## Electrochemical Synthesis of the Calix[4]resorcinol Nickel Complexes Modified with Thiophosphoryl Fragments

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**Abstract**—Nickel complexes of 1:1 composition with calix[4]resorcinols (L) modified with thiophosphyl fragments were synthesized. In the process of electrochemical reduction these complexes are capable of providing spherical homogeneous Ni(0)L particles with a narrow size distribution, stable both on the electrode and in the solution. The redox properties of the metal complexes were studied. The dimensions of the complexes obtained were estimated using the atomic force microscope (AFM) equipped with an electrochemical attachment.

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At present the supramolecular catalysis attracts much attention, suggesting the use of compounds with molecular recognition function as the components of catalytic systems: cyclodextrins and calixarenes, which, due to the presence of the hydrophobic cavity, are capable of forming *guest-host* inclusion complexes with various organic substrates. To date, despite extensive investigation of this class of compounds, examples of their application in catalysis are scarce [1, 2].

One of the promising areas to search for new catalytic systems is the creation of catalysts that combine in a single molecule the properties of metal complexes capable of molecular recognition. Calixarenes provide unique opportunity for the selective functionalization of the upper and lower rims of the macrocycle by the heteroatomic groups to form a molecular system that has multiple binding sites. It is interesting to investigate the possibility of stabilization of the transition metals in low oxidation states, first of all (0, +1), by the calixarenes with functional groups containing heteroatoms (P, N, S). The latter are effective complexing sites capable to bind a metal and form a supramolecular structure. A successful implementation of macro complexes with a narrow size distribution of particle would permit designing catalysts for various reactions. Metal nanostructures

with properties that depend on the size and shape of the particle have a variety of interesting applications, e. g., in catalysis, as the magnetic storage media of information, biosensors, in the high surface energy Raman scattering (SERS) [3–6]. In recent years, the preparation of thin films consisting of metal nanostructures is one of the hottest topics [7, 8].

Electrochemical synthesis of metal complexes in low oxidation states is well known and in some cases has significant advantages [9, 10].

Currently, the literature presents a large number of metal complexes based on calixarenes functionalized with organophosphorus fragments containing tricoordinated phosphorus atom [11-13]. However, these compounds are in most cases hydrolytically unstable, which limits their practical application. The calixarenes functionalized by organophosphorus fragments containing phosphoryl and thiophosphoryl groups may be deprived of this shortage. The presence of additional coordination sites in four organophosphorus fragments with the tetracoordinate phosphorus atom resistant to hydrolysis enhances the possibility of the synthesis of organometallic complexes with calixarenes, and extends the area of their practical use. The use of electrochemical methods for the synthesis of metal(0) complexes based on calix[4]resorcinol was

not found in the literature. The purpose of this study is to develop methods for the electrochemical synthesis of nickel(0) complexes with calix[4]resorcinol functionalized by the thiophosphoryl fragments, and the evaluation of the dimension of the structures obtained using an atomic force microscope equipped with an electrochemical attachment, which allows monitoring of the formation of products in time.

As the objects of the study we selected the calix[4] resorcinols **I–III** modified with thiophosphoryl fragments, because they have high complexing ability,

and, moreover, are resistant to hydrolysis and electrochemical oxidation. The ligands **I–III** have the *chair* conformation with *rctt*- configuration of the thiophosphoryl substituents, namely, are characterized by symmetrical arrangement of two pairs of binding sites [14]. The electrochemical properties of calix[4]resorcinols **I–III** were studied by cyclic voltammetry. In the studied range of potentials (+1.5 to -3.0 V) they are electrochemically inactive. Further we used the CVA method to study solutions of the calix[4]resorcinols **I– III** with NiBr<sub>2</sub> in DMF at various ratios.



The electrochemical reduction peak of nickel bromide contains an irreversible peak at -1225 mV, which corresponds to the transfer of two electrons. Adding equimolar amounts of ligands **I–III** to the solution of



**Fig. 1.** CVA of solution of calix[4]resorcinols **I-III** with NiBr<sub>2</sub> in DMF at the component ratio 1:1. (1) Ni(II)L<sup>I</sup>, (2) Ni(II)L<sup>II</sup>, (3) Ni(II)L<sup>III</sup>, (4) NiBr<sub>2</sub> ( $c = 5 \times 10^{-3}$  M).

