Synthesis and electrochemistry of $(5Z,5^{2})-2,2^{2}-(alkane-\alpha,\omega-diyldisulfanyldiyl)-bis(5-(2-pyridylmethylene)-3,5-dihydro-$ 4H-imidazol-4-one) complexes with cobalt(11) chloride*

E. K. Beloglazkina,* A. G. Majouga, I. V. Yudin, N. V. Zyk, A. A. Moiseeva, and K. P. Butin[†]

Department of Chemistry, M. V. Lomonosov Moscow State University, 1 Leninskie Gory, 119992 Moscow, Russian Federation. E-mail: bel@org.chem.msu.su

A series of *S*-alkylated 2-thiohydantoin derivatives containing two 5-(2-pyridylmethylene)-2-sulfanyl-3,5-dihydro-4*H*-imidazol-4-one moieties linked through a polymethylene bridge with different numbers of carbon atoms was synthesized for the first time. These compounds were obtained by the alkylation of 3-phenyl-5-(2-pyridylmethylene)-2-thiohydantoin or 3-methyl-5-(2-pyridylmethylene)-2-thiohydantoin with different α,ω -dibromoalkanes in acetone or DMF in the presence of potassium carbonate. Complexes of these compounds (L) with CoCl₂ were synthesized. In all cases, the complexes L(CoCl₂)₂ were formed regardless of the ratio of L and inorganic salt introduced into the reaction. According to electronic spectroscopic data, the cobalt atom in the complexes has a tetrahedral coordination environment. The synthesized ligands and complexes were electrochemically studied by cyclic voltammetry.

Key words: $(5Z,5'Z)-2,2'-(alkane-\alpha,\omega-diyldisulfanyldiyl)bis(5-(2-pyridylmethylene)-3,5-dihydro-4$ *H*-imidazol-4-ones, complexes with cobalt(1) chloride, electronic absorption spectroscopy, cyclic voltammetry.

2-Thiohydantoins (4-oxoimidazolidine-2-thiones) and their S-alkylated derivatives (2-alkylthio-3,5-dihydro-4H-imidazol-4-ones) attract researchers' attention in the recent time as convenient synthetic intermediates containing both electrophilic and nucleophilic carbon atoms and due to a wide spectrum of their biological activity.¹⁻³

We reported⁴ the synthesis and structural and physicochemical studies of the complexes of (5Z)-2-methylthio-3-phenyl-5-(2-pyridylmethylene)-3,5-dihydro-4*H*imidazol-4-one and 3-methyl-(5*Z*)-2-methylthio-5-(2-pyridylmethylene)-3,5-dihydro-4*H*-imidazol-4-one with Ni^{II}, Co^{II}, and Cu^{II} salts.

The present work describes the synthesis and physicochemical study of derivatives of *S*-alkylated analogs of 2-thiohydantoins containing two 5-(2-pyridylmethylene)-2-sulfanyl-3,5-dihydro-4*H*-imidazol-4-one moieties linked through a polymethylene bridge. Their complexation with Co^{II} chloride was also studied.

Synthesis of ligands

3-Phenyl-5-(2-pyridylmethylene)-2-thiohydantoin (1) and 3-methyl-5-(2-pyridylmethylene)-2-thiohydan-

toin (2), which were synthesized from phenyl or methyl isothiocyanate, glycine, and 2-pyridinecarbaldehyde according to described procedures,⁵ were chosen as the starting compounds for the syntheses of the target ligands. Ligands **3–9** were prepared by the alkylation of the thione group of compounds **1** and **2** with different α, ω -dibromoalkanes. Two procedures were used for the alkylation. According to the first procedure (method *A*), the alkylation was carried out in acetone in the presence of potassium carbonate and a catalytic amount of triethylbenzyl-ammonium chloride as the phase-transfer catalyst.⁶ According to the second procedure (method *B*), the alkylation was carried out in DMF in the presence of the same base (Scheme 1).

As found for the reactions of 3-phenyl-5-(2-pyridylmethylene)-2-thiohydantoin (1) with α,ω -dibromoalkanes, the yields of the target products are virtually the same for both alkylation methods. In the case of thiohydantoin 2, only method *B* was used. The yields of the reaction products, *viz.*, ligands L, are given in Table 1.

