

ЭЛЕКТРОХИМИЧЕСКОЕ ПОВЕДЕНИЕ И АКТИВНОСТЬ СОЛЕЙ МЕЗО – ТЕТРАКИС(1'-МЕТИЛ-ПИРИД-4- И 3-ИЛ)ПОРФИНА И КОМПЛЕКСОВ КОБАЛЬТА

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Синтезированы и охарактеризованы растворимые в воде соли 5,10,15,20-тетраakis(1'-метил-пирид-4- и -3-ил)порфин тетратозилаты $[H_2(1'-метил-Ру-4- и -3)_4P(Ts^-)_4]$ и тетраиодиды $[H_2(1'-метил-Ру-4- и -3)_4P(I^-)_4]$, 5,10,15,20-тетраakis(1'-метил-пирид-4- и -3-ил)порфирилат кобальта тетратозилат $[Co-тетраakis(1'-метил-Ру-3)_4P(Ts^-)_4]$, отличающиеся изомерией функционального мезо-заместителя молекулы порфиринов и природой противоиона (I, Ts⁻). Проведены электрохимические исследования и получены данные о редокс-поведении, эффективности использования порфириновых соединений в реакции электровосстановления молекулярного кислорода. Методом циклической вольтамперометрии установлено, что в среде аргона для лигандов наблюдаются две стадии процесса их электровосстановления, для металлокомплексов зафиксированы дополнительные переходы: один процесс электровосстановления макроцикла в области потенциалов -0,78 ... -1,36 В, и процесс окисления (восстановления) $Co^{3+} \leftrightarrow Co^{2+}$, локализованный на атоме металла при $E_{red/ox} = 0,19$ В. N-замещение пиридинного фрагмента порфиринов приводит к некоторому увеличению их восстановительной способности, по сравнению с незамещенными тетрапиридилпорфиринами $[H_2(Ру-4- и -3)_4P]$. Оценена возможность применения растворимых в воде порфиринов в электрокатализе реакции восстановления молекулярного кислорода. Показано, что природа катиона металла оказывает существенное влияние на электрокаталитическую активность соединений в реакции ионизации молекулярного кислорода в водно-щелочном растворе. Активность комплексов $Co(1'-метил-Ру-4- и -3)_4P$ тетратозилатов возрастает по сравнению с $[H_2(1'-метил-Ру-4- и -3)_4P(Ts^-)_4]$ на ~50-90 мВ, и системой без катализатора на ~140-160 мВ.

Ключевые слова: порфирины, комплексы кобальта(II), вольтамперометрия, электровосстановление, молекулярный кислород

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**ELECTROCHEMICAL BEHAVIOR AND ACTIVITY
OF MESO - TETRAKIS(1'-METHYL-PYRID-4- AND 3-YL)PORPHIN SALTS
AND COBALT COMPLEXES**

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In this work 5,10,15,20-tetrakis(1'-methyl-pyrid-4- and -3-yl)porphin tetratosylates and tetraiodide $[H_2(1'-methyl-Py-4- and -3)_4P]^{4+} (X^-)_4$, 5,10,15,20-tetrakis(1'-methyl-pyrid-4- and -3-yl)porphin tetratosylates cobalt $[Co-tetrakis(1'-methyl-Py-4- and -3)_4P]^{4+} (Ts^-)_4$ have been synthesized and characterized. These compounds were differed by the isomerism of the meso-substituent of the porphyrin molecule and the nature of the counterion (Ts^- , I^-). The data of the redox-behavior and efficiency of the use of porphyrin compounds in oxygen reduction reaction (ORR) have been obtained. The electrochemical behavior has been studied by using the cycling voltammetry method. It should be noted that two stages of the electroreduction process were observed in an argon medium for ligands. For the cobalt complexes additional processes was found. The process of the porphyrin macrocycle electroreduction in the potential region of $-0.78 \dots -1.36$ V and the $Co^{3+} \leftrightarrow Co^{2+}$, oxidation (reduction) process localized on the metal atom at $E_{red/ox} = 0.19$ V were found. The N-substitution of the pyridyl fragment of porphyrins leads to a small increase in their reducing ability, in comparison with unsubstituted tetrapyrrolylporphyrins $[H_2(Py-4- and -3)_4P]$. The possibility of using water-soluble porphyrins in the ORR electrocatalysis has been considered. It has been shown that the nature of the metal cation has a significant effect on the electrocatalytic activity of compounds in the molecular oxygen ionization reaction of in an aqueous-alkaline media. The activity of Co-complexes was increased by $\sim 50-90$ mV compared with ligands and a system without a catalyst at $\sim 140-160$ mV.

