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Synthesis and Acid–base Properties of Isomeric Tetrachlorooctabromo– and Tetrabromooctachlorotetraphenyl–porphyrins

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Reactions of Co(II)-5,10,15,20-tetra(4-bromophenyl)porphyrin chlorination with excess of the thionyl chloride and Co(II)-5,10,15,20-tetra(4-chlorophenyl)porphyrin bromination with N-bromosuccinimide were investigated. Co(II)-2,3,7,8,12,13,17,18-octabromo-5,10,15,20-tetra(chlorophenyl)porphyrin and Co(II)-2,3,7,8,12,13,17,18-octachloro-5,10,15,20-tetra(4-bromophenyl)porphyrin were synthesized and identified by UV-Vis, ^1H NMR spectroscopy and mass-spectrometry. When the halogen substituted Co(II) porphyrins were treated with a chloric and sulfuric acids mixture, corresponding porphyrin-ligands were obtained. The acid-base properties of the 2,3,7,8,12,13,17,18-octabromo-5,10,15,20-tetra(4-chlorophenyl)porphyrin and 2,3,7,8,12,13,17,18-octachloro-5,10,15,20-tetra(4-bromophenyl) porphyrin in acetonitrile were studied. Acidity and basicity constants of the synthesized porphyrin ligands were determined and the concentration intervals for their ionized forms existence were established.

Keywords: Bromination, chlorination, tetraphenylporphyrins, cobalt complexes, spectral characteristics, acid-base properties.

Синтез и кислотно–основные свойства изомерных тетрахлороктабром– и тетрабромоктахлортетрафенилпорфиринов

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Исследованы реакции хлорирования 5,10,15,20-тетра(4-бромфенил)порфирината Co(II) избытком тионилхлорида и бромирования 5,10,15,20-тетра-(4-хлорфенил)порфирината Co(II) под действием N-бромсукцинимида. Синтезированы и идентифицированы методами электронной абсорбционной, ЯМР ^1H спектроскопии и масс-спектрометрии 2,3,7,8,12,13,17,18-октабром-5,10,15,20-тетра(4-хлорфенил)порфиринат Co(II) и 2,3,7,8,12,13,17,18-октахлор-5,10,15,20-тетра(4-бромфенил)порфиринат Co(II). При обработке галогензамещенных кобальтпорфиринов смесью хлорной и серной кислот получены соответствующие порфирины-лиганды. Изучены кислотно-основные свойства 2,3,7,8,12,13,17,18-октабром-5,10,15,20-тетра(4-хлорфенил) порфирина и 2,3,7,8,12,13,17,18-октахлор-5,10,15,20-тетра(4-бромфенил)порфирина в ацетонитриле. Определены константы кислотности и основности синтезированных порфиринов-лигандов и установлены концентрационные интервалы существования их ионизированных форм.

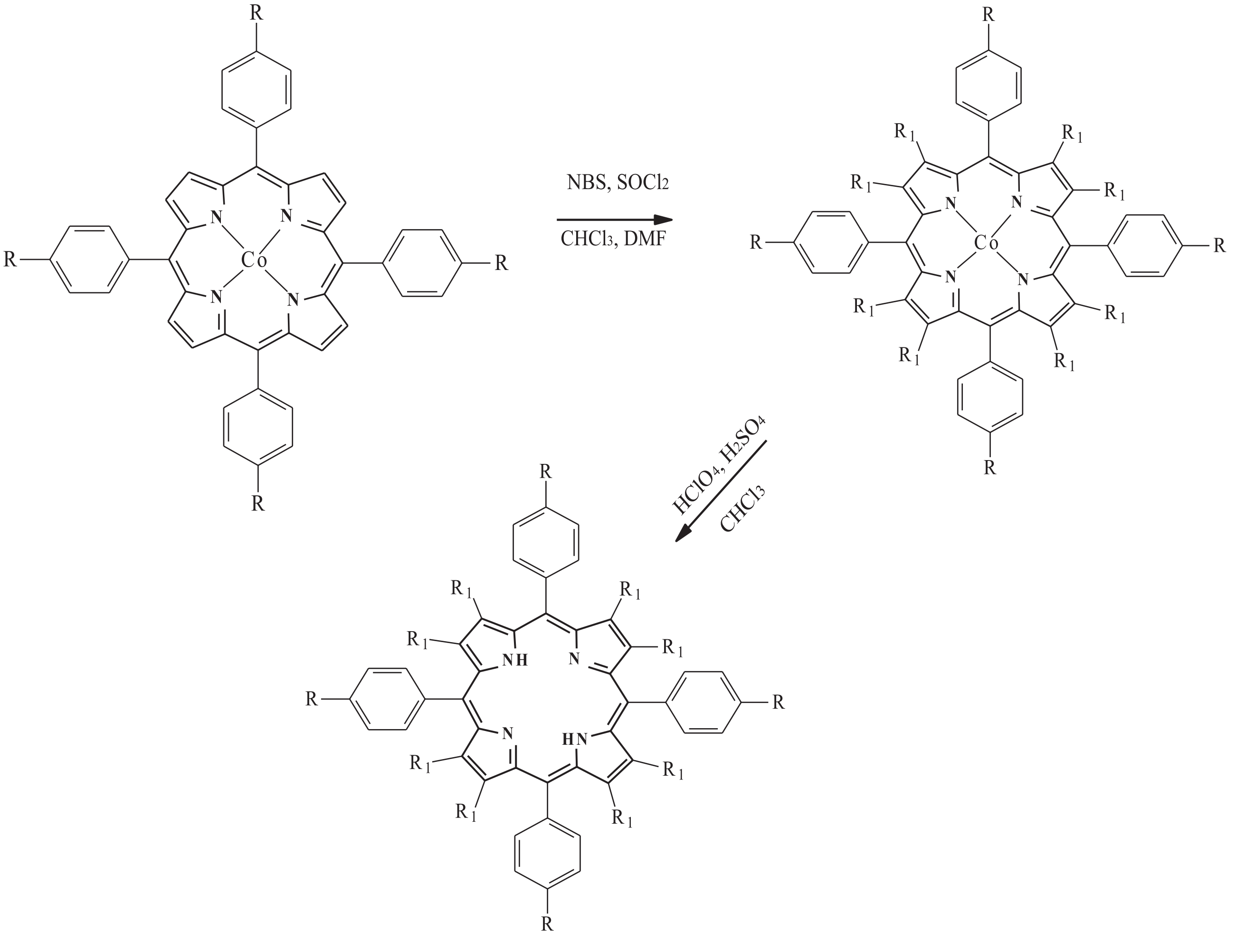
Ключевые слова: Реакции бромирования и хлорирования, тетрафенилпорфирины, комплексы Co, спектральная характеристика, кислотно-основные свойства.

