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Acid–Base Interaction of Octaaryltetraazaporphyrin Complexes in a Proton-Donor Medium

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Abstract—The processes of acid–base interactions of the octaaryltetraazaporphyrin complexes in a proton-donor environment based on acetic or trifluoroacetic acids was studied. The constants of the acidity of the protonated forms were determined. The introduction of electron-withdrawing functional groups was shown to reduce the basicity of the *meso*-nitrogen atoms of the macrocycle. The decrease in the cobalt oxidation state was shown to reduce the complex basicity.
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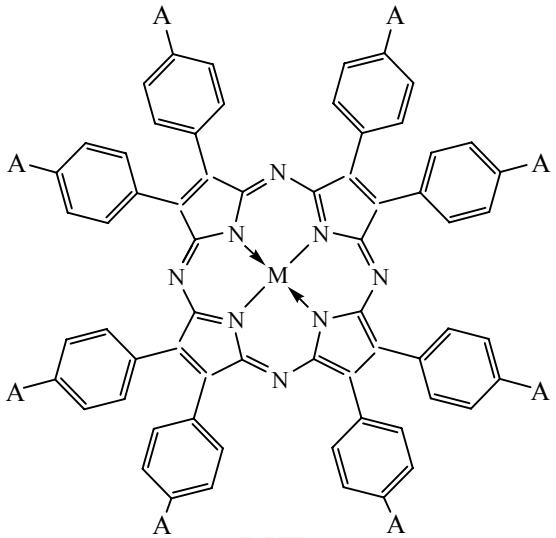
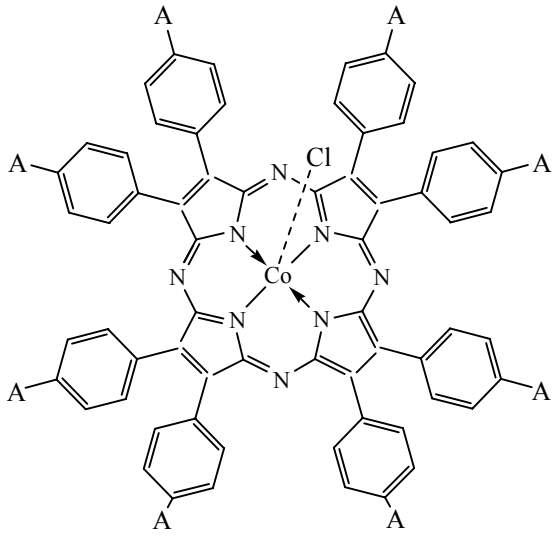
Porphyrazines are weak multi-center bases. In the case of porphyrazine metallocomplexes the acid–base interactions occur with the involvement of exocyclic (*meso*) nitrogen atoms. The process of acid–base interactions of porphyrazines is rather complicated [1–3]. The resulting acid forms differ from each other by the degree of the proton transfer from the acid molecule to the donor center. The number of the porphyrazine donor centers involved in the acid–base interaction and the constants of acidity of the produced acid forms depend on the structure and properties of the proton-donor environment of the porphyrazine. To date a large experimental material was accumulated and summarized on the study the reaction of the porphyrazines acid–base interactions [1, 2].

In this paper we first investigated the effect of the structure of octaaryltetraazaporphyrin complexes, oxidation state of the metal, and nature of the proton environment on the reactions of acid–base interaction of the complexes.

Interaction of a porphyrazine with an acid results in characteristic changes in the electron absorption spectra that register formation of various acid forms.



I, VII



II, IV, VI

I, M = Co^{2+}, A = H; **II**, A = H; **IV**, A = Br; **VI**, A = NO_2; **VII, I**, M = Pd^{2+}, A = Br.

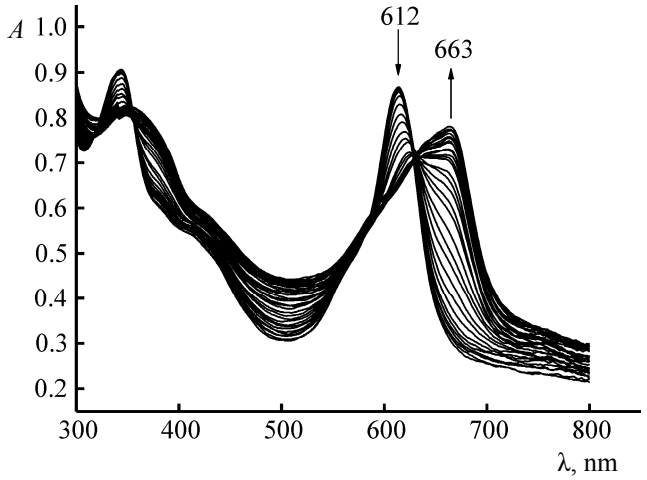


Fig. 1. Changes in the electron absorption spectrum of Co(II) octaphenyltetraazaporphyrin complex in the medium CH_2Cl_2–CF_3COOH at $c(CF_3COOH)$ = 0.01–0.02 moles per liter.