Keywords: porphyrins, cobalt-complexes, voltammetry, electroreduction, electrocatalysis, molecular oxygen

INTRODUCTION

Porphyrins and other tetrapyrrole macrocycles have a variety of functional properties [1-5], which are used in natural and artificial systems. Porphyrins, chlorines, corolles are found everywhere and represent unique molecules. They are involved in the basic processes that support living systems. Various metal centers included in the tetradentate ligand are key to achiev and regulate vital processes such as electron transfer and catalytic transformations. A special effect on the functionality of these macromolecules is also determined by the corresponding substituents [1, 5-6].

Currently, the study of the physicochemical and catalytic properties of macroheterocyclic com-

pounds of the water-soluble porphyrins is of great scientific and practical interest. This is due to the possibility of using water-soluble compounds as drugs, catalysts and inhibitors for redox reactions, photosensitizers for photodynamic therapy, in the processes of inactivation of bacteria and microbes, analytical reagents [3, 7-8].

Porphyrins are a group of heterocyclic organic compounds consisting of four modified methine-bridged pyrrole rings. They interact with carbon materials through the π - π interaction.

Electrochemical studies of TMPyP have been carried out in non-aqueous media [9-11]. The electrochemistry of $[M(TMPyP)]^{n+}(X^-)_n$ in non-aqueous media has been characterized by the processes of reduc-

tion of the conjugated π -system of the macrocycle, electron-deficient N-methyl-pyridyl substituents and, in some cases, the central metal ion. The electroreduction of $[\text{Cu}(\text{TMPyP})]^{4+}$, $[\text{Zn}(\text{TMPyP})]^{4+}$, $[\text{VO}(\text{TMPyP})]^{4+}$ has been studied in a dimethylformamide (DMF) medium. It has been established that the process occurs in three stages of addition of two electrons and includes a total of six electrons [10]. The reduction of the porphyrin π -system of the $[\text{Co}^{\text{II}}(\text{TMPyP})]^{4+}$ macrocycle in DMF is accompanied by the addition of six electrons in four stages to form $[\text{Co}^{\text{II}}(\text{TMPyP})]^{2-}$ as a final product [11]. It was found that a single one-electron oxidation transition of the complex causes the conversion of Co(II) to Co(III) in the potential range of +0.29 – -0.01 V vs to the saturated calomel electrode (SCE). The first stage of recovery occurs in the potential range of -0.49 – -0.61 V and leads to the formation of $[\text{Co}^{\text{I}}(\text{TMPyP})]^{3+}$. The second one causes the addition of one electron to the porphyrin macrocycle with the formation of $[\text{Co}^{\text{I}}(\text{TMPyP})]^{2+}$. However, intramolecular electron transfer with $[\text{Co}^{\text{I}}(\text{TMPyP})]^{2+}$ occurs in solution to form $[\text{Co}^{\text{II}}(\text{TMPyP})]^{2+}$, which is observed from spectrochemical, electrochemical studies. Two additional stages of the $[\text{Co}(\text{TMPyP})]^{2+}$ process occur at a value of $E_{1/2}$ -0.89 – -1.10 V, which causes a complete four-electron reduction of four N-methyl-pyridyl substituents in TMPyP. Due to the presence of four positive charges on pyridyl nitrogen atoms, $[\text{M}(\text{TMPyP})]^{4+}$ complexes (M = Mn, Co, Cu, Zn, and VO) are more difficult to oxidize and more easily to reduce (by 400–600 mV), compared with M(TPhP).