Introduction

Synthetic porphyrins having a planar or almost planar molecules structure have been thoroughly studied.[1-5] However, according to the data,[6-13] the porphyrin macrocycle is flexible enough and can exist in no planar conformations. The ability of spatially distorted polyhalogensubstituted metalloporphyrins to exhibit catalytic activity in oxidation reactions is of great interest.[14,15] Cobalt porphyrins are used in the SO_2 and hydrocarbons anodic oxidation catalysis with a sufficiently high efficiency.[3] The electrochemical properties of the β-bromosubstituted Co(II)-tetraphenylporphyrins were studied in.[16,17]

The authors of[17] showed that Cu(II)-tetraphenylporphyrin bromination with Br_2 in $CHCl_3$-CCl_4-Py mixture leads to the β-octabromosubstituted Cu(II) complex formation. Bromination of Cu(II)-tetra(4-chlorophenyl)porphyrin with Br_2 in $CHCl_3$-CCl_4 mixture leads to the corresponding β-octabromoderivative.[18] Octabromotetraphenylporphyrins were obtained by treatment of corresponding copper complexes with perchloric acid. When the porphyrin free base interacts with Co(II) acetate in the chloroform–methanol mixture, corresponding Co(II)-octabromoporphyrin has been synthesized.[17,19] The bromination of Ni(II)-tetraphenylporphyrin with *N*-bromosuccinimide (NBS) in chloroform-dimethylformamide (DMF) boiling mixture leads to the β-octabromosubstituted nickel(II)-porphyrin formation.[20] Co(II)-octabromotetraphenylporphyrin was obtained by the interaction of unsubstituted cobalt(II)-tetraphenylporphyrin with NBS in $CHCl_3$-DMF mixture at room temperature.[21] The authors[22,23] used thionyl chloride for the synthesis of octachlorosubstituted metalloporphyrins.

Varying the degree of the porphyrin molecule distortion due to substituents introducing is a fine tuning tool for purposeful obtaining of the macrocycles with predetermined properties. Therefore, the synthesis methods development, physical-chemical properties study of polysubstituted on the periphery porphyrins having a molecular core no planar structure are actual problems and have become the goal of our research. In this work, the reactions of Co(II)-5,10,15,20-tetra(4-chlorophenyl-porphyrin (**1**) bromination with NBS and Co(II)-5,10,15,20-tetra(4-bromophenyl)porphyrin (**2**) chlorination using thionyl chloride in a mixture of $CHCl_3$–DMF were investigated. The acid-base properties of the resulting halogensubstituted porphyrins in acetonitrile were studied.



R=Cl (**1**), R=Br (**2**), R=Cl, R_1=Br (**3**), R=Br, R_1=Cl (**4**),
R=Cl, R_1=Br (**5**), R=Br, R_1=Cl (**6**), R=H, R=Br (**7**).

Scheme 1.

Experimental

General

UV-Vis spectra were recorded on a Cary 100 (Varian) spectrophotometer at a room temperature. Mass-spectra on a Maldi TOF Shimadzu Biotech Axima Confidence mass spectrometer (matrix – dihydroxybenzoic acid) were obtained. ^{1}H NMR spectra on a Bruker AV III-500 spectrometer (internal standard was tetramethylsilane (TMS)) were recorded.

