ligand **1**. In them coordination occurs, most likely, to the deprotonated N(1) atom of the thiohydantoine fragment and thionic sulfur atom.

Mass spectrometry. The mass spectral characteristics of the cobalt and nickel complexes (**2** and **3**) differ substantially from those of the copper complex **4**. In the mass spectra of positive ions obtained by the ionization of complexes **2** and **3**, the highest intensity belongs to the fragmentation ion with *m/z* 209 corresponding, most likely, to the [**1** – MeCH=C=O] fragment. These complexes are mostly characterized by the presence of intense peaks with *m/z* 302 and 324 in the mass spectra. No peaks with *m/z* 302 and 324 are observed in the mass spectrum of compound **4**, and the maximum intensity belongs to the peak with *m/z* 235 (presumably $[PhNH—CH=S]CuCl^+$); the peak with *m/z* 591 is also observed ($[(\mathbf{1})_2Cu_2Cl_2 - PhNCS + 2\ H]^+$). The intensity ratio in isotopic clusters of the peaks agrees with the performed assignment.

For copper complex **4**, taking into account the peak with *m/z* 591 (see above) corresponding to an ion containing two chlorine atoms, one can propose the dimeric structure with the bridging chlorine atoms of type **I** or **II**. According to the IR spectral data (see Table 1) that confirm the participation of the thionic sulfur atom in coordination with the metal, structure **I** should be preferred. For compounds **2** and **3**, the dimeric structure with the bridging sulfur atoms of type **III** or polymeric structure seems to be most probable.

Note that the addition of twofold excess MeI to solutions of complexes **2—4** in DMF changes the color of the solution from yellow-brown to dark brown-red. According to available published data,[15,16] this can be related to the alkylation of the ligand to the sulfur atom, changing the coordination environment of the metal. In this case, the alkylation occurs only in the case of the complexes containing no bridging sulfur atoms. Thus, the experiment allows one to reject structure **III**. The polymeric structure of complexes **2** and **3** is confirmed by the results of electrochemical investigation (see below).

Thus, based on the spectral data, we can assume that the cobalt and nickel complexes (**2** and **3**) have polymeric structures, and copper complex **4** is dimeric with the structure of type **I** (Scheme 3).

Electrochemical investigation. The electrochemical behavior of ligand **1** and complexes **2—4** was studied by the cyclic voltammetry (CV) and rotating disk electrode (RDE) techniques on a glassy carbon (GC) electrode in DMF against a 0.05 *M* solution of Bu_4NClO_4. The potentials of electrochemical oxidation and reduction are given in Table 2.

We have earlier[17] shown that the first steps of reduction and oxidation of 5-(pyridylmethylidene)-3-phenyl-2-thiohydantoines proceed irreversibly to the C=S bond at the potentials about −1.1 V (one-electron reduction) and 1.1—1.5 V (two-electron oxidation), respectively. Comparing these data with the results obtained for substituted thiohydantoine **1**, we can mention that the oxidation of the latter is easier and its reduction is much more difficult than those in the case of pyridylmethylidene-substituted 2-thiohydantoines. This difference can be explained by the acceptor character of the pyridylmethylidene substituent in position 5 of earlier studied 2-thiohydantoines and the donor character of the 2-(methylthio)ethyl group in the case of ligand **1**.

The first step of oxidation of complexes **2—4** proceeds at potentials of 0.84—1.01 V, and the second step occurs at potentials of 1.31—1.41 V. In the first step, deprotonated