The electrochemistry of sixteen water-soluble porphyrins of the type $[\text{M}^{\text{II}}(\text{TMPyP})]^{4+}(\text{X}^-)_4$ or $[\text{M}^{\text{III}}(\text{TMPyP})\text{Cl}]^{4+}(\text{Cl}^-)_4$ in a non-aqueous medium was studied some years ago [9]. All the compounds with an inactive central metal ion were subjected to the addition of six electrons, found for most complexes with three electron transitions. More than three transitions are observed for porphyrins having a central metal ion with reduced electron deficiency for example, Cd(II).

The authors [12] considered the electrochemistry of monosodium and bis-N-alkyl-4-pyridylporphyrins with a free base in two non-aqueous solvents (pyridine (Py) and methylene chloride (CH_2Cl_2)) and tetrasubstituted N-methoxyethyl-4-pyridylporphyrin in dimethylsulfoxide (DMSO). The compound $[\text{H}_2(1\text{'-methyl-Py-4)}_4\text{P}]^{4+}(\text{I}^-)_4$ is irreversibly reduced at a cathode peak potential $E_c = -1.26$ V. The reaction product in pyridine is reoxidized one at the anode peak potential $E_a = -0.08$ V. Pyridyl and N-alkylpyridylporphyrin metal-free derivatives with one, two or four meso-pyridyl substituents are reduced similarly to tetraphenylporphyrin complexes and characterized by two

well-defined one-electron transitions. The only difference between TMPyP and TPhP is an increase in the positive potential shift with each increase in the number of pyridyl groups. The redox behavior of N-alkylpyridylporphyrins also depends on the properties of the solvent, which partially determines the dissociation/association of negatively charged ions on positively charged N-alkyl-pyridyl groups.

In an aqueous medium, unlike non-aqueous, TMPyP derivatives exist in a dissociated form, for example, $[\text{M}^{\text{II}}(\text{TMPyP})]^{4+}$ instead of $[\text{M}^{\text{II}}(\text{TMPyP})]^{4+}(\text{X}^-)_4$, and $[\text{M}^{\text{III}}\text{X}(\text{TMPyP})]^{4+}$ instead of $[\text{M}^{\text{III}}\text{X}(\text{TMPyP})]^{4+}(\text{X}^-)_4$ under the same experimental conditions. Therefore, the type of counterion can affect the electrochemical properties of metalloporphyrins in non-aqueous solvents (DMF, DMSO, Py), where the associated form can prevail in solution over the dissociated form due to the low polarity of the solvent.

In the present work, in continuation of our studies of pyridylporphyrin compounds [13], the results of studying electrochemical behavior of compounds of a number of N-substituted tetrapyridylporphyrins were presented for the first time (Fig. 1). The possibility of using these compounds in the electrocatalysis of molecular oxygen electroreduction in an aqueous-alkaline solution has been evaluated. The comparative analysis of the complex formation effect, functional substitution (4- and 3-isomerism) and the nature of the counterion (tosylate (Ts^-), iodide (I^-)) in the porphyrin molecule on the electrochemical parameters and activity of pyridylporphyrins were carried out.

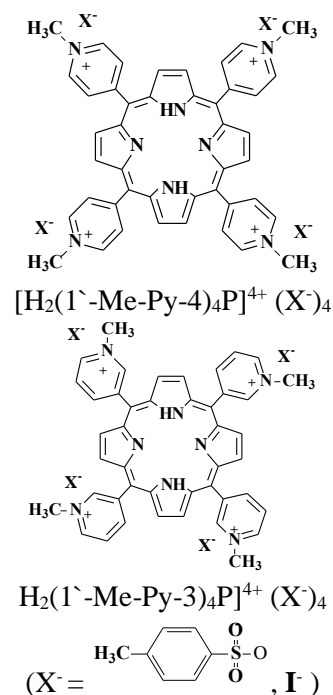


Fig. 1. Structure of porphyrins (comp. 1-4)
Рис. 1. Структура порфиринов (соед. 1-4)

EXPERIMENTAL

Ligands {5,10,15,20-tetrakis(1'-methyl-pyrid-4- and -3-yl)porphin tetratosylates (comp. **1** and **2** [H₂(1'-methyl-Py-4- and -3)₄P]⁴⁺ (Ts⁻)₄ and tetraiodide (comp. **3** and **4**) [H₂(1'-methyl-Py-4- and -3)₄P]⁴⁺ (I⁻)₄}, and metallocomplexes were synthesized according to the methods described in [14-15].