Acid-base properties of halogensubstituted porphyrins were studied in acetonitrile "Lab-Scan". The experimental procedure, preparative chemistry and experimental data processing were described in detail in Refs.[24-25] The measurements were carried out on a Cary 100 spectrophotometer in thermostated cuvettes at 298 K with least three parallel experiments at each temperature.

5,10,15,20-Tetra(4-chlorophenyl)porphyrin and 5,10,15,20-tetra(4-bromophenyl)porphyrin "Porphychem" were used in the course of the experiment. 2,3,7,8,12,13,17,18-Octabromo-5,10,15,20-tetraphenylporphyrin was synthesized according to known procedure.[20] *N*-Bromosuccinimide and thionyl chloride "Acros", alumina "Merck", DMF, $CHCl_3$, CH_2Cl_2, hexane, $Co(OAc)_2$ of "chemical pure" grade were used without additional purification.

Synthesis

*Co(II)-5,10,15,20-Tetra(4-chlorophenyl)porphyrin (**1**).* A mixture of tetra(4-chlorophenyl)porphyrin (0.04 g, 0.065 mmol) and $Co(OAc)_2$ (0.96 g, 0.65 mmol) in DMF (30 mL) was heated to reflux, it was boiled for 30 s. The reaction mixture was cooled, poured into water, NaCl was added, the precipitate was filtered off, washed with water, dried and purified by alumina chromatography using dichloromethane as eluent. Yield: 0.035 g (0.0432 mmol, 82 %). *m/z* (Ie, %): 809.02 (97) $[M]^+$ (calculated for $C_{44}H_{24}N_4Cl_4Co$: 810). ^{1}H NMR ($CDCl_3$) δ_H ppm: 15.82 br.s (8H, pyrrole), 13.00 br.s (8H, H^{o}), 8.15 d (8H, *J*=7.60 Hz, H^{m}).

Compound **2** was synthesized in a similar way.

*Co(II)-5,10,15,20-Tetra(4-bromophenyl)porphyrin (**2**).* Tetra(4-bromophenyl)porphyrin (0.04 g, 0.043 mmol), $Co(OAc)_2$ (0.75 g, 0.43 mmol), DMF (40 mL). Yield: 0.034 g (0.0344 mmol, 80 %). *m/z* (Ie, %): 986.63 (98) $[M]^+$ (calculated for $C_{44}H_{24}N_4Br_4Co$: 987.3). ^{1}H NMR ($CDCl_3$) δ_H ppm: 15.88 br.s (8H, pyrrole), 12.94 br.s (8H, H^{o}), 10.10 br.s (8H, H^{m}).

*Co(II)-2,3,7,8,12,13,17,18-Octabromo-5,10,15,20-tetra(4-chlorophenyl)porphyrin (**3**).* *N*-Bromosuccinimide (0.066 g, 0.371 mmol) was added with stirring to a solution of complex **1** (0.02 g, 0.0247 mmol) in $CHCl_3$ (12 mL) and DMF (3 mL). The mixture was refluxed for 5 min, NBS (0.044 g, 0.247 mmol) was added, refluxed another for 5 min. The reaction mixture was cooled and dichloromethane (15 mL) and water were added. The organic layer was separated, washed with water, dried over Na_2SO_4, evaporated and the residue was purified by alumina chromatography (eluent: chloroform), reprecipitated from hexane. Yield: 0.026 g (0.018 mmol, 74 %). *m/z* (Ie, %): 1439.9 (45) $[M]^+$ (calculated for $C_{44}H_{16}N_4Cl_4Br_8Co$: 1440.5). ^{1}H NMR ($CDCl_3$) δ_H ppm: 15.10 br.s (8H, H^{o}), 10.07 br.s (8H, H^{m}).

*Co(II)-2,3,7,8,12,13,17,18-Octachloro-5,10,15,20-tetra(4-bromophenyl)porphyrin (**4**).* Thionyl chloride (4 mL) was added to the compound **2** (0.02 g, 0.0203 mmol) in $CHCl_3$–DMF mixture (12 mL, 1:1). The mixture was stirred for 2 h at room temperature. The reaction mixture was evaporated to a minimum volume, DMF, water and solid sodium chloride were added, the precipitate was filtered off, washed with water, dried and purified by alumina chromatography using chloroform as eluent. Yield: 0.017 g (0.0135 mmol, 68 %). *m/z* (Ie, %): 1263.5 (42) $[M]^+$ (calculated for $C_{44}H_{16}N_4Cl_8Br_4Co$: 1262.7). ^{1}H NMR ($CDCl_3$) δ_H ppm: 14.30 br.s (8H, H^{o}), 10.13 br.s (8H, H^{m}).