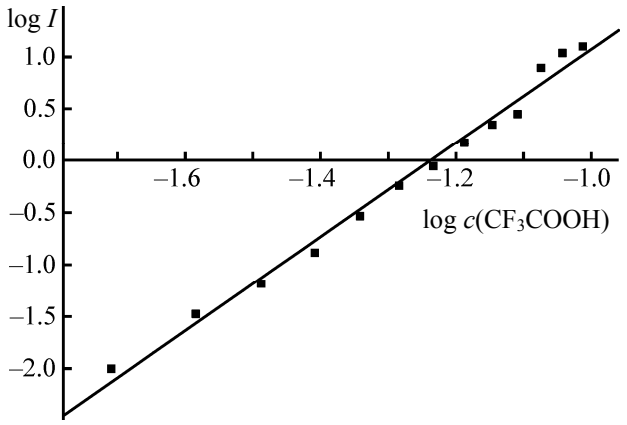


Fig. 2. Dependence on log I–log $c(CF_3COOH)$ in acid–base interaction of Co (II) octaphenyltetraazaporphyrin complex CH_2Cl_2–CF_3COOH (λ_{an} = 612 nm).

Figure 1 shows as an example the changes in the electron absorption spectrum of Co(II) octaphenyltetraazaporphyrin at adding from 0.01 to 0.02 M of trifluoroacetic acid to its solution in dichloromethane. The intensity of the absorption band at 612 nm, corresponding to the neutral form of the complex decreases, while the intensity of the band at 663 nm, corresponding to the absorption of its protonated form increases. This form is retained in 100% CF_3COOH. Such decrease in intensity of the absorption band of neutral form and the increase in intensity of the absorption bands of protonated forms, which undergo a red shift, occurs in the spectra of all complexes. According to published data [1] this corresponds to the protonation of *meso*-nitrogen atoms. In 100% trifluoroacetic acid the protonated forms are retained. In the process of acid–base interactions of the Co^{3+} complexes the extraligand Cl^- can be replaced by CF_3COO^-, although this is not registered by the spectra.

Figure 2 shows the dependence of log I (I is the indicator ratio) on log $c(CF_3COOH)$ in the process of acid–base interaction of Co(II) octaphenyltetraazaporphyrin. The slope of the dependence is greater than 1, the same occurs for all the studied complexes. It is not possible to suggest that at this stage of the acid–base interactions more than one nitrogen atom of the octaaryltetraazaporphyrin complex is protonated, because the acidity and ionizing power of the CH_2Cl_2–CF_3COOH medium are low (for dichloromethane ε = 8.9 and the CF_3COOH concentration is 0.02 M or less [3]). The value of the slope more than 1 is due to the phenomenon of homoconjugation: trifluoroacetate anion is stabilized by forming associates with one or more molecules of acid: $=NH^+\cdots\ ^-OOCCF_3(HOOCCF_3)_n$, as well as owing to the peculiarities of solvation of each complex, as has been observed previously [3].

The table shows the values of the acid concentration constants (pK) of the acid forms of complexes determined by the method of spectrophotometric titration [4]. Experimental data show that the complexes basicity decreases in the order: $(Cl)Co^{3+}TAP(C_6H_5)_8$ > $(Cl)Co^{3+}TAP(C_6H_4Br)_8$ > $(Cl)Co^{3+}TAP(C_6H_4NO_2)_8$, depending on the ligand nature. A similar sequence was found when comparing the basicity of the palladium(II) complexes. This is consistent with the electronic nature of the substituents. The table also shows that an increase in the cobalt oxidation state increases the complex basicity. The same has been observed previously in the studies of cobalt tetraneopentoxyphthalocyanine in dichlorobenzene in the presence of CF_3COOH or HCl [5]. The palladium complex basicity is less than that of the cobalt complexes.

