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Статья

Influence of Molecular Isomerism of Monopyridylporphyrin on Electrochemical and Electrocatalytic Properties in Alkaline Solution

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Dedicated to Academician of Russian Academy of Sciences, Prof. O. N. Chupakhin
on the occasion of his 80th Anniversary

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The comparative investigation of the electrochemical reduction of a number of pyridylporphyrin derivatives with alkyl substituents and their cobalt(II) complexes in 0.1 M KOH is carried out by cyclic voltammetry (CV). The influence of isomerism of the porphyrin molecule and the nature of metal on the oxidative capacity of the tetrapyrrole macrocycle and on the electrocatalytic activity of compounds studied for the oxygen electroreduction reaction is established.

Keywords: Voltammetry, pyridylporphyrin, oxygen electroreduction, metalloporphyrins.

Влияние изомерии молекулы монопиридилпорфирина на электрохимические и электрокаталитические свойства в щелочном растворе

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Посвящается Академику РАН, профессору О.Н. Чупахину по случаю его 80-летнего юбилея

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Методом циклической вольтамперометрии проведено сравнительное исследование электрохимического восстановления ряда производных пиридилпорфирина с алкильными заместителями и их комплексов с ионом кобальта(II) в 0.1 М растворе КОН. Установлено влияние изомерии молекулы порфирина и природы металла на окислительную способность тетрапиррольного макроцикла и электрокаталитическую активность изученных соединений в реакции электровосстановления молекулярного кислорода.

Ключевые слова: Вольтамперометрия, пиридилпорфирин, электровосстановление кислорода, металлопорфирины.

Introduction

Metalloporphyrins are active and selective catalysts for many redox reactions: oxidation of carbocyclic substances, ketones, fatty acids, reduction of nitrogen oxides, hydrogenation *etc*.[1,2,3] Molecular oxygen reduction is the case of heterogeneous electrocatalysis by porphyrins which is in detail studied. The development of these works is related to the decision of important challenges, in particular, the replacement of precious metals and the creation of economic electrochemical energy courses of the new generation.[1,3-8]

Electrocatalysis by metalloporpyrins belongs to the field of heterogeneous catalysis, in which organic compounds of transition metals are used for the activation of redox reactions. At present, organic complexes of *d*-metals are a hugely perspective class of electrocatalysts. Intensive fundamental and applied researches in this direction are conducted in many countries.[3,6,9-16]

As in the case of chemical heterogeneous catalysis, main effects of electrocatalysis are associated with the adsorption interaction between substrate and active site, which determines the initial structure of the activated complex and the nature of the activation energy of the considered process. And, electrocatalytic processes are implemented at the phase boundary since those accompany the heterogeneous electron transfer between the conducting phase and the reactant being located at the interface with electrolyte. The charge transfer at the interface electrocatalyst-electrolyte depends not only on the electronic structure of the transition complex, but also on the magnitude of the potential jump at this interface, which directly affects the value of the activation energy. The kinetics of electrochemical reactions significantly depends on the structure of the interphase boundary. This leads to a number of features of electrocatalytic reactions.[1]

The investigation of the structure of the interface metalloporphyrin-electrolyte involves two questions: the study of the ionic state of metalloporphyrins and the potential distribution at the interphase boundary.[1] Thus, ionic forms of *d*-metal porphyrins could participate in catalysis and electrocatalysis by them. So, the task of establishing the redox potential of metalloporphyrins and that of the identification of electrochemical conversions of electron transitions appears. And besides, the majority of works in this direction is carried out in the media of organic solvents.[12-16,17]

It was observed that metalloporphyrins and their structural analogs (porphyrazines, phthalocyanines) exhibit the high catalytic, electrocatalytic and photocatalytic activity in natural and technically important processes.[3,17] In greatest detail the oxygen electroreduction reaction is studied on organic metallocomplexes. This reaction takes place in air or oxygen cathodes of chemical current sources. It was established that the mechanism and the oxygen electroreduction reaction rate mainly depend on the chemical structure of the catalyst molecule: the type of ligand and substituents, the nature of the central metal ion, the presence of the conjugated system of monomeric units, extraligands, the conformation of the conjugated system, *etc*.[11,18-22]