Co(II)-tetrakis(pyrid-4-yl and 3-yl)porphin complexes were synthesized under action of acetates of the corresponding metals at heating in DMF.

Co(ms-(Py-4)₄)P: Yield – (55%), λ_{\max} , nm/ lg ϵ , CHCl₃: 572(3.57); 538(4.32); 413(5.70). {Co(*ms*-(Py-4)₄P)⁺(m/z): 675.486.

Co(ms-(Py-3)₄)P: Yield – (89%), λ_{\max} , nm/ lg ϵ , DMF: 588 (3.88); 549 (4.02); 432 (5.20). {Co(*ms*-(Py-3)₄P)⁺(m/z): 675.407.

Co-tetrakis(1'-methyl-pyrid-4-yl)porphin tetratosylate (comp. **5**). 0.1 g (0.148 mmol) of Co-tetrakis(pyrid-4 or -3)porphin and 0.2 g of p-toluenesulfonic acid methyl ester were dissolved in 30 ml of DMF and boiled for 1 h. Then it was cooled, diluted with 5.0 ml of benzene. The precipitate was filtered off, washed with acetone and dried. Yield – 75.0%. λ_{\max} , nm/ lg ϵ , H₂O: 581/(3.34), 547/(4.47); 434/(5.17).

Co-tetrakis(1'-methyl-pyrid-3-yl)porphin tetratosylate (comp. **6**). Yield – 89.4%. λ_{\max} , nm/ lg ϵ , H₂O: 580/(3.65); 547/(4.16); 428/(5.22).

The purity and individuality of the compounds were monitored by thin layer chromatography (Silufol C60, eluent – CHCl₃). UV-vis spectra were recorded with SF-56 spectrophotometer (LOMO, Russia).

Electrochemical measurements were performed by the method [16] in the three-electrode cell YASE-2. A saturated silver chloride electrode (Ag/AgCl) and a platinum electrode were used as the reference and counter electrodes, respectively. The working electrode was a graphite one. The working surface (0.64 cm²) was deposited with a layer (0.2-0.3 mm) of an active mass, which was prepared in an ethyl alcohol, involved the carbon support (TEC – technical elemental carbon P-514 (GOST 7885-86) with the ash content 0.45%), the fluoroplastic suspension (6% FP-4D) and studied substance in weight ratio 7:2:1.

The measurements were carried out by using the potentiostat-galvanostat «J-31P» (Elins, Russia). Potentials of cathodic (E_c) and anodic (E_a) peaks for observed processes involving studied compounds were fixed with the accuracy of ± 0.01 V. The values of redox potentials were determined as the average in a series of 5-6 parallel experiments.

RESULTS AND DISCUSSION

Electrochemical properties in an inert medium

For the electrode without a catalyst (Fig. 2, curve 1), cathodic and anodic maxima were absent on the cyclic voltammograms in the entire study region of potentials. When various porphyrin compounds are introduced into the active mass of the working electrode (Fig. 2, curve 2) in the argon atmosphere on the first cycles of cyclic voltammograms in the studied potential range for ligands, several potential regions can be identified where electrochemical transformations occur.

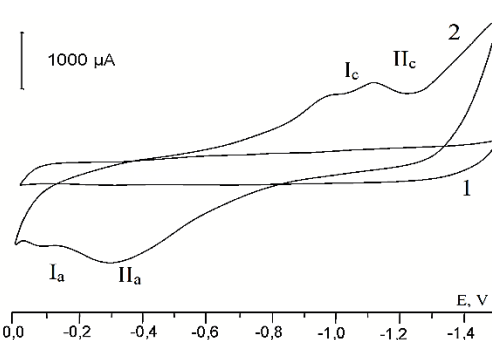


Fig. 2. I, E-curves on the electrode: 1- without catalyst, 2 – modified with comp. **2** in 0.1M KOH solution under argon (3 cycle). A scan rate is 0.02 V·s⁻¹

Рис. 2. I, E-кривые для электродов: 1 - без катализатора, 2 – модифицированный соед. **2** в растворе 0,1М KOH в среде аргона (3 цикл). Скорость сканирования потенциала 0,02 В·с⁻¹

Comp. **1-4** undergoes to two electrochemical processes. The first process is associated with the electroreduction of the π -conjugated system in the potential region $\Delta E_{\text{red/ox}}$, V (-0.55... -0.66) and the formation of the radical anion ($L \leftrightarrow L^{\cdot -}$). The second process depending on the functional substitution and nature of the counterion corresponds to the localization of the second electron in the π -electron system of the macrocycle at $\Delta E_{\text{red/ox}}$, V (-0.73... -0.83) ($L^{\cdot -} \leftrightarrow L^{2-}$) (Table 1).