NiBr<sub>2</sub> in DMF results in disappearance of initial reduction peak and appears a new peak at -1165 (NiL<sup>II</sup>), (NiL<sup>III</sup>), (NiL<sup>1</sup>), -1299-1370 mV respectively. The reduction current of each of these peaks decreases (Fig. 1). This is probably due to the coordination of NiBr<sub>2</sub> with the ligand and a corresponding decrease in the diffusion coefficient. The binding of nickel with the calixarene molecule follows also from the decrease in the adsorption currents. Similar examples were described in the literature: In the study of the binding of nitroxide ligands with Co, Ni, and Mn by the CVA method the complexation criterion was the shift of the peaks of the metal reduction [15, 16]. Further increase in the concentration of nickel bromide in the investigated solutions led only to an increase in the Ni(II)/Ni(0) reduction current. After passing through the electrolyte (a solution of a ligand I-III in DMF with NiBr<sub>2</sub> at a ratio of 1:1) 2  $e^{-}$  of electricity per one mol of Ni, in the voltammograms at a potential of -1200 mV the disappearance of the peak of Ni(II)/Ni(0) was observed. In the studied range of potentials (+1.5 to -3.0 V) on the polarization curves of Ni(0)L<sup>I-III</sup> the peaks of reduction-oxidation were also absent, which

may be indicative of the electrochemical stability of the obtained complexes.

Analysis of the electrochemical characteristics obtained at the registration of CVA of calix[4] resorcinols I–III solutions with NiBr<sub>2</sub> in DMF at different ratios showed that the shift of the peak of Ni(II)/Ni(0) reduction with respect to the source nickel bromide occurs at the 1:1 ratio of the reagents. The complex Ni(II)L<sup>I</sup> is reduced easier than nickel bromide, and the complexes Ni(II)L<sup>II,III</sup> are reduced in a more negative region, which is probably due to differences in the structure of the initial ligands (calix [4]resorcinol) and the stability of the complexes formed.

The composition of metal complexes Ni(II)L<sup>I-III</sup> was determined by the Bent-French limited logarithm method [17], which allows to find the coefficient n in the equation: Ni(II) + nL = Ni(II) Ln, using a logarithmic dependence of the optical density of the solution on the concentration of one component. The absorption bands of the compounds studied are shown in Table 2. Changes in optical density with increasing concentration of ligand were observed at 290 (280) nm. The coefficient n for the ligands I–III was found equal to 0.84, 0.74, and 0.79, respectively. Thus, by calculating the slope we found that the metal: ligand stoichiometry of the complexes formed was 1:1 (Fig. 2).

Joint electrochemical reduction of calix[4]resorcinols **I–III** with nickel bromide was carried out in a separated electrolytic cell with platinum cathode and anode, in DMF. 2 F of electricity per 1 mole of nickel salt was passed through the solution. During the synthesis the reaction mixture changed color from orange to dark cherry. The resulting reduction products were studied by <sup>31</sup>P, <sup>1</sup>H NMR spectroscopy, IR, UV spectroscopy, and mass spectrometry. In the IR spectra of the isolated metal complexes Ni(0)L<sup>I–III</sup> is observed

 Table 1. Electrochemical characteristics of solutions of calix[4]resorcinols I–III complexes with NiBr<sub>2</sub> in DMF

Compound	$-E^{\rm red}$ , mV	<i>I</i> , mA	$\Delta E^{\rm red},{ m mV}^{ m a}$	
Ni(II)L <sup>I</sup>	1165	0.0275	64	
Ni(II)L <sup>II</sup>	1299	0.0146	70	
Ni(II)L <sup>III</sup>	1370	0.0464	141	
NiBr <sub>2</sub>	1229	0.1212		

<sup>a</sup>  $\Delta E^{\text{red}}$  is difference of the reduction potentials of complexes Ni(II)L<sup>1-III</sup> and pure NiBr<sub>2</sub>.

a shift of the absorption band of thiophosphoryl group P=S to the low-frequency region by 20-30 cm<sup>-1</sup> relative to free calix[4]resorcinols I-III. This shift may indicate the formation of the P=S→Ni coordination bond. Similar shift of the absorption bands of the P=S bond vibration was observed by the example of complexes of Ni(II) with N-thiophosphorylthioureas [18]. The <sup>31</sup>P NMR spectra of the initial ligands I–III are characterized by a singlet signal in the range of 63.0–78.4 ppm. When the calixarene was mixed with the nickel bromide at subsequent electrochemical reduction of the complex Ni(II)L to Ni(0)L there was only a slight shift of the resonance signal of the phosphorus atom (1–0.5 ppm). In the <sup>1</sup>H NMR spectra of the complexes obtained the greatest shift of the peaks, by 1.2–1.6 ppm, was observed for the methylene protons of ethoxy groups located at the phosphorus atom, in the Ni(0)L<sup>1,11</sup> complexes, or endocyclic methylene protons in the complex Ni(0)  $L^{III}$ . The values of molecular weights of the Ni(0) $L^{II,III}$ complexes determined by the MALDI mass spectrometry indicate the formation of 1:1 complexes. The composition of the complexes was confirmed by elemental analysis with the atomic-emission spectrometer.