The compositions of the compounds synthesized were confirmed by the elemental analysis data, and their structures were determined by the data of ¹H and ¹³C NMR and IR spectroscopies. In the ¹H NMR spectra of compounds **3**–**9**, the signal from the NH groups disappears, while it is present in the spectra of the corresponding thiohydantoins **1** and **2**, and a signal of protons of CH₂S

Published in Russian in Izvestiya Akademii Nauk. Seriya Khimicheskaya, No. 9, pp. 2099-2104, September, 2005.

1066-5285/05/5409-2163 © 2005 Springer Science+Business Media, Inc.

^{*} Dedicated to Academician N. S. Zefirov on the occasion of his 70th birthday.

[†] Deceased.

Beloglazkina et al.



R = Ph (1, 3–6), Me (2, 7–9) n = 2 (3), 4 (7), 6 (4, 8), 8 (5), 10 (6, 9)

Reagents and conditions: *i*. Method *A*: K_2CO_3 , acetone, Et₃BnNCl, 20 °C; *ii*. Method *B*: K_2CO_3 , DMF, 20 °C.

at 3.2 ppm appears. The IR spectra of the compounds synthesized exhibit an absorption band of the C=N group at 1670 cm⁻¹.

Synthesis of complexes

According to published data, 2-thiohydantoins and their *S*-alkylated derivatives with transition metal salts form complexes in which the metal ion can coordinate to the nitrogen or sulfur atom, or simultaneously to both of these atoms.^{8–15}

To obtain the target complexes, we used the method of slow diffusion of a solution of ligand L (3, 5–7) in CH_2Cl_2 into an alcoholic solution of $CoCl_2 \cdot 6H_2O$,^{5,7,16}

Table 1. Yields of compounds 3-9 prepared by methods *A* and *B*

Starting 5-(2-pyri-	Starting α,ω-dibromo-	Pro- duct	Yield of product (%)	
dylmethylene)- 2-thiohydantoin	alkane n		A	В
1	1,2-Dibromoetha 1,6-Dibromohexa	ne 3 .ne 4	64	73 68
	1,8-Dibromoocta 1,10-Dibromodec	ne 5 ane 6	62 67	
2	1,4-Dibromobuta 1,6-Dibromohexa 1,10-Dibromodec	ne 7 ne 8 ane 9		67 71 69

due to which powdered precipitates of the complexes were formed.

It has previously been shown^{4,17} that the reactions of the (5Z)-2-methylthio-3-phenyl(or 3-methyl)-5-(2-pyridylmethylene)-3,5-dihydro-4H-imidazol-4-one ligands with Co^{II} and Cu^{II} chlorides afford complexes LMCl₂, in which the metal ion has a tetrahedral ligand environment and coordinates to two nitrogen atoms (of the pyridine and imidazole moieties) and two chloride anions. Each of the ligands studied in the present work (L) has two 5-(2-pyridylmethylene)-3,5-dihydro-4H-imidazol-4-one moieties. Therefore, we can expect a priori that they would form 1:1 (LCoCl₂) or 1:2 [L(CoCl₂)₂] complexes in the reactions with cobalt chloride. However, the 1:2 complexes $[L(CoCl_2)_2]$ were isolated in all cases, regardless of the ratio of ligand L and inorganic salt introduced into complexation. The compositions of the resulting compounds were determined from the elemental analysis data. All the complexes are green and poorly soluble in DMF and DMSO and do not melt at temperatures below 300 °C. The data on the composition of the complexes are given in Table 2.

Complexes 3a, 5a, 6a, and 7a were characterized by the data of electronic and IR spectroscopies. The IR spectra of all the complexes contain the shift of the absorption band of the C=O group of the ligand toward higher fre-

Table 2. Composition, yield, and elemental analysis data for complexes 3a and 5a-7a