Scheme 3

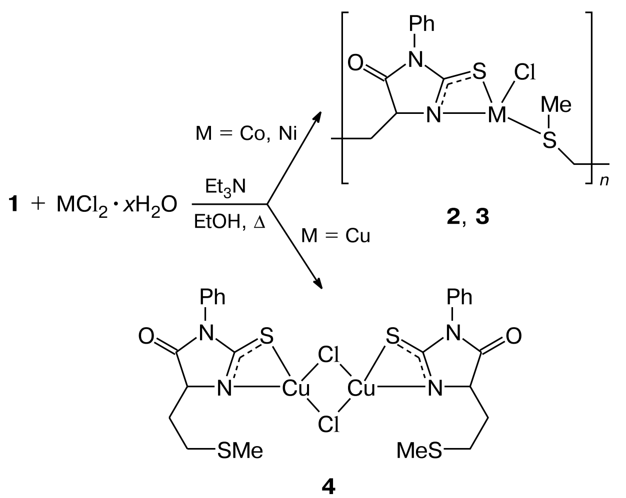


Table 2. Electrochemical reduction (E^{Red}) and oxidation (E^{Ox}) potentials of compounds **1—4** measured *vs.* Ag/AgCl/KCl(sat.) by the CV (E_p is the peak potential) and RDE ($E_{1/2}$ is the half-wave potential) methods on the GC electrode[a]

Compound	E_p^{Red}	$E_{1/2}^{Red}$	E_p^{Ox}	$E_{1/2}^{Ox}$
	V			
1	−1.96, −2.50	−2.14, −2.55	1.14	1.23
2	−0.78, −1.47, −2.07/0.04[b]	−0.72, −1.40, −2.10	1.01, 1.31	1.07, 1.41
3	−0.77, −1.53, −1.96	−0.77, −1.97	1.30	1.24
4	0.36/056[c], 0.05/0.16, −0.54, −0.93/0.12[b], −2.01	0.53[c], 0.12, −0.62, −1.28, −1.96	1.36	1.19, 1.44

[a] DMF, 0.05 *M* solution of Bu_4NClO_4; peak potentials in reverse scan of the CV curves are given after slash.

[b] Peak of oxidative desorption of M^0.

[c] Initial potential of 0.7 V.

organic ligand **1** is oxidized, probably, similarly to the process described in Ref. 5. The second oxidation step corresponds in potential to the oxidation of the coordinated chloride anions.[17]

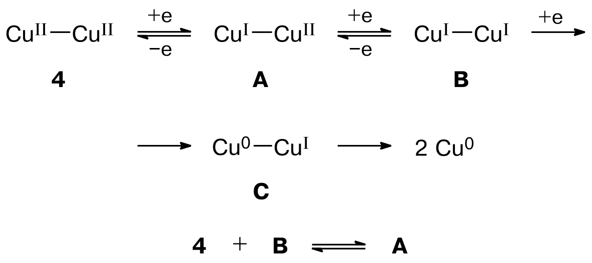
Compared to the CV curve of the free ligand, the CV curves of the cobalt and nickel complexes (**2** and **3**) exhibit three reduction peaks with less negative potentials (for example, –0.77, –1.47, and –2.07 V for complex **2**), which correspond, most likely, to the transitions

$$\mathrm{M^{II} \rightarrow M^{I} \rightarrow M^{0}}\ (\mathrm{M = Co, Ni})$$

and to the reduction of the anionic organic ligand. Note that complex **2** decomposes to form metallic cobalt when the potential of the third cathodic redox potential is achieved, which is indicated by the appearance of a black film of $\mathrm{Co^0}$ on the electrode surface and the oxidative desorption peak in the reverse scan of the CV curve at $E_p = 0.04$ V (Fig. 1).

Binuclear copper complex **4** is reduced through the formation of mixed-valent complexes, which is confirmed by the appearance of four additional reduction peaks in the CV curve compared to that of the free ligand (Scheme 4).

Scheme 4



$$\underset{\mathbf{4}}{\mathrm{Cu^{II}{-}Cu^{II}}} \underset{-e}{\overset{+e}{\rightleftharpoons}} \underset{\mathbf{A}}{\mathrm{Cu^{I}{-}Cu^{II}}} \underset{-e}{\overset{+e}{\rightleftharpoons}} \underset{\mathbf{B}}{\mathrm{Cu^{I}{-}Cu^{I}}} \xrightarrow{+e} \underset{\mathbf{C}}{\mathrm{Cu^{0}{-}Cu^{I}}} \longrightarrow 2\,\mathrm{Cu^{0}}$$

$$\mathbf{4} + \mathbf{B} \rightleftharpoons \mathbf{A}$$

Under the experimental conditions, compound **4** and product **B** interact, most likely, with each other giving compound **A**. This is confirmed by the fact that in the CV curve the intensity of the reverse peak of the first reduction wave (Fig. 2, peak *A*′) is higher than the intensity of the forward peak (peak *A*).