So, the values of the redox potential of $E_{\text{red/ox}}^1$ of the first electroreduction process for compounds **1** and **2** are slightly lower than for compounds with counter ion I⁻. From the $E_{\text{red/ox}}^1$ values, it can be concluded that the 4-isomer is reduced in comparison with the 3-isomer in the region of more positive potentials (potential shift is from 40 to 60 mV). This is due to the different position of the atom in the pyridyl fragments of the porphyrin molecule. The same dependence is also observed for unsubstituted 4- and 3-pyridylporphyrins described in [17].

Thus, the N-substitution of the pyridyl fragment of porphyrins leads to a slight increase in their reducing ability, in comparison with unsubstituted tetrapyrrolylporphyrins.

Table 1

Electrochemical parameters of redox process (E, V vs Ag/AgCl) in 0.1 M KOH solution in argon medium.
 $\nu = 0.02 \text{ V}\cdot\text{s}^{-1}$

Таблица 1. Электрохимические параметры окислительно-восстановительных процессов (E, V vs Ag/AgCl) в растворе 0,1 М КОН в среде аргона. $\nu = 0,02 \text{ В}\cdot\text{с}^{-1}$

Compounds	$L \leftrightarrow L^{\cdot-}$			$L^{\cdot-} \leftrightarrow L^{2-}$		
	E_c^I	E_a^I	$E_{red/ox}^I$	E_c^{II}	E_a^{II}	$E_{red/ox}^{II}$
1	-0.82	-0.29	-0.55	-1.00	-0.45	-0.73
2	-1.06	-0.12	-0.59	-1.19	-0.32	-0.76
3	-0.86	-0.33	-0.60	-1.02	-0.54	-0.78
4	-1.02	-0.29	-0.66	-1.16	-0.50	-0.83
H ₂ (Py-4) ₄ P [17]	-0.60	-0.29	-0.45	-0.88 *-1.19	-0.54 *-	-0.71 *-1.12
H ₂ (Py-3) ₄ P [17]	-0.61	-0.48	-0.54	0.81 *-1.06	0.61 *-0.94	-0.71 *-1.00

Note: * - $L^{2-} \leftrightarrow L^{3-}$

$E_{red/ox} = (E_c + E_a)/2$

Примечание: * - $L^{2-} \leftrightarrow L^{3-}$

$E_{red/ox} = (E_c + E_a)/2$

In an argon atmosphere, metal complexes **5** and **6** undergoes three electrochemical transformations of the macrocycle. The first process is associated with the electroreduction of the π -conjugated system in the potential region ΔE_c , V (-0.53... -0.57) and the formation of the radical anion. The second process corresponds to the localization of the second electron in the π -electron system of the macrocycle at $\Delta E_{red/ox}$, V (-0.78... -1.05), depending on the functional substitution and nature of the counterion. The third process is associated with further electroreduction of the macrocycle and the formation of a trianion form in the potential region - 1.33 ... - 1.36 V (Fig. 3, Table 2). An additional electronic transition was observed for the complexes, associated with the oxidation (reduction) of $\text{Co}^{3+} \leftrightarrow \text{Co}^{2+}$, localized on the metal atom at $E_{red/ox} = 0.19$ V.