Ligand	Complex	Composition of complex	Yield (%)	Found Calculated (%)		(%)	Molecular formula
				C	Н	N	
3	3a	$3 \cdot 2 \text{CoCl}_2$	65	<u>44.96</u>	<u>2.76</u>	<u>9.59</u>	$C_{32}H_{24}Cl_4Co_2N_6O_2S_2$
5	50	5 2CoC1 2U O	74	45.30	2.85	9.91	
5	5a	5·2C0Cl ₂ ·3H ₂ O	/4	<u>46.07</u> 46.26	<u>4.20</u> 4.29	<u>8.52</u> 8.52	$C_{38} \Pi_{42} C_{14} C_{02} \Pi_{6} O_{5} S_{2}$
6	6a	$6 \cdot 2 Co Cl_2 \cdot 2 H_2 O$	80	<u>48.15</u>	<u>4.34</u>	<u>8.22</u>	$C_{40}H_{44}Cl_4Co_2N_6O_4S_2$
				48.21	4.45	8.43	
7	7a	$7 \cdot 2 \text{CoCl}_2 \cdot 2 \text{H}_2 \text{O}$	68	<u>36.30</u> 36.57	<u>3.53</u> 3.58	<u>10.45</u> 10.66	$C_{24}H_{28}Cl_4Co_2N_6O_4S_2$



Fig. 1. IR spectra (Nujol) at $1550-1750 \text{ cm}^{-1}$ of ligand 7 (1) and its complex with CoCl₂ 7a (2).

quencies compared to those of the starting compounds (Fig. 1). On the contrary, the vibrational frequencies of the C=N and C=C bonds decrease.

The electronic absorption spectra of ligands 5-7 contain absorption bands only in the UV region corresponding to the π - π ^{*}- and n- π ^{*}-transitions. For the starting CoCl₂•6H₂O in which the metal ion has an octahedral ligand environment, the spectrum exhibits three mediumintensity bands of the d-d-transitions in the visible region (500-700 nm). When complexation occurs, the intensity of the absorption bands of the ligand in the UV region decreases and the bands of the d-d-transitions of the metal shift along with the simultaneous decrease in their intensity (Table 3 and Fig. 2), which is usually observed when the geometry of the complex changes from octahedral to tetrahedral. The electronic absorption spectra suggest that the coordination environment of the metal in the complexes under study is similar to that in similar mononuclear cobalt complexes containing (5Z)-(2-pyridylmethylene)-3,5-dihydro-4*H*-imidazol-4-one⁴ as a ligand. Thus, according to the data of elemental analysis and spectroscopy, we ascribe the following structures to all of the complexes synthesized.



n = 2, 4, 6, 8, 10

Electrochemical studies

The behavior of compounds 3 and 5–7 and their complexes (Table 4, Fig. 3) was electrochemically studied in DMF solutions in the presence of $0.05 M Bu_4NCIO_4$ as a

Table 3. Data of electronic absorption spectroscopy in the UV and visible regions for $CoCl_2 \cdot 6H_2O$, ligands 5–7, and complexes 3a and 5a–7a (CH₃CN, $C = 4 \cdot 10^{-3}$ mol L⁻¹)

Compound	λ/nm (logε)			
CoCl ₂ •6H ₂ O	214 (3.9), 255 (3.6), 570 (3.5), 613 (2.5),			
	678 (2.7)			
5	272 (4.79), 364 (5.08)			
6	271 (4.69), 361 (4.97)			
7	275 (4.85), 364 (5.15)			
3a	262(3.81), 372(3.78), 552 (3.25), 634 (3.38)			
5a	276 (3.74), 380 (3.97), 560 (3.05), 660 (3.09)			
6a	259 (3.77), 379 (3.65), 584 (2.91), 675 (3.00)			
7a	279 (3.56), 380 (3.84), 555 (1.96), 634 (2.15)			



Fig. 2. Electronic absorption spectra of ligand 7 (*I*), complex **7a** (*2*), and CoCl₂·6H₂O (*3*) in the visible region (CH₃CN, $C = 4 \cdot 10^{-3}$ mol L⁻¹).

supporting electrolyte at a glassy-carbon (GC) disk electrode by the methods of cyclic voltammetry (CV) and rotating disk electrode (RDE).



Fig. 3. Cyclic voltammograms (200 mV s⁻¹) in a DMF/0.05 *M* Bu₄NClO₄ solution of ligand **3** ($C = 10^{-3} \text{ mol } L^{-1}$) (*I*), beforehand synthesized complex **3a** ($C = 10^{-3} \text{ mol } L^{-1}$) (*2*), and a mixture of ligand **3** ($C = 10^{-3} \text{ mol } L^{-1}$) and CoCl₂·6H₂O ($C = 2 \cdot 10^{-3} \text{ mol } L^{-1}$) 5 min after mixing (*3*).