Thus, the aim of the present work is to study the electro-reduction process of a number of monopyridylporphyrin derivatives with alkyl substituents in β-positions and their cobalt(II) complexes in 0.1 M KOH, as well as of the influence
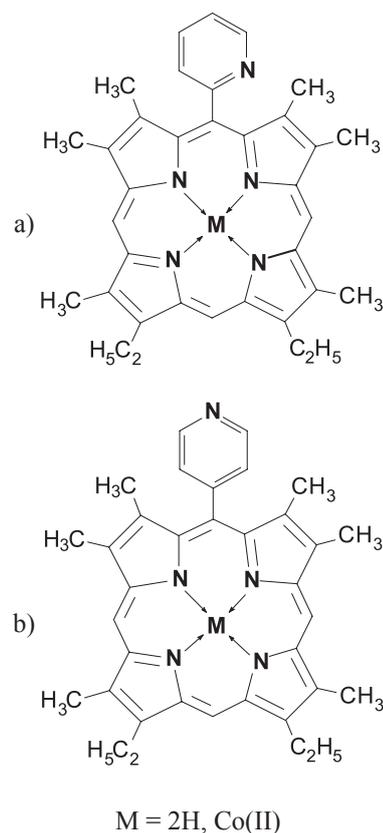

M = 2H, Co(II)

Figure 1. Structures of the studied porphyrin compounds.

of porphyrin molecule isomerism and the nature of metal on the oxidative capacity of the tetrapyrrole macrocycle and on the electrocatalytic activity of the compounds studied for the oxygen electroreduction reaction.

Experimental

Synthesis of monopyridylporphyrin derivatives with alkyl substituents in β-positions and their cobalt(II) complexes (Figure 1) was performed with methods described in [23,24].

The electrochemical studies were carried out by CV in aqueous solution of potassium hydroxide (0.1 M) of the reagent grade. Measurements were carried out in a three-electrode electrochemical glass cell. Platinum was used as the counter electrode, saturated silver-chloride electrode served as the reference electrode. The working electrode represented a graphitized carbon rod with a surface area being equal to 0.64 cm², the side surface insulated with a fluoroplastic coating. The end of the rod was covered with a thin layer of active mass involving the carbon support (TEC - technical elemental carbon with the ash content 2 %), fluoroplastic particles (6 % FP-4D) and the studied compound in the mass ratio of 7:2:1. After ending experiments, the active mass was easily removed. The operation of new layer application could be repeated many times.

Potentials of the cathodic (E_c) and anodic (E_a) peaks in voltammograms were fixed for observed processes by using a PC. The values of redox potentials were determined as the average in a series of 5-6 parallel experiments ($E_{red/ox}=(E_c+E_a)/2$). Water used in preparing of KOH solution was twice distilled immediately before experiments and cleaned according to recommendations.[25]

Results and Discussion

In contract to the previously studied alkylporphyrin derivatives,[20,21] chemical compounds investigated have a

Table 1. Redox potentials for electrodes with studied compounds. The potential scan rate $v = 0.020$ V·s^{-1}.

