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Spectrophotometric Study of Acid–Base and Coordination Properties of 2,3,7,8,12,13,17,18-Octamethyl-5,10,15,20-tetrakis(thiophen-2-yl)porphyrin

Yu. B. Ivanova[a], O. V. Razgonyaev[b], A. S. Semeikin[b], and N. Zh. Mamardashvili[a]

[a] *Krestov Institute of Solution Chemistry, Russian Academy of Sciences, ul. Akademicheskaya 1, Ivanovo, 153045 Russia*
e-mail: jjiv@yandex.ru

[b] *Ivanovo State University of Chemistry and Technology, Sheremetevskii pr. 7, Ivanovo, 153000 Russia*

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Abstract—2,3,7,8,12,13,17,18-Octamethyl-5,10,15,20-tetrakis(thiophen-2-yl)porphyrin has been synthesized, and its acid–base and complexing properties have been studied by spectrophotometry in the systems $HClO_4$–acetonitrile (298 K) and $Zn(OAc)_2$–acetonitrile. The basicity constants and kinetic parameters for the formation of zinc complexes of 2,3,7,8,12,13,17,18-octamethyl-5,10,15,20-tetrakis(thiophen-2-yl)porphyrin in the above systems have been determined, and the effect of *meso*-thienyl substituents on the reactivity of octamethylporphyrin derivative has been discussed. Acid–base and complexing properties of 2,3,7,8,12,13,17,18-octamethyl-5,10,15,20-tetrakis(thiophen-2-yl)porphyrin have been compared with those of 5,10,15,20-tetrakis(4-*tert*-butylphenyl)-2,3,7,8,12,13,17,18-octamethylporphyrin.

Keywords: porphyrins, acid–base properties, protonated forms, coordination properties

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Porphyrins and their metal complexes are typical representatives of tetrapyrrole macroheterocycles that widely occur in nature and are very important for biological processes, such as oxygen transfer and storage, transformation of solar energy into chemical energy, electron transfer, and catalysis of redox reactions, as well as for data storage and transformation and many other applications [1–12]. High catalytic activity of porphyrins is determined by the aromatic character of the macrocycle, ability to form strong complexes with many metals, and facile variation of the oxidation state of the central metal ion. An important factor is chemical stability of porphyrins as free bases, as well as of their cationic and anionic forms. Natural porphyrins possess a complex set of substituents that considerably affect all properties of the macrocycle. Optimization of modern methods for the synthesis of porphyrins provides the possibility of their modification with a view to obtaining compounds possessing required physicochemical properties. Some modified chromophore systems are capable of absorbing in the near-IR and IR region, the properties intrinsic to the porphyrin core being retained [13, 14]. Such derivatives (in particular thiadiazolylporphyrins) are used in medicine as molecular probes and photosensors for cancer therapy and in geology as geochemical standards [15]. The mechanism of generation of optical response due to interaction of porphyrins with metal cations is an important factor in the design of compounds with desired coordination, physicochemical, and acid–base properties. For this purpose, in the present work we studied by spectro-photometry the acid–base and complexing properties of 2,3,7,8,12,13,17,18-octamethyl-5,10,15,20-tetrakis-(thiophen-2-yl)porphyrin (**I**) containing thienyl substituents in the *meso* positions.

Porphyrin **I** was synthesized as described below (see Experimental). Its complexing and acid–base properties were studied in the systems $Zn(OAc)_2$–MeCN and $HClO_4$–MeCN (298 K) (Scheme 1).

The complexation of porphyrins is of first kinetic order in the ligand [1] (Fig. 1). In all cases, the electronic absorption spectra of the reaction mixtures displayed distinct isosbestic points.