Table 4. Electrochemical potentials of reduction (E^{red}) and oxidation (E^{ox}) of the ligands and their complexes measured by the CV (E_{p} is the peak potential) and RDE methods ($E_{1/2}$ is the half-wave potential) at the GC electrode in DMF/0.05 *M* Bu₄NClO₄ (CV 200 mV s⁻¹, RDE 20 mV s⁻¹, 2800 min⁻¹)

Com-	$E_{\rm p}^{\rm red}$	$E_{1/2}^{\text{red}}$	E _p ox	$E_{1/2}^{\text{ox}}$
pound		V		
3	-1.20	-1.18 (2e)	1.56	1.54 (1.7e)
	-1.82	-1.90 (1e)		
	-2.18	-2.26 (1e)		
3a	-0.67	-0.64 (2e)	1.28	1.24 (2e)
	-1.19	-1.05 (2e)		
	-1.74	-1.48		
	-2.22	-1.95		
5	-1.25	-1.22 (2e)	1.52	1.48 (2e)
	-1.17*	-1.95 (1e)		
	-1.90	-2.21	-2.35 (1e)	
5a	-0.72	-0.65 (2e)	1.26	1.20 (2e)
	-1.20	-1.08 (2e)		
	-1.78	-1.44		
	-2.20	-2.00		
6	-1.35	-1.18 (2e)	1.60	1.62 (2e)
	-1.88	-1.83 (2e)		
6a**	-0.71	-0.66 (2e)	1.26	1.20 (2e)
	-0.59*	-0.94		
	-1.24	-1.40		
	-2.16	-1.90		
7	-1.20	-1.14 (1e)	1.60	1.58 (2e)
	-1.10	-1.82 (1e)		
	-1.74*			
	-2.12			
7a	-0.68	-0.62 (1e)	1.30	1.34 (2e)
	-0.97	-1.44		
	-1.70			
	-2.22			
$CoCl_2 \cdot 6H_2O$	-0.86 (1e)	-1.30 (2e)	1.53	1.50 (1e)
- 2	-1.21 (1e)		1.70	1.70 (1e)
	0.35			

Note. The number of electrons transferred in this step and determined using the RDE method by a comparison with the wave of one-electron oxidation of ferrocene.

* Peak potentials in inverse scans of the CV curves.

** Low solubility.

The complexes of ligands 3 and 5–7 with cobalt chloride are reduced much more easily than the corresponding ligands. All the complexes under study are stable and do not dissociate in DMF to the free ligand and CoCl₂. In addition, the complexes are formed rather rapidly from the corresponding ligands and CoCl₂·6H₂O, which are taken in stoichiometric and comparatively low concentrations (10^{-3} mol L⁻¹), directly in an electrochemical cell. In 2–3 min, the CV curve of the mixture exhibits the appearance of a new peak in the near-cathodic region (–0.60 V). This peak is absent from the CV of the starting substrates, and its intensity increases for 5–10 min (for different ligands) after the reactants were mixed, after which it stops changing.

The typical CV curves of the ligand, isolated complex, and a ligand— $CoCl_2$ mixture obtained 5 min after dissolution are presented in Fig. 3 for ligand **3** and its complex **3a**. It is seen that the voltammogram of a ligand—transition metal salt mixture corresponds completely to that for the complex synthesized beforehand. We observed a similar pattern for all other systems under study. Thus, the electrochemical method provides preliminary information on a possibility of synthesis of chelate complexes with ligands of this type in a chosen solvent and on the complexation rate.

The first reduction peak of the complexes under study corresponds to the two-electron process (which was proved by the electrochemical study on the RDE as compared to the wave of the one-electron oxidation of ferrocene). This means that two cobalt atoms are independent of each other, *i.e.*, the reduction of the first metal center (Co^{II} \rightarrow Co^I) has no effect on the second cobalt atom, which is reduced, therefore, at the same potential (about -0.7 V). Probably, this is related to the fact that one coordinated cobalt atom is considerably remote from another atom and the donating nitrogen atoms are not connected by any conjugated system of bonds *via* which electrons could be transferred.

Experimental

The starting compounds 1 and 2 were synthesized from phenyl isothiocyanate (or methyl isothiocyanate), glycine, and 2-pyridinecarbaldehyde according to earlier described procedures.⁵ The course of the reactions was monitored by TLC on Silufol plates.