Compound	$Co^{2+} \leftrightarrow Co^{3+}$			$L \leftrightarrow L^-$			$L^- \leftrightarrow L^{2-}$ Py			$L^{2-} \leftrightarrow L^{3-}$		
	E_c, V	E_a, V	$E_{red/ox}$, V	E^I_c, V	E^I_a, V	$E^I_{red/ox}$, V	E^{II}_c, V	E^{II}_a, V	$E^{II}_{red/ox}$, V	E^{III}_c, V	E^{III}_a, V	$E^{III}_{red/ox}$, V
H$_2$(DEtHMePy[2]P)	–	–	–	-0.896(8)	-0.526(5)	-0.711(7)	-1.252(5)	-0.677(4)	–0.965(5)	-1.362(5)	–	–
H$_2$(DEtHMePy[3]P)[23]	–	–	–	-0.861(7)	-0.600(3)	-0.731(5)	-1.065(7)	-0.727(5)	–0.896(6)	-1.233(6)	-1.160(3)	-1.196(4)
H$_2$(DEtHMePy[4]P)	–	–	–	-0.867(6)	-0.603(2)	-0.737(4)	-1.213(5)	-0.702(5)	–0.958(5)	-1.332(4)	–	–
Co^{II}(DEtHMePy[2]P)	0.201(7)	0.325(8)	0.263(8)	-0.748(9)	-0.571(7)	-0.660(8)	-1.101(4)	-0.929(3)	–1.015(3)	-1.348(3)	–	–
Co^{II}(DEtHMePy[3]P)[23]	0.168(5)	0.324(7)	0.246(6)	-0.716(7)	-0.565(4)	-0.640(5)	-1.107(5)	–	–	–	–	–
Co^{II}(DEtHMePy[4]P)	0.156(5)	0.360(4)	0.258(5)	-0.724(5)	-0.560(3)	-0.642(4)	-1.081(8)	–	–	–	–	–

Potential values are shown with respect to saturated silver-chloride electrode.

Table 2. Redox potentials of $Co^{2+} \leftrightarrow Co^{3+}$, half-wave potentials, maximum potentials and effective number of electrons for oxygen electroreduction. The potential scan rate $v = 0.020$ V·s^{-1}.

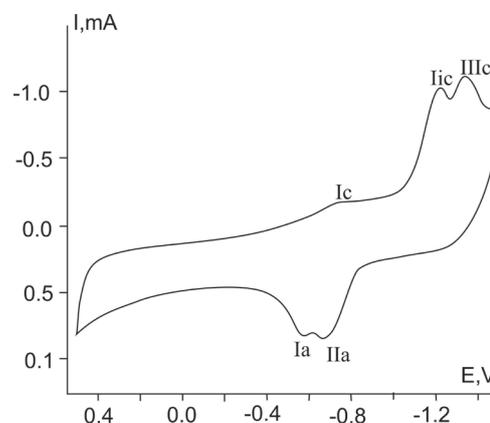| Compound	$E_{red/ox}$, V $Co^{2+} \leftrightarrow Co^{3+}$	$E_{1/2}(O_2)$, V	$E_{max}(O_2)$, V	n
H$_2$(DEtHMePy[2]P)	–	-0.222(6)	-0.283(5)	2.2
H$_2$(DEtHMePy[3]P)[23]	–	-0.222(4)	-0.284(4)	2.3
H$_2$(DEtHMePy[4]P)	–	-0.234(4)	-0.301(3)	2.1
Co^{II}(TMeTBuP)[19]	0.190(8)	-0.130(5)	-0.220(3)	Not defined
Co^{II}(DEtHMePy[2]P)	0.263(8)	-0.097(3)	-0.143(2)	3.5
Co^{II}(DEtHMePy[3]P)[23]	0.246(6)	-0.092(4)	-0.140(5)	3.9
Co^{II}(DEtHMePy[4]P)	0.258(5)	-0.099(5)	-0.153(4)	3.6
TEC	–	-0.300(6)	–	2.0

pyridyl moiety in the porphine *meso*-position. Moreover, as seen from given structural formulas of compounds, nitrogen atoms of pyridyl moieties are both in *ortho*- (Figure 1a) and in *para*- (Figure 1b) positions, M(DEtHMePy[2]P) and M(DEtHMePy[4]P), respectively, where M = H$_2$, Co(II). Therefore, it was interested to follow the effect of the position of nitrogen heteroatoms in pyridyl moieties on the values of redox potentials for conversion processes of porphyrin ligands and cobalt ion, *i.e.* on the ability of the tetrapyrrole macrocycle and the central metal to electroreduction (electrooxidation).