 Table 2. Spectral characteristics of the products of electrochemical reduction of calix[4]resorcinols I–III complexes with nickel bromide

L	IR, v, $cm^{-1}$ (P=S)		$^{31}$ P NMR, $\delta_{P}$ , ppm (DMSO)		Mass-spectrum (MALDI) <i>m</i> / <i>z</i>		UF, nm (DMF)	
	L	Ni(0)L	L	Ni(0)L	L	Ni(0)L 1:1	L	Ni(0)L 1:1
Ι	830	799	63.0	61.9		1523.1	290, 350	290, 360
II	820	802	62.1	61.8	1519.6	1578.9	290	290, 370
III	832	797	78.4	78.0	1400.0	1459.9	280	280, 370



 $-\log c(L)$ 

Fig. 2. The logarithmic dependence of the optical density of the solution on the concentration of the ligands I–III.

The size of the Ni(0)L particles was studied by means of atomic force microscopy with an electrochemical attachment. When a current was passed through a solution of Ni(II)L<sup>I</sup> in DMF spherical particles formed with an average size of 100 nm (Fig. 3), and this size did not vary with the time of the electrolysis.

The investigation of solution of the complex Ni(II)  $L^{III}$  in DMF using atomic force microscopy showed that in the first minutes of electrolysis the solution began rapidly to darken, and on the HOPG substrate appear dark formations of various shapes, poorly connected with it. Therefore, to monitor the process we used optical microscopy that showed the formation of mostly spherical particles in 5 min (Fig. 4).

These particles do not differ much from each other by size. After the break in the electrical circuit in the cell the substrate began to clear from the deposited particles. This process was very fast: within a few minutes the surface became completely clean. It also confirms the weak binding of the deposited particles by the substrate. A similar pattern was observed at the electrolysis of a solution of the complex Ni(II)L<sup>II</sup>. Therefore, the size of particles of the resulting complexes Ni(0)L<sup>I-III</sup> was studied after the completion of electrolysis, extraction of sample from the liquid medium and drying it on a substrate for 1 h at 60°C, using intermittent contact atomic force microscopy. The results obtained showed that at the electrochemical reduction of the complex Ni(II)L<sup>I</sup> individual spherical particles are formed with an average size of 450 nm (Fig. 5).

Reduction of the Ni(II)L<sup>II</sup> complex resulted in the formation of ensembles with an average size of 600 nm combined of individual particles (Fig. 6).

After electrolysis of the solution of the complex Ni(II)L<sup>III</sup>, the entire surface of the substrate was covered with a dense layer of particles. As in the case of the complex based on calixarene **II** the ensembles consisting of individual particles could be distinguished. The average size of these ensembles is 350 nm (Fig. 7).

Thus, the data on the dimensions of the particles of Ni(0) complexes with calix[4]resorcinols **I–III**, obtained by atomic force microscopy, indicate the formation of particles with narrow size distribution, which is an important factor in the development of catalytic systems based on them.

#### **EXPERIMENTAL**

Electrochemical measurements were performed in the regime of cyclic voltammetry using a potentiostat E2P of BAS Epsilon (USA), consisting of a measuring unit, a Dell Optiplex 320 computer with the installed



Fig. 3. Atomic force microscopy image of particles formed at the reduction of the complex of calix[4] resorcinol I with NiBr<sub>2</sub> (1:1 ratio) in DMF in the process of electrolysis, and their size distribution.



**Fig. 4.** The image of the electrode surface with the particles formed at the reduction of the complex of calix[4]-resorcinol **III** with NiBr<sub>2</sub> (1:1 ratio) in DMF in the process of electrolysis in an optical microscope at 400× magnification.

software EpsilonES-USB-V200, and the electrochemical cell C3. As working electrodes a stationary glassy carbon electrode, Ag/AgCl reference electrode for voltammetric measurements, and auxiliary electrode of platinum wire of 0.5 mm diameter were used. Measurements were carried out under argon atmosphere.