We studied basicity of the complexes $(Cl)Co^{3+}TAP\cdot(C_6H_5)_8$, $(Cl)Co^{3+}TAP(C_6H_4Br)_8$, and $(Cl)Co^{3+}TAP\cdot(C_6H_4NO_2)_8$ in the CH_3COOH–H_2SO_4 medium in the H_2SO_4 concentration range from 0.14 to 0.89 M. Figure 3 shows as an example the changes in the electron absorption spectra of $(Cl)Co^{3+}TAP(C_6H_4NO_2)_8$ in this environment. As seen, only one absorption band that suffered a red shift increased in intensity.

The H_2SO_4 acidity function for the concentration range under study is unknown, so we determined the concentration dependence of acidity constants of

The values of acidity constants of protonated forms of complexes (pK) of octaaryltetraazaporphyrins in the proton-donor media

Complex[a]	pK (CH_2Cl_2–CF_3COOH)	pK (CH_3COOH–H_2SO_4)
$Co^{2+}TAP(C_6H_5)_8$	1.23±0.05	3.32±0.02
$(Cl)Co^{3+}TAP(C_6H_5)_8$	2.56±0.02	3.32±0.01
$(Cl)Co^{3+}TAP(C_6H_4Br)_8$	1.12±0.01	2.58±0.02
$(Cl)Co^{3+}TAP(C_6H_4NO_2)_8$	0.55±0.01	–
$Pd^{2+}TAP(C_6H_4Br)_8$	0.77±0.01	–
$Pd^{2+}TAP(C_6H_5)_8$	0.94±0.01	–

[a] TAP is tetraazaporphyrin.

protonated forms. In the CH_3COOH–H_2SO_4 mixture the proton-donor moiety is the protonated acetic acid $CH_3COOH_2^+$. The concentration of the $CH_3COOH_2^+$ species was calculated using the equation of the H_2SO_4 dissociation in acetic acid {pK(H_2SO_4) = 4.25 [6]}.

Figure 4 shows the dependence of log I on log c($CH_3COOH_2^+$) for $(Cl)Co^{3+}TAP(C_6H_4NO_2)_8$. For all the studied complexes this dependence is linear with the slope equal to 1, which allows us an assumption on the formation in the studied H_2SO_4 concentration range of the complexes monoprotonated at the *meso*-nitrogen atom. The pK values of the generated acid forms are listed in the table.

EXPERIMENTAL

Trifluoroacetic acid was purified by fractional distillation over concentrated H_2SO_4 (bp 72.5ºC). Dichloromethane was distilled over monoethanolamine (bp 40ºC). Glacial acetic acid of the reagent grade was subjected to repeated freezing out and boiled with the calculated amount of acetic anhydride, and then the fractional distillation was carried out (bp 118ºC). Anhydrous 100% H_2SO_4 was prepared from 60% oleum and 96% H_2SO_4.

Studies of acid-base interaction were determined by spectrophotometric titration using a spectrophotometer Shimadzu UV-1800 at 298 K as described in [9]. The concentration ratio of acid-base forms in equilibrium (indicator ratio) was determined by Eq. (1).

$$I_i = (A_i - A_0)/(A_\infty - A_i). \quad (1)$$

Here A_0 is the initial optical density of the solution on the analytical wavelength, A_∞ is the optical density of the solution after complete transition of the base into the protonated form, A_i is the optical density of the solution in the ith experiment, I_i is the indicator ratio.

The values of concentration stability constants of acidic forms were determined by Eq. (2).

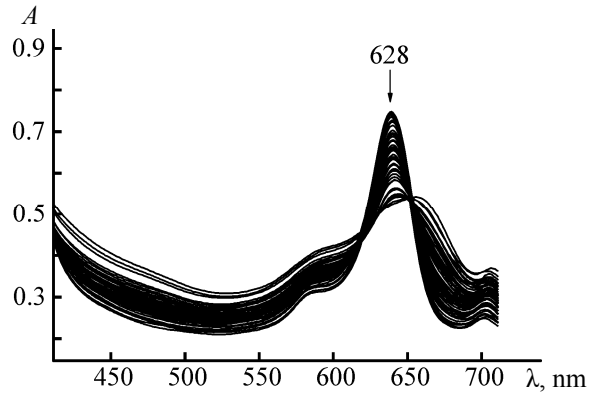


Fig. 3. Changes in the electron absorption spectrum of Co(III) octa(*p*-nitrophenyl)tetraazaporphyrin complex in a mixture CH_3COOH–H_2SO_4 with H_2SO_4 = 0.14–0.89 moles per liter.