*2,3,7,8,12,13,17,18-Octabromo-5,10,15,20-tetra(4-chlorophenyl)porphyrin (**5**).* Chloric acid (3 mL) and sulfuric acid (2.5 mL) were added to the solution of compound **3** (0.02 g, 0.0139 mmol) in chloroform (10 mL). The solution was stirred for 1 h at room temperature. The organic layer was separated, washed with water and ammonia, with water again, dried over Na_2SO_4, evaporated. The residue was purified by alumina chromatography using dichloromethane as eluent and finally it was reprecipitated from hexane. Yield: 0.014 g (0.0101 mmol, 72 %). *m/z* (Ie, %): 1385 (42) $[M]^+$ (calculated for $C_{44}H_{18}N_4Cl_4Br_8$: 1383.7). UV-Vis (acetonitrile) λ_{max} (lgε) nm: 372 (4.44), 474 (5.09), 646 (4.17), 763 (3.94). UV-Vis (CH_2Cl_2) λ_{max} (lgε) nm: 374 (4.45), 470 (5.43), 569 (4.07), 626 (4.17), 742 (4.10) (lit. data:[18] 373 (4.41), 470 (5.37), 571 (3.87), 628 (4.08), 742 (3.79)). ^{1}H NMR ($CDCl_3$) δ_H ppm: 8.14 d (8H, *J*=7.70 Hz, H^{o}), 7.78 d (8H, *J*=7.60 Hz, H^{m}) (lit. data:[18] 8.05 d (8H, H^{0}), 7.69 d (8H, H^{m}), -1.73 br.s (2H, NH-protons)).

*2,3,7,8,12,13,17,18-Octachloro-5,10,15,20-tetra(4-bromophenyl)porphyrin (**6**).* 3 mL of chloric and 2.5 mL of sulfuric acids were added to solution of compound **4** (0.02 g, 0.0158 mmol) in chloroform (10 mL). The solution was stirred for 3 h at room temperature. The organic layer was separated, chloric (3 mL) and sulfuric (2.5 mL) acids were added, then it was stirred for 2 h and treated as described above in **5**, chromatography by alumina using mixture dichloromethane-hexane (1:1) as eluent. Yield: 0.01 g (0.0083 mmol, 54 %). *m/z* (Ie, %): 1207.3 (53) $[M]^+$ (calculated for $C_{44}H_{18}N_4Cl_8Br_4$: 1205.9). UV-Vis (acetonitrile) λ_{max} (lgε) nm: 372 (4.44), 458 (5.04), 554 (4.07), 623 (4.16), 732 (3.99). ^{1}H NMR ($CDCl_3$) δ_H ppm: 8.04 d (8H, *J*=7.70 Hz, H^{o}), 7.92 d (8H, *J*=7.60 Hz, H^{m}).

Results and Discussion

It is shown that the bromination of the compound **1** with NBS (molar ratio 1:20) in $CHCl_3$–DMF mixture at room temperature proceeds *ca.* by an order of magnitude slower than in the case of unsubstituted Co(II) tetraphenylporphyrin.[21] A mixture of β-octabromosubstituted Co(II) and Co(III) porphyrins is formed by interaction of **1** with NBS (molar ratio 1:25 – 1:35) in boiling $CHCl_3$–DMF (4:1) mixture within 10 min (spectrophotometric control). The UV-Vis spectrum of the sample dissolved in $CHCl_3$ has bands with λ_{max} at 370, 466, 588 and 638 nm (Figure 1). Co(II) 2,3,7,8,12,13,17,18-octabromo-5,10,15,20-tetra-(4-chlorophenyl)porphyrin (**3**) was obtained by alumina chromatography of octabromosubstituted cobalt-porphyrins

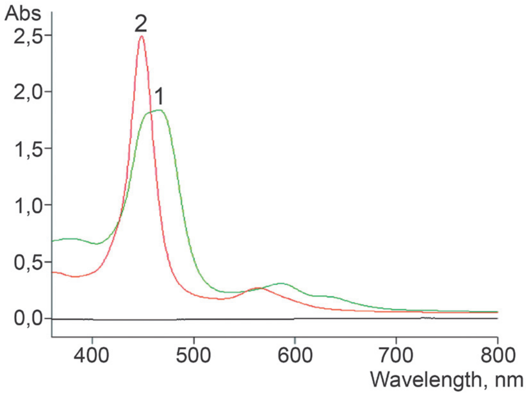


Figure 1. UV-Vis spectra in $CHCl_3$: 1 – the mixture of β-octabromosubstituted Co(II) and Co(III) porphyrins; 2 – Co(II)-2,3,7,8,12,13,17,18-octabromo-5,10,15,20-tetra(4-chlorophenyl) porphyrin.

(eluent – chloroform) (Figure 1). There are broadened signals of *ortho*- and *meta*-protons at 15.10, 10.07 ppm in the ^{1}H NMR spectrum of resulting compound. Similar spectra for paramagnetic Co(II) tetraphenylporphyrins (configuration 3d^7) are given in.[19,21] For example, signals of *ortho*- and *meta*-protons of Co(II) tetra(4-bromophenyl)porphyrin appear as broadened singlets and are located in a weak field at 12.94 and 10.10 ppm. On the contrary, signals of *ortho*- and *meta*-protons of diamagnetic Co(III) tetra(4-bromophenyl)porphyrin (configuration 3d^6) appear as doublets and are located in a strong field at 8.10, 7.92 ppm.[19]

Compound **3** is also formed by dissolving the Co(II) and Co(III) porphyrins in a strongly coordinating solvent – DMF. There are bands with λ_{max} at 457 and 567 nm of the complex **3** in DMF in the UV-Vis spectrum.