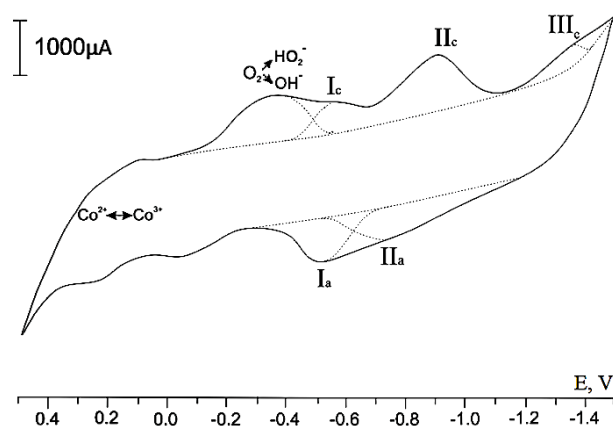


Fig. 3. CV-curves on the electrode modified with comp. 6 in 0.1M KOH under argon (3 cycle). A scan rate is 0.020 V·s⁻¹

Рис. 3. I, E-кривые электродов модифицированных соед. 6 в 0,1М КОН в среде аргона (3 цикл). Скорость сканирования потенциала 0,02 В·с⁻¹

Table 2

Electrochemical parameters (E, V vs Ag/AgCl) of tetrapyrrolylporphyrines complexes in 0.1M KOH solution in argon medium. $\nu = 0.02 \text{ V}\cdot\text{s}^{-1}$

Таблица 2. Электрохимические параметры (E, V vs Ag/AgCl) комплексов тетрапирридилпорфиринов в растворе 0,1М КОН в среде аргона. $\nu = 0,02 \text{ В}\cdot\text{с}^{-1}$

Compounds	$M^{3+} \leftrightarrow M^{2+}$			$L \leftrightarrow L^{\cdot-}$			$L^{\cdot-} \leftrightarrow L^{2-}$		
	E_c	E_a	$E_{red/ox}$	E_c^I	E_a^I	$E_{red/ox}^I$	E_c^{II}	E_a^{II}	$E_{red/ox}^{II}$
5	0.16	0.21	0.19	-0.57	-	-	-1.02 *-1.33	-0.86	-0.94
6	0.12	0.25	0.19	-0.56	-0.53	-0.55	-0.92 *-1.36	-0.78	-0.85
Co(Py-4) ₄ P [17]	0.15	0.25	0.20	-0.58	-0.40	-0.49	-0.98 *-1.15	-0.62	-0.80
Co(Py-3) ₄ P [17]	0.14	0.28	0.21	-0.60	-0.45	-0.53	-0.90 *-1.09	-0.56 *-0.87	-0.73 *-0.98

Note: ** - $L^{2-} \leftrightarrow L^{3-}$

$E_{red/ox} = (E_c + E_a)/2$

Примечание: ** - $L^{2-} \leftrightarrow L^{3-}$

$E_{red/ox} = (E_c + E_a)/2$

From the values of the redox potentials ($E_{\text{red/ox}}^I$, $E_{\text{red/ox}}^{II}$ и $E_{\text{red/ox}}^{III}$) of the processes of electroreduction of the complexes, it can be concluded that they are reduced at lower values of the potential, in comparison with the unsubstituted complexes $\text{Co(Py-4)}_4\text{P}$ and $\text{Co(Py-3)}_4\text{P}$.

The effect of the isomerism of the pyridyl substituent of the compounds **5-6** is characterized by a shift of the redox potentials of the macrocycle reduction processes. So, in the case of metal complexes, the 3-isomer is reduced at lower potentials, compared with the 4-isomer.

Electrocatalytic activity of ligands and metal complexes of tetrapyrrolylporphyrins

Interest for the investigation in the field of catalysis of the electrochemical reduction of molecular respiration continues and will continue to grow, which will lead to the need to develop important technologies for electrochemical stability. Work on the creation of non-platinum electrocatalysts for the reduction of oxygen in alkaline media, due to modern applied tasks of reducing the cost and size amplitude of current sources while simultaneously increasing their current characteristics, continues [18-21].

In order to analyze of the electrocatalytic activity of porphyrin compounds in the ORR, voltammetric curves corresponding to the limiting saturation of the electrolyte with oxygen, were obtained.