¹H and ¹³C NMR spectra were measured on a Varian-XR-400 instrument with a working frequency of 400 and 100 MHz, respectively, in CDCl₃. IR spectra were recorded on an UR-20 instrument in Nujol and on an IR-200 FTIR spectrometer (ThermoNicolet, USA) with a resolution of 4 cm^{-1} . UV spectra were recorded on a Perkin-Elmer, λ -25 instrument in CH₃CN. Mass spectra were obtained on a Finnigan MAT 95 XL instrument (ionization energy 70 eV, temperature of the source 200 °C, temperature-programmed regime of the rod 30–290 °C/15 deg min⁻¹). Oxidation and reduction potentials were measured on a PI-50-1.1 potentiostat connected with a PR-8 programmer. Cyclic voltammograms and waves on the RDE were recorded on a two-coordinate recorder. The working electrode was a glassy-carbon disk electrode. Potentials were measured relative to the standard potential of the ferrocene/ferrocenium ion (Fc/Fc⁺) redox system using a silver chloride Ag/AgCl/KCl(sat.) reference electrode. The supporting electrolyte was tetrabutylammonium perchlorate $(C_4H_9)_4NClO_4$ (highest purity grade (99.8%), Fluka).

Reactions of 3-phenyl-2-thioxo-5((Z)-2-pyridylmethylene)imidazol-4-one (1) and 3-methyl-2-thioxo-5((Z)-2-pyridylmethylene)imidazol-4-one (2) with α,ω -dibromoalkanes (general procedure). A. α,ω -Dibromoalkane (2.5 mmol) was added for 5 min with stirring to a mixture of compound 1 (1.4 g, 5 mmol), dry K₂CO₃ (1.04 g, 7.5 mmol), and a catalytic amount of triethylbenzylammonium chloride (0.57 g, 0.25 mmol) in acetone (10–15 mL). The reaction mixture was stirred for 1 h at ~20 °C, and a precipitate that formed was filtered off and washed with acetone. The filtrate was evaporated *in vacuo* to dryness, and a precipitate that formed was recrystallized from ethyl acetate.

B. α , ω -Dibromoalkane (2.5 mmol) was added for 5 min with stirring at -10 °C to a mixture of compound 1 (1.4 g, 5 mmol) or compound 2 (1.1 g, 5 mmol) and dry K₂CO₃ (1.04 g, 7.5 mmol) in DMF (15 mL). The reaction mixture was stirred for 2 h at -10 °C and then for 2 h at room temperature. Then water (50 mL) was added to the mixture. A precipitate that formed was filtered off, washed with water, and recrystallized from ethyl acetate.

(5*Z*,5´*Z*)-2,2´-(Ethane-1,2-diyldisulfanyldiyl)bis(3-phenyl-5-(2-pyridylmethylene)-3,5-dihydro-4*H*-imidazol-4-one) (3), m.p. 259 °C. ¹H NMR, δ : 8.75 (d, 1 H, H_{α -Py}, *J* = 7.9 Hz); 8.66 (d, 1 H, H_{β '-Py}, *J* = 4.0 Hz); 7.81 (td, 1 H, H_{β -Py}, *J*₁ = 7.3 Hz, *J*₂ = 2.3 Hz); 7.42 (m, 3 H, Ph); 7.29 (m, 2 H, Ph); 7.11 (td, 1 H, H_{γ -Py}, *J*₁ = 7.5 Hz, *J*₂ = 1.0 Hz); 7.18 (s, 1 H, CH=); 3.11 (t, 2 H, SCH₂, *J* = 7.5 Hz). ¹³C NMR, δ : 169.43, 166.77, 154.33, 150.96, 140.46, 136.86, 132.76, 130.43, 129.07, 128.02, 125.61, 124.14, 108.10, 30.22. IR, v/cm⁻¹: 1710 (C=O); 1670 (C=N); 1640 (C=C). Mass spectrum, *m/z* (*I*_{rel} (%)): 588 [M]⁺ (2). Found (%): C, 65.28; H, 4.10; N, 14.11. C₃₂H₂₄N₆S₂O₂. Calculated (%): C, 65.31; H, 4.08; N, 14.29.