Electrochemical Behavior of Monopyridylporphyrin Ligands H$_2$(DEtHMePy[2]P), H$_2$(DEtHMePy[4]P)

Figure 2 presents *I,E*-curve obtained for the monopyridylporphyrin *para*-isomer. Free ligand being in the active mass, in cathodic and anodic parts of the potentiodynamic curve a number of cathodic and anodic maxima are observed, that related to the electrochemical conversion of the π-conjugated system and the pyridyl substituent in the porphyrin molecule.

On cathodic part of the voltage-current curve for H$_2$(DEtHMePy[4]P) there are three peaks corresponding to ligand electroreduction processes. Process I$_c$ is associated with the accession of the first electron in the π-electron system and the formation of a monoanionic form in the potential range -0.70 ÷ -0.90 V. On anodic part of the *I,E*-curve peak I$_a$ of the reserve electrochemical process being in the potential range -0.5 ÷ -0.65 V can be detected. At more negative potentials on the cathodic part of the *I,E*-curve two surrounding peaks are

Figure 2. *I,E*-curve obtained for electrode with the ligand H$_2$(DEtHMePy[4]P) in Ar. The potential scan rate $v = 0.020$ V·s^{-1}.

observed. Two these peaks are located in the potential range -1.15 ÷ -1.50 V. Process II$_c$, in our opinion, is due to electroreduction of the pyridyl group in the porphyrin molecule that is in good agreement with the research results.[21] The accession of the third electron leading to the formation of a trianionic form (process III$_c$) is observed in the potential area -1.25 ÷ -1.45 V. It should be noted that the second maximum (II$_c$) has a corresponding anodic peak (II$_a$), which lies in the potential interval -0.60 ÷ -0.75 V. The third process in the given experimental conditions is electrochemically irreversible. The experimental and calculated values of potentials for observed conversion processes of monopyridylporphyrin *para*-isomer are shown in Table 1.

Similar results of the electrochemical behavior for *ortho*-isomer (DEtHMePy[2]P) were obtained (Figure 3, Table 1).
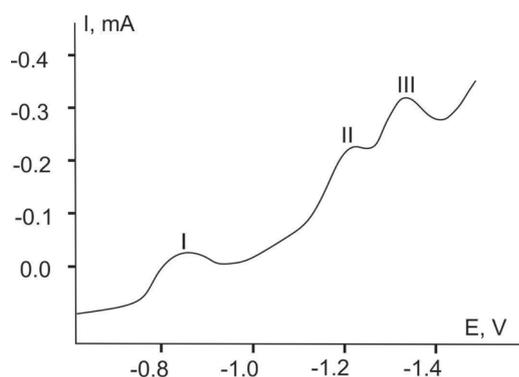

Figure 3. Fragment of the cathodic part of *I,E*-curve for electrode with the ligand H₂(DEtHMePy[2]P) in Ar. The potential scan rate $v = 0.020$ V·s⁻¹.

Carrying out a comparative analysis of the obtained values of redox potentials characterizing each electroreduction process of porphyrin ligand molecule, we could make the following conclusions:

– Electroreduction process of dianionic (L^{2-}) to trianionic form (L^{3-}) for *ortho*- and *para*-isomers is electrochemically irreversible (Scheme 1). This can be explained, perhaps, that the addition of a third electron to the doubly charged anion leads to the formation of a stable dianionic form.

– $E_{red/ox}$ magnitude of electroreduction of the pyridyl moiety for *ortho*- and *para*-isomers lies in a more negative region (potential shift is 60-70 mV), than for *meta*-isomer, previously studied.[21] This indicates that the pyridyl moiety with the nitrogen atom in the *meta*-position is easier reduced, than others.

– The isomerism of nitrogen atom in the pyridyl moiety, though not strongly, but affects the reductive ability (the first step) of the porphyrin ligand. Indeed, the values of redox potentials of the process attaching the first electron to the π-conjugated system of the porphyrin molecule decreases in a row: *ortho*-, *meta*-, *para*-isomer (-0.711, -0.731, -0.737 V). The change of potentials really is not big, but for such wispy interaction effects this fact should be noted.