The bromosubstituted cobalt-porphyrin **2** chlorination with excess of thionyl chloride in $CHCl_3$-DMF mixture (1:1) within 2 hours results in the octachlorosubstituted Co(II) and Co(III)-porphyrins formation. The UV-Vis spectrum of the sample dissolved in DMF has bands with λ_{max} at 456, 580 and 639 nm (Figure 2). The nature of spectrum in DMF does not change significantly after isolation of the obtained compounds from the reaction mixture. Co(II) 2,3,7,8,12,13,17,18-octachlro-5,10,15,20-tetra(4-bromophenyl)porphyrin (**4**) is formed in DMF solution after 1.5 hours. There are bands with λ_{max} at 446 and 555 nm in the UV-Vis spectrum of compound **4** in DMF (Figure 2). Chromatographic purification of octachlorosubstituted cobalt-porphyrins on alumina also results in the formation of Co(II) complex **4**. Only the last fraction contains a mixture of cobalt-porphyrins with λ_{max} at 445, 558 and 624 nm according to the data of UV-Vis spectrum in chloroform.

The ^{1}H NMR spectrum of compound **4** in $CDCl_3$ contains signals of *ortho*- and *meta*-protons at 14.30 and 10.13 ppm (Figure 3).

According to,[17] the use of perchloric acid for the octabromotetraphenylporphyrin formation does not lead to 100 % copper-porphyrin demetallization. Free base twice protonated form ($H_4Br_8T(4\text{-}ClPh)P^{2+}$) is formed by the treatment of compound **3** in chloroform with a mixture of chloric and sulfuric acids (4:3) within 60 min. The UV-Vis spectrum of $H_4Br_8T(4\text{-}ClPh)P^{2+}$ in chloroform has bands with λ_{max} at 434, 499 and 746 nm (Figure 4). The 2,3,7,8,12,13,17,18-octabromo-5,10,15,20-tetra(4-chlorophenyl)porphyrin (**5**) was obtained after mineral acids removal and treatment of the protonated form with ammonia solution (Figure 4). ^{1}H NMR spectrum of the bromosubstituted porphyrin **5** in $CDCl_3$ contains signals of *ortho*- and *meta*-protons at 8.14 and 7.78 ppm.

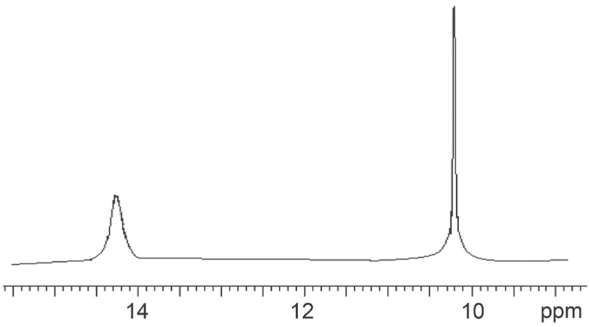


Figure 3. The informative fragment of the ^{1}H NMR spectrum of Co(II) 2,3,7,8,12,13,17,18-octachloro-5,10,15,20-tetra(4-bromophenyl)porphyrin in $CDCl_3$.

Under similar conditions, when the complex **4** is treated with a mixture of chloric and sulfuric acids within 3 hours, 100 % demetallization of the cobalt-porphyrin is not observed. The chlorosubstituted porphyrin twice protonated form ($H_4Cl_8T(4\text{-}BrPh)P^{2+}$) is formed by the repeated addition to solution of the porphyrin free base and cobalt-complex of chloric and sulfuric acids. UV-Vis spectrum of $H_4Cl_8T(4\text{-}BrPh)P^{2+}$ in chloroform has bands with maxima at 422, 489 and 734 nm. 2,3,7,8,12,13,17,18-Octachloro-5,10,15,20-tetra-(4-bromophenyl)porphyrin (**6**) was obtained after mineral acids removal and treatment of $H_4Cl_8T(4\text{-}BrPh)P^{2+}$ with ammonia solution. In the ^{1}H NMR spectrum of porphyrin **6** in $CDCl_3$ signals of *ortho*- and *meta*-protons were recorded at 8.04 and 7.92 ppm.