(5*Z*,5´*Z*)-2,2´-(Hexane-1,6-diyldisulfanyldiyl)bis(3-phenyl-5-(2-pyridylmethylene)-3,5-dihydro-4*H*-imidazol-4-one) (4), m.p. 240 °C. ¹H NMR, δ : 8.77 (d, 1 H, H_{α -Py}, *J* = 7.9 Hz); 8.66 (d, 1 H, H_{β '-Py}, *J* = 3.9 Hz); 7.75 (td, 1 H, H_{β -Py}, *J*₁ = 7.3 Hz, *J*₂ = 2.3 Hz); 7.45 (m, 3 H, Ph); 7.30 (m, 2 H, Ph); 7.17 (s, 1 H, CH=); 7.13 (dd, 1 H, H_{γ -Py}, *J*₁ = 7.5 Hz, *J*₂ = 0.9 Hz); 3.32 (t, 2 H, SCH₂, *J* = 7.5 Hz); 1.86 (quint, 2 H, CH₂, *J* = 7.6 Hz); 1.54 (quint, 2 H, CH₂, *J* = 7.5 Hz). ¹³C NMR, δ : 153.86, 150.04, 135.94, 132.22, 129.50, 129.20, 127.28, 126.76, 124.05, 123.12, 52.03, 50.05, 38.47, 30.89, 28.80, 28.40. IR, v/cm⁻¹: 1700 (C=O); 1670 (C=N); 1630 (C=C). Found (%): C, 66.71; H, 5.04; N, 12.65. C₃₆H₃₂N₆S₂O₂. Calculated (%): C, 67.06; H, 5.00; N, 13.03.

(5*Z*,5´*Z*)-2,2´-(Octane-1,8-diyldisulfanyldiyl)bis(3-phenyl-5-(2-pyridylmethylene)-3,5-dihydro-4*H*-imidazol-4-one) (5), m.p. 242 °C. ¹H NMR, δ : 8.77 (d, 1 H, H_{α -Py}, *J* = 7.9 Hz); 8.65 (d, 1 H, H_{β '-Py}, *J* = 3.9 Hz); 7.73 (td, 1 H, H_{β -Py}, *J*₁ = 7.3 Hz, *J*₂ = 2.3 Hz); 7.45 (m, 3 H, Ph); 7.30 (m, 2 H, Ph); 7.17 (s, 1 H, CH=); 7.15 (dd, 1 H, H_{γ -Py}, *J*₁ = 7.5 Hz, *J*₂ = 0.9 Hz); 7.19 (s, 1 H, CH=); 1.82 (quint, 2 H, SCH₂, *J* = 14.1 Hz); 1.64 (m, 2 H, CH₂); 1.42 (m, 4 H, CH₂--CH₂). IR, v/cm⁻¹: 1680 (C=O); 1660 (C=N); 1610 (C=C). Mass spectrum, *m*/*z* (*I*_{rel} (%)): 672 [M]⁺ (13).

(5*Z*,5´*Z*)-2,2´-(Decane-1,10-diyldisulfanyldiyl)bis(3-phenyl-5-(2-pyridylmethylene)-3,5-dihydro-4*H*-imidazol-4-one) (6), m.p. 243 °C. ¹H NMR, δ : 8.83 (d, 1 H, H_{α -Py}, *J* = 7.9 Hz); 8.69 (d, 1 H, H_{β '-Py}, *J* = 3.9 Hz); 7.77 (td, 1 H, H_{β -Py}, *J*₁ = 7.3 Hz, *J*₂ = 2.3 Hz); 7.40 (m, 3 H, Ph); 7.30 (m, 2 H, Ph); 7.20 (s, 1 H, CH=); 7.13 (dd, 1 H, H_{γ -Py}, *J*₁ = 7.5 Hz, *J*₂ = 0.9 Hz); 3.32 (t, 2 H, CH₂, *J* = 7.3 Hz); 1.42 (m, 2 H, CH₂); 1.24 (m, 6 H, (CH₂)₆). IR, v/cm⁻¹: 1690 (C=O); 1670 (C=N); 1600 (C=C). Found (%): C, 68.23; H, 5.95; N, 11.67. C₄₀H₄₀N₆O₂S₂. Calculated (%): C, 68.54; H, 5.75; N, 11.09. (5*Z*,5´*Z*)-2,2´-(Butane-1,4-diyldisulfanyldiyl)bis(3-methyl-5-(2-pyridylmethylene)-3,5-dihydro-4*H*-imidazol-4-one) (7), m.p. 220 °C. ¹H NMR, δ : 8.82 (d, 1 H, H_{α -Py}, *J* = 7.9 Hz); 8.59 (d, 1 H, H_{β '-Py}, *J* = 4.0 Hz); 7.71 (td, 1 H, H_{β -Py}, *J*₁ = 7.3 Hz, *J*₂ = 2.3 Hz); 7.38 (m, 3 H, Ph); 7.31 (m, 2 H, Ph); 7.23 (s, 1 H, CH=); 7.13 (dd, 1 H, H_{γ -Py}, *J*₁ = 7.5 Hz, *J*₂ = 0.9 Hz); 3.41 (t, 2 H, SCH₂, *J* = 7.5 Hz); 3.08 (s, 3 H, NMe); 2.19 (quint, 2 H, CH₂, *J* = 7.5 Hz). IR, v/cm⁻¹: 1700 (C=O); 1660 (C=N); 1600 (C=C). Mass spectrum, *m/z* (*I*_{rel} (%)): 492 [M]⁺ (13).