Electrochemical Properties of Cobalt Complexes of ortho- and para-Isomers: Co^{II}(DEtHMePy[2]P), Co^{II}(DEtHMePy[4]P)

The study of electrochemical properties of monopyridylporphyrin cobalt(II) complexes was carried out by analyzing *I,E*-curves obtained under the same experimental conditions as well as for monopyridylporphyrin ligands.

A number of features of the electrochemical behavior of cobalt complexes ought to be noted (Table 1). Firstly, the presence of maximum with an insignificant intensity in the

potential range -0.1 ÷ -0.4 V on the cathodic site of *I,E*-curve is characterized for the first measured cycles. This cathodic current maximum corresponds to the electroreduction process of oxygen molecule adsorbed on the catalyst surface that indicates the presence of oxygen adduct Co-O₂. It should be emphasized that the tendency to formation of the oxygen adduct is observed for all porphyrin cobalt complexes. [1,18,21,22]

Secondly, when administering studied cobalt complexes in the electrode active mass on voltage-current curves in the investigated potential region, together with electrochemical processes in the porphyrin macrocycle the reversible oxidation (reduction) process of metal ion is found. In the potential range 0.4÷0.0 V a pair of maxima is observed, which according to the literature is related to a reversible process $Co^{2+} \leftrightarrow Co^{3+}$.

Thirdly, one should particularly notice that for the monopyridyl cobalt complex – Co^{II}(DEtHMePy[4]P) the cathodic hydrogen separation process has already occurred at potential -1.15 V, so on cyclic *I,E*-curves the third electron transfer being related to the formation of the trianionic form isn't fixed. The same consistent pattern of the electrochemical behavior is observed for Co^{II}(DEtHMePy[3]P).[21]

Fourthly, for the *ortho*-isomer cobalt complex the similar course of *I,E*-curves is observed as well as for Co^{II}(DEtHMePy[4]P). The difference was only the reversibility shift of the cobalt ion electrooxidaton process to side of the formation of oxidized form Co^{3+} and the possibility of fixing the cathodic process of the formation of a complex trianionic form.

In order to comparatively analyze electrochemical pro-perties of studied monoporphyrin cobalt complexes, Table 1 shows the values of redox potentials for observed processes.

Analysis of experimental and calculated data (Tables 1 and 2) showed that:

– The complexation leads to the shift of redox potentials, characterizing the electroreduction of the tetrapyrrole macrocycle with the formation of a monoanionic form, aside positive potential values (about 80÷90 mV). It means that the complexation leads to decreasing the reductive ability of the macrocycle. It can be explained that the formation of σ-bonds Co←N in complexes leads to the partial release of the four electron pair coordinating to nitrogen atoms from the conjugated system (σ-effect) that finally promotes the electron adoption of the π-conjugated system of an organic ligand.

– Redox potentials of the conversion process of metal ion Co(II) and macrocycle on the first stage ($L \leftrightarrow L^-$) are virtually unchanged. Therefore, for structures of the similar type, when the isomerism is related to the pyridyl moiety, which doesn't include directly in the conjugated system with the macrocycle, its influence on the more remote central metal ion could be exhibited in a small extent.

$$[Co(III)P]^+ \underset{-e}{\overset{+e}{\rightleftarrows}} Co(II)P \underset{-e}{\overset{+e}{\rightleftarrows}} Co(II)P^{-\bullet} \underset{-e}{\overset{+e}{\rightleftarrows}} Co(II)P^{2-} \underset{-e}{\overset{+e}{\rightleftarrows}} Co(II)P^{3-}$$

cationic form   anion-radical form   dianionic form   trianionic form

Scheme 1. Electrochemical conversion of monopyridylporphyrin cobalt complexes.