Preparative electrolysis was performed in a three electrode 30 ml cell using a DC source B5-49. The value of the potential of the working electrode was registered with a DC voltmeter B7-27. The working surface of the cylindrical platinum cathode used as the working electrode was equal to  $20.0 \text{ cm}^2$ . In experiments with separation of anodic and cathodic spaces was used a ceramic diaphragm with the pore size 900 nm. As anode served a platinum spring, the anolyte was a saturated solution of the background electrolyte used in the catholyte, Bu<sub>4</sub>NBF<sub>4</sub> in DMF. During electrolysis, the electrolyte was stirred with a magnetic stirrer at a constant flow of argon passed through a drying system.

<sup>1</sup>H NMR spectra were recorded on a multinuclear spectrometer Bruker Avance DRX 400 (400 MHz), with respect to the signal of residual protons of deuterated solvent as an internal reference. IR spectra were recorded on a Bruker Vector-22 spectrometer in the frequency range 400–3600 cm<sup>-1</sup> in mineral oil. Mass spectra were obtained on a MALDI mass spectrometer ULTRAFLEX-III. UV spectra were recorded on a Perkin Elmer Lambda 35 spectrophotometer.

Microscopic studies were performed with a Veeco (USA) scanning probe microscope MultiMode V with



**Fig. 5.** Atomic force microscopy image of particles formed at the reduction of the complex of calix[4]resorcinol I and NiBr<sub>2</sub> (1:1 ratio) in DMF after drying the substrate, and their size distribution.

an electrochemical cell of MMTMEC model (Veeco). When scanning, we used the rectangular cantilevers RTESP (Veeco) with silicon probes. The resonant frequency of the cantilevers occurs in the region 250-350 kHz, and the radius of curvature of the probe is 10<sup>-13</sup> nm. The microscopic images were obtained with a resolution of 256×256 pixels per frame at the scan rate 1 Hz. We used a scanner 8279JV with the largest field of scanning. To eliminate the distortion associated with the vibration of the microscope under the influence of external noise, a vibration system SG0508 was used, able to smooth out the vibrations with a frequency of 0.5 Hz (lower limit). The electrochemical cell contained a silver electrode and a platinum auxiliary electrode. The working electrode was the HOPG substrate for atomic force microscopy (highly oriented pyrolytic graphite).

Elemental analysis data were obtained on an atomic emission spectrometer iCAP 6300 DUO.

DMF was dried over potassium carbonate and then distilled over CaH<sub>2</sub>. Benzene was distilled over sodium, diethyl ether was refluxed over  $P_2O_5$  followed by distillation, to remove water traces. After purification, the solvents were stored in an atmosphere of dry argon.



**Fig. 6.** Atomic force microscopy image of particles formed at the reduction of the complex of calix[4]resorcinol **II** and NiBr<sub>2</sub> (1:1 ratio) in DMF after drying the substrate, and their size distribution.

All syntheses were carried out in an atmosphere of dry argon.

General procedure of synthesis of Ni(0)L<sup>I-III</sup>. Electrochemical cell was charged with  $2.5 \times 10^{-4}$  mol calix[4]resorcinol dissolved in 20 ml of DMF, a solution of  $2.5 \times 10^{-4}$  mol of nickel bromide trihydrate was added, and the mixture was stirred with a magnetic stirrer. Through the electrolyte 2 F of electricity per one mole of nickel bromide trihydrate (134 mA h) was passed. At the end of electrolysis the solvent was removed on a rotary evaporator at 60°C, the dry residue was washed with water (3×30 ml), insoluble precipitate was filtered off, washed with diethyl ether, and dried in a vacuum (50°C, 0.04 mm Hg) to constant weight.

Nickel 4,6,10,12,16,18,22,24-octahydroxy-2,8,14,20tetra[4-(diethyl thiophosphoryloxy)phenyl]pentacyclo[19.3.1.1<sup>3,7</sup>,1<sup>9,13</sup>,1<sup>15,19</sup>]octacosa-1(25),3,5,7(28),9,11,-13(27),15,17,19(26),21,23-dodecaenylate, brick-red powder, yield 0.30 g (78.9%), mp >350°C. <sup>1</sup>H NMR spectrum (DMF- $d_7$ ,  $\delta$ , ppm): 0.98 t (24H, C<u>H</u><sub>3</sub>CH<sub>2</sub>, <sup>3</sup> $J_{\text{HH}}$  7.08 Hz), 3.70 m (16H, CH<sub>3</sub>CH<sub>2</sub>); 5.63 s (4H, CH); 5.39 and 6.10, two s (4H, H<sub>Ar</sub><sup>h,v</sup>); 6.15 and 6.23