(5*Z*,5*´Z*)-2,2*´*-(Hexane-1,6-diyldisulfanyldiyl)bis(3-methyl-5-(2-pyridylmethylene)-3,5-dihydro-4*H*-imidazol-4-one) (8), m.p. 205 °C. ¹H NMR, δ : 8.74 (d, 1 H, H_{α -Py}, *J* = 7.9 Hz); 8.63 (d, 1 H, H_{β '-Py}, *J* = 3.9 Hz); 7.69 (td, 1 H, H_{β -Py}, *J*₁ = 7.3 Hz, *J*₂ = 2.3 Hz); 7.35 (m, 3 H, Ph); 7.29 (m, 2 H, Ph); 7.17 (s, 1 H, CH=); 7.11 (dd, 1 H, H_{γ -Py}, *J*₁ = 7.5 Hz, *J*₂ = 1.0 Hz); 3.34 (t, 2 H, SCH₂, *J* = 7.4 Hz); 3.07 (s, 3 H, NMe); 1.91 (quint, 2 H, CH₂, *J* = 7.5 Hz); 1.59 (quint, 2 H, CH₂, *J* = 7.5 Hz). ¹³C NMR, δ : 170.60, 168.20, 154.70, 150.8, 141.34, 136.64, 127.62, 124.02, 123.68, 30.64, 29.05, 28.49, 26.71. IR, v/cm⁻¹: 1700 (C=O); 1670 (C=N); 1610 (C=C). Mass spectrum, *m/z* (*I*_{rel} (%)): 524 [M]⁺ (6).

(5*Z*,5´*Z*)-2,2´-(Decane-1,10-diyldisulfanyldiyl)bis(3-methyl-5-(2-pyridylmethylene)-3,5-dihydro-4*H*-imidazol-4-one) (9), m.p. 191 °C. ¹H NMR, δ : 8.81 (d, 1 H, H_{α-Py}, *J* = 7.9 Hz); 8.67 (d, 1 H, H_{β´-Py}, *J* = 3.9 Hz); 7.71 (td, 1 H, H_{β-Py}, *J*₁ = 7.3 Hz, *J*₂ = 2.3 Hz); 7.41 (m, 3 H, Ph); 7.29 (m, 2 H, Ph); 7.21 (s, 1 H, CH=); 7.10 (dd, 1 H, H_{γ-Py}, *J*₁ = 7.5 Hz, *J*₂ = 0.9 Hz); 3.37 (t, 2 H, SCH₂, *J* = 7.4 Hz); 3.18 (s, 3 H, NMe); 1.86 (quint, 2 H, CH₂, *J* = 7.3 Hz); 1.46 (m, 4 H, CH₂--CH₂). ¹³C NMR, δ : 184.2, 166.2, 150.9, 143.7, 143.0, 136.8, 128.2, 123.6, 106.0, 42.8, 39.5, 29.6, 29.15, 29.0. IR, v/cm⁻¹: 1700 (C=O); 1670 (C=N); 1600 (C=C). Mass spectrum, *m/z* (*I*_{rel} (%)): 580 [M]⁺ (13).