The characteristics of UV-Vis spectra of the synthesized cobalt-porphyrins are given in Table 1. Halogenation of cobalt tetraphenylporphyrins β-positions leads

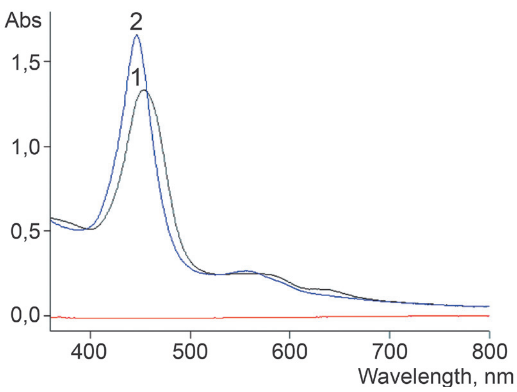


Figure 2. UV-Vis spectra in DMF: 1 – the mixture of β-octachlorosubstituted Co(II) and Co(III) porphyrins; 2 – Co(II)-2,3,7,8,12,13,17,18-octachloro-5,10,15,20-tetra(4-bromophenyl)porphyrin.

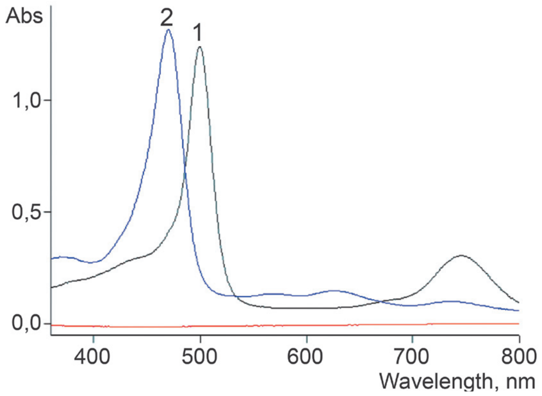


Figure 4. UV-Vis spectra in chloroform:
1 – twice protonated form of 2,3,7,8,12,13,17,18-octabromo-5,10,15,20-tetra(4-chlorophenyl)porphyrin (**5**),
2 – porphyrin **5**.

Table 1. The parameters of UV-Vis spectra of Co(II) tetraphenylporphyrins.

Complex	Solvent	Soret band, λ (lgε), nm	*Q*-band, λ, (lgε) nm
1	$CHCl_3$	410 (5.32)	529 (4.23)
2	$CHCl_3$	411 (5.57)	528 (4.50)
3	$CHCl_3$	449 (5.04)	564 (4.17)
3	DMF	457 (5.12)	567 (4.29)
4	$CHCl_3$	438 (5.01)	554 (4.16)
4	DMF	446 (5.07)	557 (4.31)

to the bathochromic shift of the absorption bands compared to unsubstituted complexes **1-2**.

m/z Signals of halogenated cobalt complexes and their porphyrin-ligands are fixed in mass-spectra corresponding to the molecular ions of the compounds **1-6** (Figures S1-4, Experimental).

A special place in chemistry of porphyrins is given to the study of the acid-base properties of these unique molecules.[1-4] It is well known that porphyrins (H_2P) exhibit amphoteric properties in organic solvents and can be protonated and deprotonated through intra-cyclic nitrogen atoms in the presence of acids and bases.

$$H_4P^{2+} \xrightleftharpoons{k_{b1}} H_3P^+ + H^+, \qquad (1)$$

$$H_3P^+ \xrightleftharpoons{k_{b2}} H_2P + H^+, \qquad (2)$$

$$H_2P \xrightleftharpoons{k_{a1}} HP^- + H^+, \qquad (3)$$

$$HP^- \xrightleftharpoons{k_{a2}} HP^{2-} + H^+, \qquad (4)$$

where H_2P, HP^-, P^{2-}, H_3P^+, H_4P^{2+} are the molecular, mono- and double-deprotonated and protonated forms of the porphyrins. The dissociation constants of the porphyrins protonated forms and the state of dissociation of molecular forms are traditionally designated K_b and K_a.[24-26,30]

In this work, acid-base properties of porphyrins **5-6** in comparison with 2,3,7,8,12,13,17,18-octabromo-5,10,15,20-tetraphenylporphyrin (**7**) have been studied by the method of spectrophotometric titration[24,25] in acetonitrile (AN) – $HClO_4$ (5) and AN – 1,8-diazabicyclo[5.4.0]undec-7-ene (DBU) (6) at 298 K.

$$\textbf{5-7} - HClO_4 - CH_3CN \qquad (5)$$

$$\textbf{5-6} - DBU - CH_3CN \qquad (6)$$

Figure 5 and Figures S5-6 show the UV-Vis spectra of compounds **5-7** in AN with titration by 0.01 M $HClO_4$ acetonitrile solution. Figure 6 and Figure S7 show the compounds **5-6** UV-Vis spectra in AN with titration by 0.01 M DBU acetonitrile solution. The abscissa scale shows the lg concentration of the titrant in mol/L.