Electrochemical Activity of Monopyridyporphyrins and Their Cobalt Complexes in the Oxygen Electroreduction Reaction in Alkaline Solution (0.1 M KOH)

In addition to the investigation of the electrochemical behavior of monopyridylporphyrin derivatives with alkyl substituents and their cobalt complexes in alkaline solution, experiment of studying the oxygen electroreduction process on the electrodes activated H_2(DEtHMePy[2]P), H_2(DEtHMePy[4]P), Co^{II}(DEtHMePy[2]P) and Co^{II}(DEtHMePy[4]P) was performed.

Upon the introduction of gaseous oxygen into the electrolyte the characteristic feature of *I,E*-curves is that the additional intensive maximum in the potential range $0.10 \div -0.35$ V (Figure 4) appears, which corresponds to the oxygen electroreduction process.
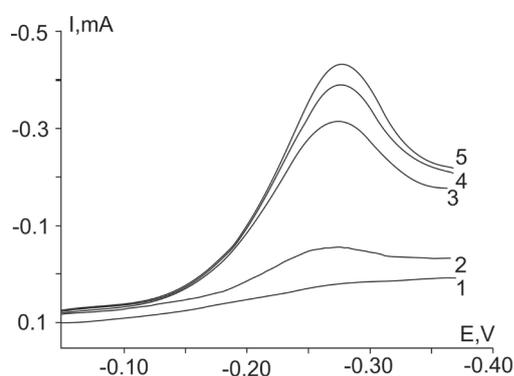

Figure 4. Fragment of the cathodic part of *I,E*-curve for electrode with ligand H_2(DEtHMePy[4]P) upon saturation of the solution with molecular oxygen, cycles: 1- 0, 2- 5, 3- 15, 4- 25, 5- 40. The potential scan rate $v = 0.020$ V·s^{-1}.

To carry out a comparative analysis of the electrocatalytic activity of studied compounds, we measured *I vs. E* curves corresponding to the limiting saturation of the electrolyte with gaseous oxygen, when further cycling did not change their shape.

To assess the electrocatalytic activity of compounds, the current density values were compared at a constant potential value. Due to the different values of peak currents for this process that depends on the amount of active mass applied on the working electrode, we believe that the half-wave potential of molecular oxygen electroreduction $E_{1/2}(O_2)$ or the potential at maximum

current of this process $E_{max}(O_2)$ can serve as the reliable parameter for assessing the depolarizing effect of catalysts.

Based on experimental data (Table 2), we can make the following conclusions:

– Compared with free ligands, for cobalt complexes the essential shift of $E_{1/2}(O_2)$ into the potential region of positive values (over 0.1 V) is observed. This indicates that metal complexes exhibit higher depolarizing effect on this process. Hence, they have higher electrocatalytic activity in the oxygen electroreduction reaction.

– Within the error, $E_{1/2}(O_2)$ values for each series of compounds (ligands or complexes) are close to each other. It is also a confirmation that the molecular isomerism of monopyridylporphyrin affects insignificantly on the electrocatalytic effect of studied compounds.

– For the cobalt complexes (Table 2) the introduction of pyridyl group into the *meso*-position of porphine molecule leads to the shift of $E_{1/2}(O_2)$ in side of positive values (more 30 mV), *i.e.* activity increases. So, in spite of that pyridyl group exhibits π-electron-withdrawing properties, its presence in the molecule shows the positive effect on the electroreduction process of molecular oxygen. In our opinion, it could be related to that after the molecular oxygen is adsorbed on the ion Co by forming σ-bond between the oxygen p_x-MO and the d_{z2}-orbital of metal ion, there is the movement of electron density to the anti-bonding p_x*-MO of oxygen simultaneously from the d_{xz}-orbital of Co and the sp^2-hybrid orbital of nitrogen atom containing a lone pair of electrons (σ-donor). So the O-O bond is strongly weakened and lengthened. This creates favorable conditions for the rupture of the O-O bond and for reduction to hydroxide ions (OH$^-$) without the formation of an intermediate – peroxide ion (HO$_2^-$). The described mechanism of oxygen reduction is called the dual-site one (metal ion and nitrogen atom) (see Figure 5).