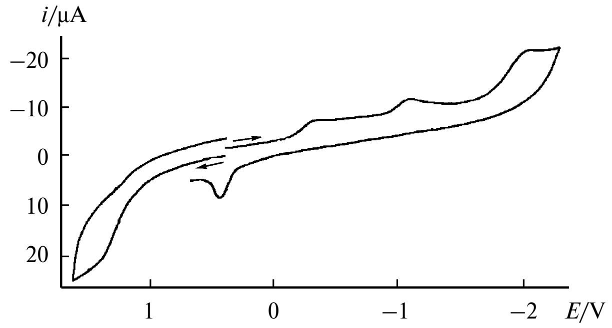


Fig. 1. Cyclic voltammogram of complex **2** (DMF, 10^{-3} mol $\mathrm{L^{-1}}$) on the glassy carbon electrode.

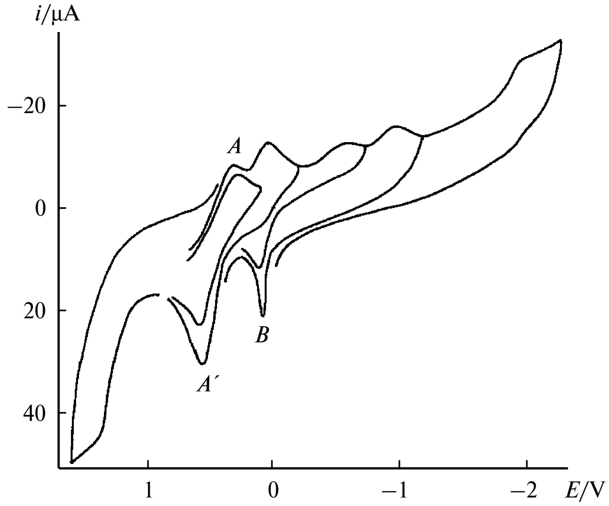


Fig. 2. Cyclic voltammogram of complex **4** (DMF, 10^{-3} mol $\mathrm{L^{-1}}$) on the glassy carbon electrode.

Copper(I)-containing reduction products **A** and **B** are rather stable in time and do not decompose with formation of the free metal under the conditions of CV curve recording (sweep rate 200 mV $\mathrm{s^{-1}}$). However, product **C** that formed by electrolysis at the potential of the third peak ($E_p = -0.54$ V) decomposes gradually, most likely, resulting in the destruction of the complex. As a result, the peak of oxidative desorption of zero-valent copper is observed in the reverse anodic scan of the CV curve (see Fig. 2, peak *B*). When the potential of the fourth reduction peak is achieved, the desorption peak becomes more intense and is identified in the reverse scan without electrolysis, which indicates the fast decomposition of the complex. The reduction peaks of ligand **1** are observed at more negative potential values.

Note that for this series of compounds the experiments on the RDE are impeded by the strong adsorption of both the initial compounds and reduction (or oxidation) products on the electrode surface, which results in the formation of non-conducting films. This is indicated by the current decrease in the RDE curves and very low current values (1/9—1/12 e).

Generalizing the results of electrochemical investigation, we can conclude that the primary reduction of all the complexes studied proceeds to the metal and the oxidation occurs to the coordinated thiohydantoine anion. The electrochemical data also confirm structural similarity of complexes **2** and **3** and the dimeric structure of copper complex **4**.

Experimental

The course of the reactions and individual character of the products were monitored by TLC on a stationary silica gel layer (Silufol). ^{1}H NMR spectra were recorded on a Varian-XR-400 instrument with a working frequency of 400 MHz in $CDCl_3$. IR spectra were measured on a UR-20 instrument in Nujol and on an IR200 FT-IR spectrometer (TermoNicolet) with a resolution of 4 cm^{-1}. Mass spectra of laser ionization of positive ions were obtained on a Vision 2000 time-of-flight mass spectrometer with an N_2 laser (radiation wavelength 336 nm).