Titrant solutions of 0.01 mol/L DBU and 0.01 mol/L perchloric acid were prepared on the basis of dry acetonitrile (Lab-Scan, water content not more than 0.03 %) was used as the solvent. Perchloric acid (66.76 % aqueous solution) was used to prepare the working solution of 0.01 mol/L perchloric acid in acetonitrile. At the end of the titration in the system at the end point, the total content of the titrant was ~ $7.76 \cdot 10^{-7}$ mol/L; therefore, the introduced water was ~ $5.18 \cdot 10^{-7}$ mol/L. The results of the work[29] indicate that the effect of water in acetonitrile is manifested when the water concentration in the system is greater than ~ 0.1 mol/L. 1,8-Diazabicyclo[5.4.0]undec-7-ene (DBU) (98 %) was used to prepare a working solution of 0.01 mol/L in acetonitrile and the water content in the system was meager.

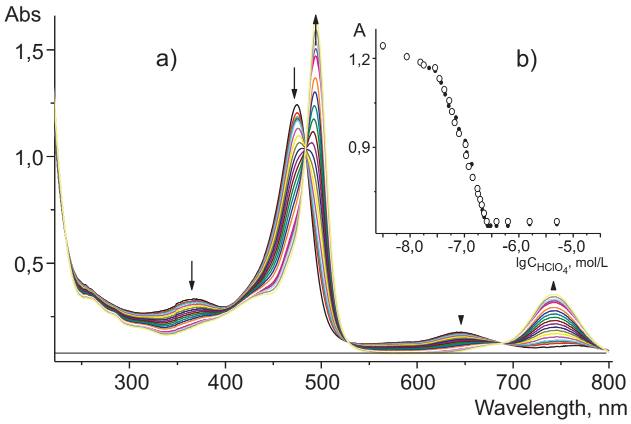


Figure 5. The change in the UV-Vis spectra (a) and the spectrophotometric titration curve (λ=475 nm) (b) of 2,3,7,8,12,13,17,18-octabromo-5,10,15,20-tetra(4-chlorophenyl)porphyrin in the AN-$HClO_4$ system ($C_{porp.}=1.01 \cdot 10^{-5}$ mol/L, $C_{HClO_4}=0 \div 2.51 \cdot 10^{-5}$ mol/L), T=298 K.

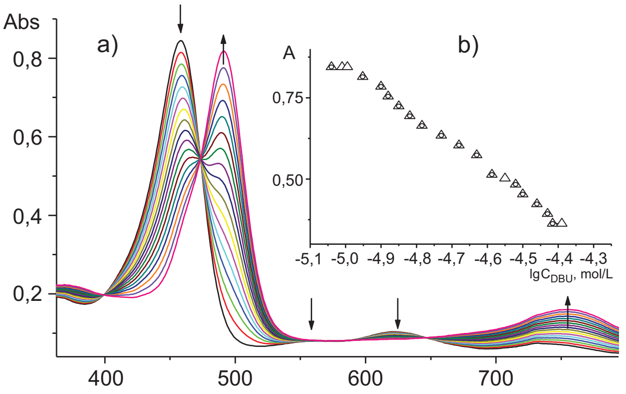


Figure 6. The change in the UV-Vis spectra (a) and the spectrophotometric titration curve (λ=458 nm) (b) of 2,3,7,8,12,13,17,18-octachloro-5,10,15,20-tetra(4-bromophenyl)porphyrin in the AN-DBU system ($C_{porp.}=0.77 \cdot 10^{-5}$ mol/L; $C_{DBU}=0 \div 3.84 \cdot 10^{-5}$ mol/L), T=298 K.

The obtained data analysis showed that with the increase in the concentration of $HClO_4$ in the system (5) and DBU in the system (6), two families of spectral curves were formed in the UV-Vis spectra of the studied porphyrins, each corresponding to its own set of isosbestic points. The presence of two families of isosbestic points in the UV-Vis spectra is for the stepwise protonation processes characteristic. However, the spectrophotometric titration curves based on the experimental data did not have pronounced steps that does not negative stepwise ionization processes but assumes close values of each reaction protonation constants.[26] The isosbestic points presence and the UV-Vis spectra nature indicate that the ratio between the ionized forms during protonation is not disturbed as the concentration of two porphyrin molecule absorbing centres changes. Extinction coefficients for all forms of the investigated porphyrins participating in the Equilibria (1-4) for systems (5) and (6) were determined using the UV-Vis spectra data and the total particle concentration of each porphyrin (Table 2). The total protonation constant for the processes (1) and (2) was calculated from the Equation (7).

$$pK_{b1,2}=-\lg K_{b1,2}=\lg(Ind) + pH, \qquad (7)$$

where *K* – protonation constant, *Ind* – the indicator ratio $[H_4P^{2+}]/[H_2P]$.

The p*H* – $\lg C_{HClO4}$ dependence was established earlier,[27-31] using previously received spectropotentiometric research data of glass electrode PH function to AN and temperature calibration of the electrode system – silver chloride electrode, filled with Et_4NCl solution, saturated at 293 K for *m*-nitroaniline (pK_a=7.6).[27-30] (Figure 7). These data were used in the protonation constants calculation.