**Fig. 7.** Atomic force microscopy image of particles formed at the reduction of the complex of calix [4] resorcinol **III** and NiBr<sub>2</sub> (1:1 ratio) in DMF after drying the substrate, and their size distribution.

two s (4H,  $H_{Ar}^{h,v}$ ); 6.61 m (16H, CH=); 8.04 and 8.25 two s (8H, OH<sup>h,v</sup>). <sup>31</sup>P NMR spectrum (DMF,  $\delta$ , ppm): 61.97. IR spectrum (mineral oil, v, cm<sup>-1</sup>): 799 (P=S), 3174 (–OH). MALDI mass-spectrum, *m/z*: 1523.1 [*M*]<sup>+</sup>. Found, %: Ni 3.05. C<sub>68</sub>H<sub>76</sub> NiO<sub>20</sub>P<sub>4</sub>S<sub>4</sub>. Calculated, %: Ni 3.87;

Nickel 4,6,10,12,16,18,22,24-octahydroxy-2,8,14,20tetra[3-(diethyl thiophosphoryloxy)phenyl]-5,11,17,23tetramethylpentacyclo[19.3.1<sup>13,7</sup>.1<sup>9,13</sup>.1<sup>15,19</sup>]octacosa-1(25),3,5,7(28),9,11,13(27),15,17,19(26),21,23-dodecaenylate, dark red powder, yield 0.29 g (74%), mp > 350°C. <sup>1</sup>H NMR spectrum (DMF- $d_7$ ,  $\delta$ , ppm): 0.94 t (24H, C<u>H</u><sub>3</sub>CH<sub>2</sub>, <sup>3</sup>*J*<sub>HH</sub> 7.14 Hz), 3.72 m (16P, CH<sub>3</sub>C<u>H</u><sub>2</sub>); 1.93 and 2.08 two s (12H, CH<sub>3</sub><sup>h,v</sup>); 5.73 s (4H, CH); 5.28 and 6.9 two s (4H, H<sub>Ar</sub><sup>h,v</sup>); 6.64 m (16H, CH=); 7.40 and 7.65 two s (8H, OH<sup>h,v</sup>). <sup>31</sup>P NMR spectrum (DMF,  $\delta$ , ppm): 61.87. IR spectrum (mineral oil, v, cm<sup>-1</sup>): 802 (P=S), 1057 (POC), 3539 (–OH). MALDI mass-spectrum, *m/z*: 1578.9 [*M*]<sup>+</sup>. Found, %: Ni 2.98. C<sub>72</sub>H<sub>84</sub> NiO<sub>20</sub> P<sub>4</sub>S<sub>4</sub>. Calculated, %: Ni 3.74;

Nickel 4,6,10,12,16,18,22,24-octahydroxy-2,8,14,20tetra[4-(1,2,3-dioxothiophosphoryloxy)phenyl]-5,11,17,23-tetramethylpentacyclo[19.3.1<sup>13,7</sup>.1<sup>9,13</sup>.1<sup>15,19</sup>]- octacosa-1(25),3,-5,7(28),9,11,13(27),15,17,19(26),21,23dodecaenylate, dark-orange powder, yield 0.31 g (85.1%), mp > 350°C. <sup>1</sup>H NMR spectrum (DMF- $d_7$ ,  $\delta$ , ppm): 1.90 and 2.07 two s (12H, CH<sub>3</sub><sup>h,v</sup>); 3.18 m (16H, *p*-CH<sub>2</sub>); 5.47 s (4H, CH); 5.76 and 6.15 two s (4H, H<sub>Ar</sub><sup>h,v</sup>); 6.42 m (16H, CH=); 7.01 and 7.45 two s (8H, OH<sup>h,v</sup>). <sup>31</sup>P NMR spectrum (DMF,  $\delta$ , ppm): 78.0. IR spectrum (mineral oil, v, cm<sup>-1</sup>): 797 (P=S), 3407 (OH). MALDI mass-spectrum, *m/z*: 1459.9 [*M*]<sup>+</sup>. Found, %: Ni 3.76. C<sub>64</sub>H<sub>60</sub>Ni<sub>4</sub>O<sub>20</sub>P<sub>4</sub>S<sub>4</sub>. Calculated, %: Ni 4.04.

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