A PI-50-1.1 potentiostat connected to a PR-8 programmer was used for electrochemical investigation. Working electrodes were glassy carbon (d = 2 mm), platinum (d = 3 mm), and gold (d = 2 mm) disks. The supporting electrolyte was a 0.05 *M* solution of Bu_4NClO_4 in DMF, the reference electrode was Ag/AgCl/KCl(sat.), and the counter electrode was the platinum plate. In the CV studies the potential sweep rate was 200 mV s^{-1}, and that for the RDE studies was 20 mV s^{-1}. The potentials are given with account for *iR*-compensation. The number of transferred electrons in redox processes was determined by comparison of the limiting current of the wave in RDE experiments with the current of one-electron oxidation of ferrocene taken in an equal concentration.

All measurements were carried out in dry argon. Samples were dissolved in the pre-deaerated solvent. Dimethylformamide (pure grade) was stirred over freshly calcined K_2CO_3 for four days followed by distillation *in vacuo* first over P_2O_5 and then over anhydrous $CuSO_4$.

5-[2-(Methylthio)ethyl]-3-phenyl-2-thioxoimidazolidin-4-one (1) was synthesized according to a described procedure.[8] A 2 *M* solution of NaOH was added to a solution of L-methionine (2 g, 0.013 mol) in a water—pyridine (1 : 1) mixture (20 mL) to pH 9, and this pH value was maintained constant during the whole reaction. The mixture was heated to 40 °C, phenyl isothiocyanate (1.81 g, 0.013 mol) was added, and the mixture was stirred for 1 h at 40 °C with periodical pH measurement. Pyridine and excess isothiocyanate were removed by the extraction of the reaction mixture with an equal volume of benzene. Concentrated HCl (3 mL) was added to the aqueous fraction, and the mixture was refluxed for 2 h. The reaction mixture was concentrated by evaporating to 1/2 volume under reduced pressure and cooled down to 20 °C. The pale yellow precipitate that formed was filtered off and recrystallized from MeOH. The yield was 2.93 g (85%), m.p. 133—134 °C (*cf.* Ref. 8: m.p. 133 °C).

Synthesis of complexes 2—4 (general procedure). Ligand **1** was dissolved in minimum hot EtOH, and 1 equiv. of a metal salt dissolved in minimum EtOH was added. Triethylamine (1 equiv.) was added to the boiling mixture, and reflux was continued for 10 h. The mixture was cooled to ~20 °C, and the precipitate that formed was filtered off.

Complex 2. Dark brown complex **2** was synthesized from ligand **1** (0.20 g, 0.75 mmol), $CoCl_2 \cdot 6H_2O$ (0.08 g, 0.75 mmol), and Et_3N (0.075 g, 0.75 mmol). The yield was 0.08 g (57%), m.p. 282 °C (with decomp.). Calculated (%): C, 40.06; H, 3.64; N, 7.79. $C_{12}H_{13}N_2OS_2 \cdot CoCl$. Found (%): C, 39.38; H, 4.22; N, 7.18.

Complex 3. Yellow complex **3** was synthesized from ligand **1** (0.20 g, 0.75 mmol), $NiCl_2 \cdot 6H_2O$ (0.08 g, 0.75 mmol), and Et_3N (0.075 g, 0.75 mmol). The yield was 0.09 g (64%), m.p. 317 °C (with decomp.). Calculated (%): C, 40.06; H, 3.64; N, 7.79. $C_{12}H_{13}N_2OS_2 \cdot NiCl$. Found (%): C, 39.89; H, 3.99; N, 7.57.

Complex 4. Brown complex **4** was synthesized from ligand **1** (0.20 g, 0.75 mmol), $CuCl_2 \cdot 2H_2O$ (0.06 g, 0.75 mmol), and Et_3N (0.075 g, 0.75 mmol). The yield was 0.08 g (55%), m.p. 266 °C. Calculated (%): C, 39.56; H, 3.60; N, 7.69. $C_{12}H_{13}N_2OS_2 \cdot CuCl$. Found (%): C, 39.85; H, 3.75; N, 7.66.

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