In the case of the processes (3), (4), Equation (8) was used to calculate the acidity constant.

$$\lg K_{a1,2}=\lg(Ind) + n\lg C_{DBU}, \qquad (8)$$

where $K_{a1,2}$ is the total acidity constant, C_{DBU} is the analytical value of the DBU concentration in the solution, *Ind* is the indicator ratio P^{2-}/H_2P, *n* is the number of dissociated protons (*n*=2), $pK_{a1,2}=-\lg K_{a1,2}$. The error in constants measuring did not exceed 3–5 %.

The porphyrins protonation and deprotonation constants values of **5**-**6** in particular showed (Table 2) that the introduction of bromine and chlorine atoms into the β-positions of tetraphenylporphyrins leads to the change in the macrocycle π-electron density and promotes reduction of the basic and correspondingly increase of the acid properties as compared with unsubstituted compound.

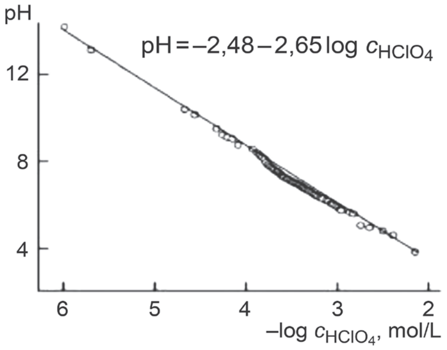


Figure 7. Dependence of p*H* on log C_{HClO4} at T=298 K according to the results of spectropotentiometric titration of the solution of 3-nitroaniline in acetonitrile with perchloric acid.[25]

In the case of the β-substituted chlorine derivative **6**, this effect is maximized and the difference between the basicity constants is more than **5** orders of magnitude. As the acidity increases, the compounds can be arranged in a row:

$H_2Br_8TPP < H_2Br_8T(4\text{-}ClPh)P < H_2Cl_8T(4\text{-}BrPh)P$.

The presence of electron-withdrawing chlorine and bromine atoms in *para*-positions of phenyl rings also contributes to the decrease in the electron density at the reaction centre nitrogen atoms compared to unsubstituted tetraphenylporphyrin and, as a consequence, it should enhance the ligand acid properties. The phenyl rings having weak electron-acceptor properties limit the possibility of electron density transfer from the functional substituent to the porphyrin reaction centre *via* the conjugated bond system making the induction effect of the substituents in a priority.

Table 2. The parameters of UV-Vis spectra of porphyrins molecular and ionic forms in acetonitrile, he corresponding basicity and acidity constants values.

Forms of porphyrins	Soret band, λ (lgε) nm	*Q*-bands, λ (lgε) nm	$pK_{b1,2}$	$pK_{a1,2}$
H_2TPP	413 (5.02)	512 (3.56), 546 (3.12), 589 (2.92), 646 (2.96)	19.8[30]	
H_3TPP^+	413 (5.01)	512 (3.69), 547 (3.42), 660 (3.47)	18.61[31]	
H_4TPP^{2+}	441 (5.04)	661 (4.17)		
H_2Br_8TPP (**7**)	471 (5.14)	646 (4.16), 765 (3.92)	16.60	10.77[32]
$H_4Br_8TPP^{2+}$	490 (5.19)	741 (4.52)		
Br_8TPP^{2-} [32]	497 (5.30)	734 (4.80)		
$H_2Br_8T(4\text{-}ClPh)P$ (**5**)	475 (5.09)	646 (4.17), 763 (3.94)	16.06	10.15
$H_4Br_8T(4\text{-}ClPh)P^{2+}$	495 (5.21)	743 (4.54)		
$Br_8T(4\text{-}ClPh)P^{2-}$	500 (4.96)	733 (4.18)		
$H_2Cl_8T(4\text{-}BrPh)P$ (**6**)	458 (5.04)	554 (4.07), 623 (4.16), 732 (3.99)	14.76	9.66
$H_4Cl_8T(4\text{-}BrPh)P^{2+}$	486 (5.23)	736 (4.56)		
$Cl_8T(4\text{-}BrPh)P^{2-}$	491 (5.03)	755 (4.32)		

The aggregate of all these factors contributed to the change in acid-base properties of the studied porphyrins **5-7**.

Conclusions

The bromination reaction of β-positions of Co(II) tetra(4-chlorophenyl)porphyrin with an excess of *N*-bromosuccinimide is observed in a boiling chloroform–dimethylformamide mixture. The complete chlorination of the pyrrole rings of Co(II) tetra(4-bromophenyl)porphyrin with a large excess of the thionyl chloride in $CHCl_3$–DMF mixture takes place at room temperature. When the halogen substituted Co(II) porphyrins are treated with a chloric and sulfuric acids mixture, corresponding porphyrin-ligands are obtained. Acidity and basicity constants of the synthesized porphyrins were determined and the concentration intervals for their ionized forms existence were established. The introduction of bromine and chlorine atoms into β-positions of the tetraphenylporphyrin promotes reduction of the basic properties and correspondingly increase acid properties of the porphyrin-ligands studied as compared with unsubstituted compound. Varying the degree of porphyrin molecule distortion by introducing substituents makes it possible to purposefully synthesize compounds with predetermined properties.

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