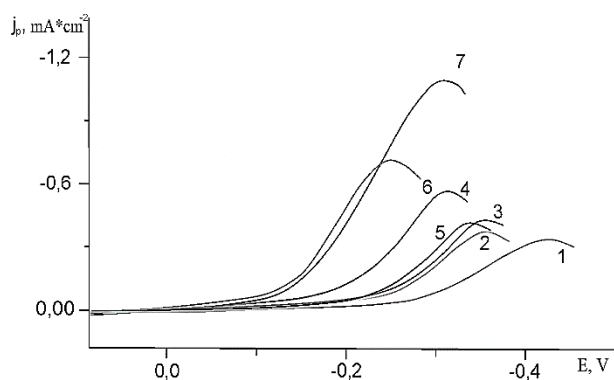


Fig. 4. Fragment of I,E-curves for ORR of: 1- without catalyst, 2- comp. **2**, 3- comp. **1**, 4 - comp. **4**, 5- comp. **3**, 6 - comp. **6**, 7- comp. **5**

Рис. 4. Фрагмент I,E-кривых процесса электровосстановления молекулярного кислорода с различными катализаторами.: 1- без катализатора, 2- соед. **2**, 3- соед. **1**, 4 - соед. **4**, 5- соед. **3**, 6 - соед. **6**, 7- соед. **5**

The increase in the catalytic activity of the compounds leads to the depolarization effect, which is appeared in the shift of the electroreduction wave of molecular oxygen and the half-wave potential

$[E_{1/2}(\text{O}_2)]$ into the region of positive values in comparison with the system without a catalyst ($E_{1/2}(\text{O}_2) = -0.35$ V). This indicates the participation of the studied ligands and complexes in the electrocatalysis of the considered process.

The catalytic activity of the studied compounds in the ORR increases, according to a decrease in the electroreduction potential of O_2 [$E_{1/2}(\text{O}_2)$] in the series: **2** < **1** < **6** < **5**, **4** < **3**.

An important characteristic of the ORR is the number of electrons (n) involved in the reaction. In order to clarify the mechanism of the process, using the Randles–Sevcik equation for a fixed electrode [22], we calculated the number of electrons for voltammograms obtained at different scanning speeds.

$$i_p = 272n^{3/2}SC_A D_A^{1/2}v^{1/2},$$

where i_p – maximum current (peak current), (mA); S – surface of the electrode, (cm^2); C_A – solubility of the substance O_2 , ($\text{mol}\cdot\text{l}^{-1}$); D_A –diffusion coefficient O_2 , ($\text{cm}^2\cdot\text{s}^{-1}$); v – scan rate, ($\text{V}\cdot\text{s}^{-1}$).

An analysis of the effective number of electrons n (Table 3), calculated in the maximum region using the Randles–Sevcik equation with parameters [23] shows that for all the studied catalysts n is in the range 2.0-3.0. This suggests that the ORR for the studied catalysts proceeds in parallel according to the 2 and 4 electronic mechanism through the formation of oxygen-containing intermediates.

The depolarization effect for complexes **6** < **5** $\Delta E_{1/2}(\text{O}_2)$ are 0.14 and 0.16 V, respectively, which is slightly higher than for the unsubstituted complexes $\text{Co(Py-3)}_4\text{P}$ and $\text{Co(Py-4)}_4\text{P}$ (Table 3).

Table 3
The values of half-wave potential ($E_{1/2}(\text{O}_2)$, V) and the effective number of electrons (n) at $v = 0.02$ V·s⁻¹
Таблица 3. Значения потенциала полуволны ($E_{1/2}(\text{O}_2)$, В) и эффективное число электронов (n) при $v = 0,02$ В·с⁻¹

Compounds	$E_{1/2}(\text{O}_2)$	n
1	-0.29	2.0
2	-0.30	2.0
3	-0.26	2.2
4	-0.28	2.2
5	-0.19	3.0
6	-0.21	2.9
$\text{Co(Py-4)}_4\text{P}$ [17]	-0.18 (without catalyst = -0.30)	-
$\text{Co(Py-3)}_4\text{P}$ [17]	-0.15 (without catalyst = -0.30)	-
without catalyst	-0.35	2.0

CONCLUSION

Thus, functionally substituted tetrapyrrolylporphyrins and their Co-complexes studied are quite effective systems that can be of interest when using them as heterogeneous and homogeneous catalysts of oxidation processes with participation of molecular oxygen.

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The authors declare the absence a conflict of interest warranting disclosure in this article.

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