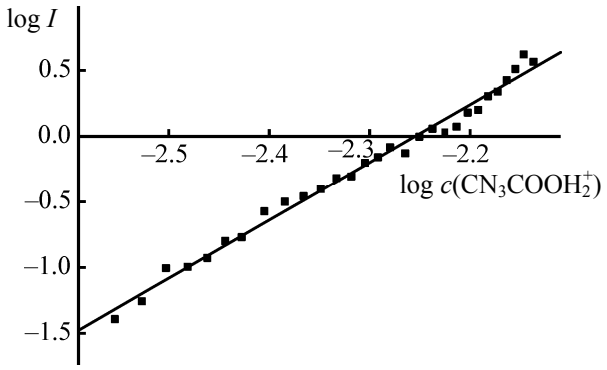


Fig. 4. Dependence on log I–log c($CN_3COOH_2^+$) in acid–base interaction Co(III) octa(*p*-nitrophenyl)tetraazaporphyrin complex in a mixture CH_3COOH–H_2SO_4 (λ_{an} = 628 nm).

$$\log K = \log (c_i/c_{i-1}) - n\log c_{HA}. \quad (2)$$

Here HA denotes CF_3COOH or $CH_3COOH_2^+$.

The Mg^{2+} complex with octaphenyltetraazaporphyrin was synthesized by the method of Linstead [7]. Octa(*p*-bromophenyl)tetraazaporphyrin and octa(*p*-nitrophenyl)tetraazaporphyrin were prepared along the procedures in [8, 9].

The Co^{2+} complex with octaphenyltetraazaporphyrin (I). 0.1 g of octaphenyltetraazaporphyrin–Mg complex and 0.14 g of $CoCl_2$ (molar ratio 1:10) were dissolved in 20 ml of DMF, the mixture was heated to boiling and cooled. The reaction mixture was transferred to a glass frit filter with neutral alumina, and the complex was eluted with dimethylformamide. The filtrate was poured into water, the precipitate formed was filtered off, washed with water and methanol, and dried. 0.08 g (0.0817 mmol, 77%) of the complex was isolated, R_f = 0.85 ($CHCl_3$–CCl_4, 1:1). Found, %: C 78.38, H 4.07; N 11.37. $C_{64}H_{40}N_8Co$. Calculated, %: C 78.45, H 4.11; N 11.43.

^{1}H NMR spectrum, δ, ppm ($CDCl_3$): 7.86 d (16H) 7.58 (16H), 7.44 t (8H).

IR spectrum, ν, cm^{-1}: 1157 s, 1004 s, 991 s (δ_{C-H}), 747 s, 695 s (γ_{C-H}), 3048 m, 2925 s, 2852 m (ν_{C-H}), 1444 m, 1372 m (skeletal C=N), 1647 m, 1630 m, 1587 m, 1561 w (skeletal C=C), 1074 w, 747 m, 611 m (pyrrole ring), 596 w. 507 (ν_{Co-N}).

The $(Cl)Co^{3+}$ complex with octaphenyltetraazaporphyrin (II). Synthesis is analogous to that of the Co^{2+} complex **I**. After the synthesis, in the cooled reaction mixture was added 4 ml of hydrochloric acid, the mixture was kept for 15 min, 50 ml of chloroform and 100 ml of water was added to it, the organic layer was separated, evaporated to a minimum volume, and reprecipitated into hexane. 0.075 g (70%) of compound **II** was obtained, R_f = 0.82 ($CHCl_3$–CCl_4, 1:1). Found, %: C 71.40, H 3.69; N 10.45. $C_{64}H_{40}N_8ClCo$. Calculated, %: C 71.48, H 3.75; N 10.42. ^{1}H NMR spectrum, δ, ppm ($CDCl_3$): 7.72 d (16H) 7.52 t (16H), 7.39 t (8H).

The Co^{2+} complex with octa(*p*-bromophenyl)tetraazaporphyrin (III). 0.1 g of octa(*p*-bromophenyl)tetraazaporphyrin and 0.083 g of $CoCl_2$ (molar ratio 1:10) were dissolved in 20 ml of DMF. The reaction mixture was kept for 3 h at 25°C and transferred to a glass frit filter with neutral aluminum oxide (eluent DMF), the eluate was poured into water, the precipitate was filtered off, washed with water and methanol, and dried. 0.085 g (0.0528 mmol, 84%) of compound **III** was isolated, R_f = 0.87 ($CHCl_3$–CCl_4, 1:4). Found, %: C 47.65, H 1.96; N 6.88. $C_{64}H_{32}Br_8N_8Co$. Calculated, %: C 47.71, H 2.00; N 6.96.

^{1}H NMR spectrum (δ, ppm, CDCl 3): 7.73 d (16H), 7.57 d (16H).