The number of electrons (*n*) involving in the reaction was an important parameter for characterizing the electroreduction of molecular oxygen. To elucidate the mechanism of molecular oxygen electroreduction, the Randles-Shevchic equation for stationary electrode (1) being used,[17] the number of electrons was calculated based on voltammograms measured with different potential scan rates:

$$i_p = 272 n^{3/2} SCD^{1/2} V^{1/2} \qquad (1),$$

where i_p is the peak current; S is the electrode surface, cm^2; C is the O_2 solubility, M; D is the O_2 diffusivity, cm^2·s^{-1}; V is the potential scan rate, V·s^{-1}.
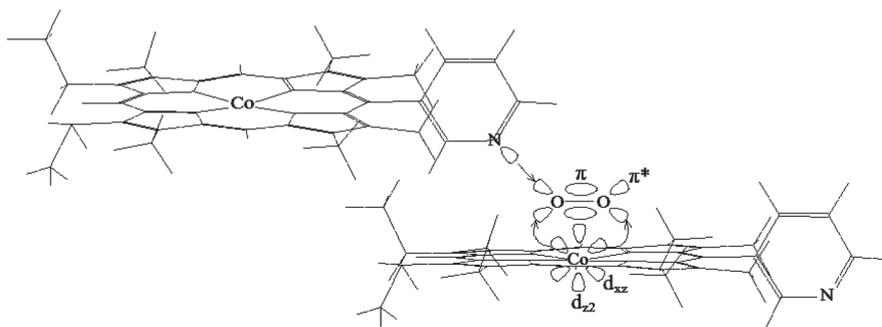

Figure 5. Supposed scheme of the dual-site mechanism of oxygen reduction for Co^{II}(DEtHMePy[3]P).

The following values of the parameters involving in equation (1): $S = 0.64$ cm^2, $C = 1.34 \cdot 10^{-3}$ mol·l^{-1} and $D = 2.601 \cdot 10^{-5}$ cm^2·s^{-1} were employed in calculations. Table 2 shows the calculated n values.

The analysis of data indicates that the oxygen electroreduction process for studied compounds parallel occurs by two- and four-electron mechanism. Like, for monopyridylporphyrin ligands the considered process proceeds mainly by two-electron mechanism, and for metal complexes – by four-electron mechanism. The rising electrochemical activity for studied cobalt complexes is related to the change of mechanism in the direction of the four-electron mechanism with the rupture of the O-O bond.

The obtained values of half-wave potentials for the electroreduction process of molecular oxygen $E_{1/2}(O_2)$ and the effective number of electrons (n) testified the symbatic changes in these magnitudes. Based on the obtained data (Table 2) it is clear that all studied porphyrins have higher electrocatalytic activity, comparing with the system without a catalyst ($E_{1/2}(O_2) = -0.300$ V). In addition, Table 2 shows that the cobalt complex having the more positive value $E_{red/ox}$ Co(III)/(II) exhibits better catalytic activity. The linear correlation between the catalytic activity of cobalt complexes with the electron configuration d^7 and the redox potential of Co(III)/(II) was reported previously.[26]

Conclusions

It was established that the isomerism of the nitrogen atom in the pyridyl moiety, though not strongly, but affects on the electrochemical and electrocatalytic properties of studied porphyrins. The present of the cobalt ion in molecule decreases the reductive ability of the π-conjugated system and increases the electrocatalytic effect on the oxygen electroreduction.

The electrocatalytic activity of cobalt complexes increases in the order: Co^{II}(DEtHMePy[4]P) < Co^{II}(DEtHMePy[2]P) < Co^{II}(DEtHMePy[3]P).

The dual-site mechanism of oxygen reduction was defined, where the active sites are cobalt ion and nitrogen atom of the pyridyl substituent.

The linear relationship between the catalytic activity of cobalt complexes and the redox potentials Co(III)/(II) was noted.

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