Synthesis of complexes (general procedure). Ethanol (3 mL) was carefully (over the flask wall) added to a solution of ligand 3 or 5-7 (0.034 mmol) in CH₂Cl₂ (2-3 mL) in such a manner that a two-phase system was formed. Then a solution of CoCl₂•6H₂O (16 mg, 0.068 mmol) in EtOH (2-3 mL) was slowly added. The flask with the reaction mixture was tightly closed and kept until a precipitate was formed. The precipitate was filtered off and dried in air. $(5Z,5^2)-2,2^2$ -(Ethane-1,2-divldisulfanyldivl)bis(3-phenyl-5-(2-pyridylmethylene)-3,5dihydro-4*H*-imidazol-4-one)dinickel(11) tetrachloride (3a), (5Z,5'Z)-2,2'-(octane-1,8-dividisulfanyldivi)bis(3-phenyl-5-(2-pyridylmethylene)-3,5-dihydro-4*H*-imidazol-4-one)dinickel(II) tetrachloride trihvdrate (5a), $(5Z,5^{2}Z)-2.2^{2}$ -(decane-1,10-diyldisulfanyldiyl)bis(3-phenyl-5-(2-pyridylmethylene)-3,5-dihydro-4H-imidazol-4-one)dinickel(11) tetrachloride dihydrate (6a), and (5Z,5'Z)-2,2'-(butane-1,4-diyldisulfanyldiyl)bis(3-methyl-5-(2-pyridylmethylene)-3,5-dihydro-4H-imidazol-4-one)dinickel(II) tetrachloride dihydrate (7a) were thus obtained.

The data on the composition of the complexes and the yields of the compounds synthesized are presented in Tables 1 and 2. Their spectral data are given in Table 3.

This work was financially supported by the Russian Foundation for Basic Research (Project No. 04-03-32845) and the Foundation "Universities of Russia" (Grant 05.03.046).

References

- 1. US Pat. 3994904; Chem. Abstr., 1976, 86, 10658m.
- 2. Czech. Pat. 151744; Chem. Abstr., 1974, 81, 63633b.
- 3. US Pat. 4452798A; Chem. Abstr., 1985, 101, 38476b.
- 4. A. G. Majouga, Ph. D. (Chem.) Thesis, M. V. Lomonosov Moscow State University, Moscow, 2005, 137 pp. (in Russian).
- V. Zubenko, *Tr. L'vov. Med. In-ta* [Works of Lvov Medical Institute], 1957, **12**, 83 (in Russian); *Chem. Abstr.*, 1960, **54**, 21059h.
- K. Kiec-Kononowicz and J. Karolak-Wojciechowska, *Phosphorus, Sulfur, Silicon*, 1992, 73, 235.
- J. Casas, E. Castellano, A. Macfas, N. Playa, A. Sanchez, J. Sordo, and J. Zukerman-Schpector, *Inorg. Chim. Acta*, 1995, 238, 129.
- R. S. Srivastava, R. R. Srivastava, and H. N. Bhargava, Soc. Chim. Fr., 1991, 128, 671.
- D. Kushev, G. Gorneva, V. Enchev, E. Naydenova, J. Popova, S. Taxirov, L. Maneva, K. Grancharov, and N. Spassovska, J. Inorg. Biochem., 2002, 89, 203.

- M. Choudhry, A. Burrows, M. Mingos, J. White, and D. Williams, *Chem. Commun.*, 1995, 1521.
- M. Chowdhry, M. Mingos, A. White, and D. Williams, *Chem. Commun.*, 1996, 899.
- J. Casas, A. Castineiras, N. Playa, A. Sanchez, J. Sordo, J. Varela, and E. Vazquez-Lopez, *Polyhedron*, 1999, 18, 3653.
- J. Casas, E. Castellano, A. Masias, N. Playa, A. Sanchez, J. Sordo, J. Varela, and E. Vazquez-Lopez, *Polyhedron*, 2001, 20, 1845.
- 14. P. Molina, A. Tarrada, D. Curiel, and C. Ramirez de Arellano, *Tetrahedron*, 1999, **55**, 1417.
- M. Arca, F. Demartin, F. Devillanova, A. Garau, F. Isaia, V. Lippolis, and G. Verani, *Inorg. Chem.*, 1998, **37**, 4164.
- 16. A. Hassaan, Sulfur Lett., 1991, 13, 1.
- A. G. Majouga, E. K. Beloglazkina, S. Z. Vatsadze, A. A. Moiseeva, K. P. Butin, and N. V. Zyk, *Mendeleev Commun.*, 2004, 14, 115.

Received February 28, 2005; in revised form June 21, 2005