IR spectrum, ν, cm^{-1}: 2920 s, 2847 m, 2639 w, 1633 m, 1491 m, 1268 w, 1372 m, 1158 s, 1072 s, 992 s, 825 m, 750 m, 694 s, 600 w, 563 w.

The $(Cl)Co^{3+}$ complex with octa(*p*-bromophenyl) tetraazaporphyrin (IV) was synthesized by analogy with the Co^{2+} complex **III**. Subsequent operations were carried out as in the synthesis of complex **II**. 0.085 g (0.0517 mmol, 80%) of compound **IV** was isolated, R_f = 0.85 ($CHCl_3$–CCl_4, 1:4). Found, %: C 46.61, H 1.92; N 6.74. $C_{64}H_{32}Br_8N_8$ ClCo. Calculated, %: C 46.69, H 1.96; N 6.81. ^{1}H NMR spectrum, δ, ppm ($CDCl_3$): 7.81 d (16H), 7.63 d (16H).

The Co^{2+}complex with octa(*p*-nitrophenyl)tetraazaporphyrin (V). 0.1 g of octa(*p*-nitrophenyl) tetraazaporphyrin and 0.1 g of $CoCl_2$ (molar ratio 1:10) were dissolved in 15 ml of DMF and the mixture was kept at room temperature for 20 min. The reaction mixture was transferred to a glass frit filter with neutral aluminum oxide (eluent DMF). The filtrate was poured into water, the precipitate was filtered off, washed with water and methanol, and dried. 0.082 g (0.612 mmol, 78%) of compound **V** was isolated, R_f = 0.88 ($CHCl_3$–CCl_4, 1:4). Found, %: C 57.30, H 2.37; N 16.77. $C_{64}H_{32}N_{16}O_{16}Co$. Calculated, %: C 57.37, H 2.41; N 16.73. ^{1}H NMR spectrum, δ, ppm ($CDCl_3$): 7.80 d (16H), 7.49 d (16H).

IR spectrum, ν, cm^{-1}: 2923 s, 2853 m, 1749 w, 1642 s, 1580 w, 1510 m, 1455 s, 1350 m, 1160 w, 1148 s, 1025 s, 860 w, 835 w, 430 w.

The $(Cl)Co^{3+}$ complex with octa(*p*-nitrophenyl)-tetraazaporphyrin (VI). 0.1 g of compound **V** was dissolved in 15 ml of DMF, 1 ml of HCl was added. The mixture was stirred for 10 min, and 50 ml of chloroform and 100 ml of water was added to it. The organic layer was separated, evaporated to a minimum volume, and precipitated into hexane. 0.086 g (0.0681 mmol, 80%) of compound **VI** was isolated, R_f = 0.86 ($CHCl_3$–CCl_4, 1:4). Found, %: C 55.82, H 1.61; N 16.34. $C_{64}H_{32}N_{16}O_{16}ClCo$. Calculated, %: C 55.89; H 1.64; N 16.29.

^{1}H NMR spectrum, δ, ppm ($CDCl_3$): 7.87 d (16H), 7.59 d (16H).

The Pd^{2+} complex with octaphenyltetraazaporphyrin (VII) was prepared by the method [8]. 0.1 g of octaphenyltetraazaporphyrin and 0.19 g of $PdCl_2$ (molar ratio 1:10) were dissolved in 40 ml of DMF, the mixture was heated to boiling, boiled for 30 minutes, then another 0.19 g of $PdCl_2$ was added and the boiling was continued for 30 min. The mixture was then cooled, poured into water, the precipitate was filtered off, washed with water, dried, and chromatographed on alumina, using as eluent a pyridine–diethyl ether mixture, 1:4. 0.073 g (65%) of compound **VII** was isolated, R_f = 0.67 ($CHCl_3$–CCl_4, 1:1).

The Pd^{2+} complex with octa(*p*-bromophenyl)tetraazaporphyrin (VIII) was prepared by the method [8]. 0.1 g of octa(*p*-bromophenyl)tetraazaporphyrin and 0.23 g of $PdCl_2$ (molar ratio 1:20) were dissolved in 20 ml of DMF, heated to boiling, boiled for 10 min, cooled, poured into water, filtered, washed with water, dried, and chromatographed on silica gel (eluent chloroform), and then reprecipitated from methanol. 0.1 g of compound (90%) was isolated. R_f = 0.41 (CCl_4). Found, %: C 46.38, H 1.88; N 6.69. $C_{64}H_{32}Br_8N_8Pd$. Calculated, %: C 46.35; H 1.93; N 6.76.

ACKNOWLEDGMENTS

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