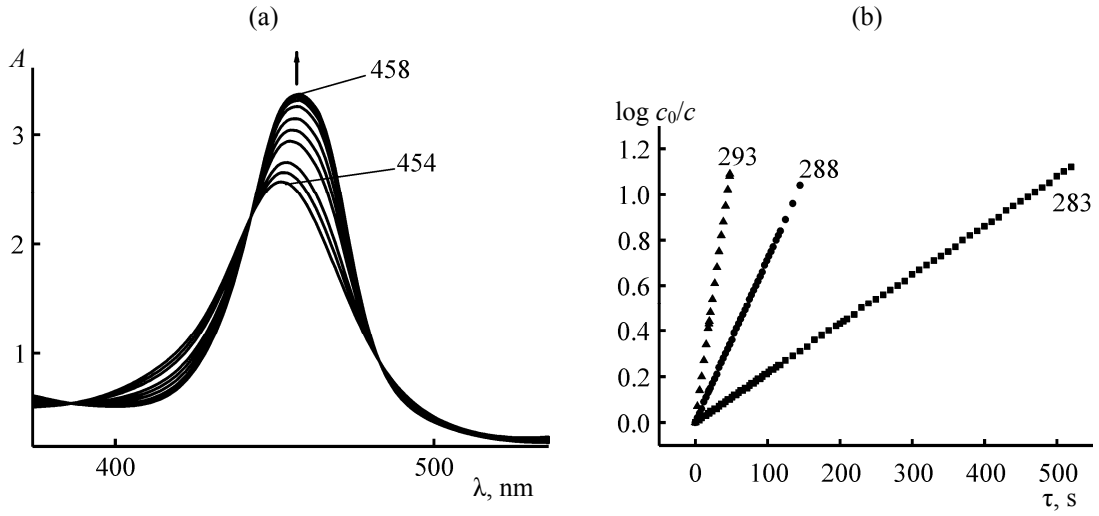


Fig. 1. (a) Variation of the electronic absorption spectrum in the reaction of porphyrin **I** with zinc(II) acetate in acetonitrile at 283 K; $c_{\mathbf{I}} = 1.38 \times 10^{-5}$ M, $c[Zn(OAc)_2] = 1.5 \times 10^{-3}$ M; (b) plots of ln (c_0/c_i) versus time for the reaction of porphyrin **I** with zinc(II) acetate in acetonitrile at 283–293 K; $c_{\mathbf{I}} = 0.69 \times 10^{-5}$ M, $c[Zn(OAc)_2] = 0.75 \times 10^{-3}$ M.

Kinetic experiments were carried out using excess $Zn(OAc)_2$ with respect to porphyrin **I**, so that the effective rate constants k_{ef} for reaction (1) could be calculated by Eq. (2).

$$H_2P + Zn(OAc)_2 \rightarrow ZnP + 2AcOH, \quad (1)$$

$$k_{ef} = (1/\tau)\ln [(A_0 - A_\infty)/(A - A_\infty)]. \quad (2)$$

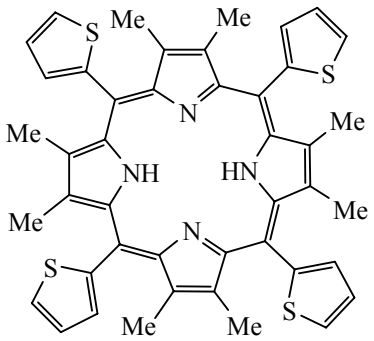
Here, A_0, A, and A_∞ are the optical densities of the reaction solution at the initial moment, time τ, and by the end of the reaction, respectively.

The $(n+1)$-order rate constants were calculated using Eq. (3):

$$k_{n+1} = k_{ef}/c^n[Zn(OAc)_2], \quad (3)$$

where n is the order of reaction (1) in zinc(II) acetate, which was determined from the $\log k_{ef}$–$\log c[Zn(OAc)_2]$ dependence ($n = 1$ in acetonitrile; Fig. 2).

Scheme 1.



H_2P (**I**)

The energy of activation (E_a) for the examined temperature range was calculated by the Arrhenius equation (4), and the entropy of activation $\Delta S^{\neq}$ was determined using Eq. (5):

$$E_a = 19.1[(T_1 T_2)/(T_2 - T_1)]\log(k_2/k_1); \quad (4)$$

$$\Delta S^{\neq} = 19.1 \log k_v + E_a/298 - 253. \quad (5)$$

The electronic absorption spectrum of the zinc complex of **I** contained the following bands, λ_{max}, nm ($\log\varepsilon$): 458 (5.43), 595 (4.35), 649 (4.19). The kinetic parameters for the complexation of zinc with ligand **I** in acetonitrile are given in Table 1.

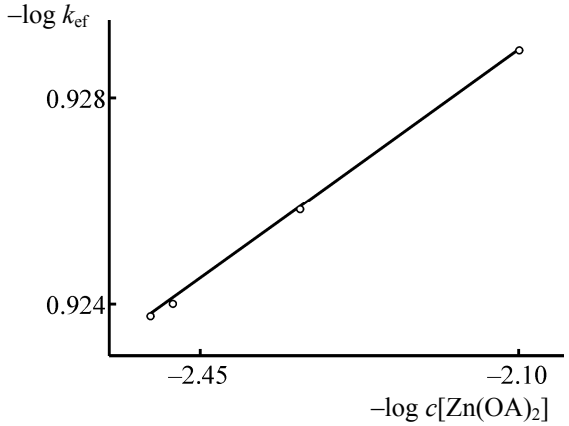


Fig. 2. Plot of $\log k_{ef}$ vs $\log c[Zn(OAc)_2]$ for the reaction of porphyrin **I** with zinc(II) acetate in acetonitrile at 298 K ($\tan\alpha = 0.999$, $r = 0.9998$).

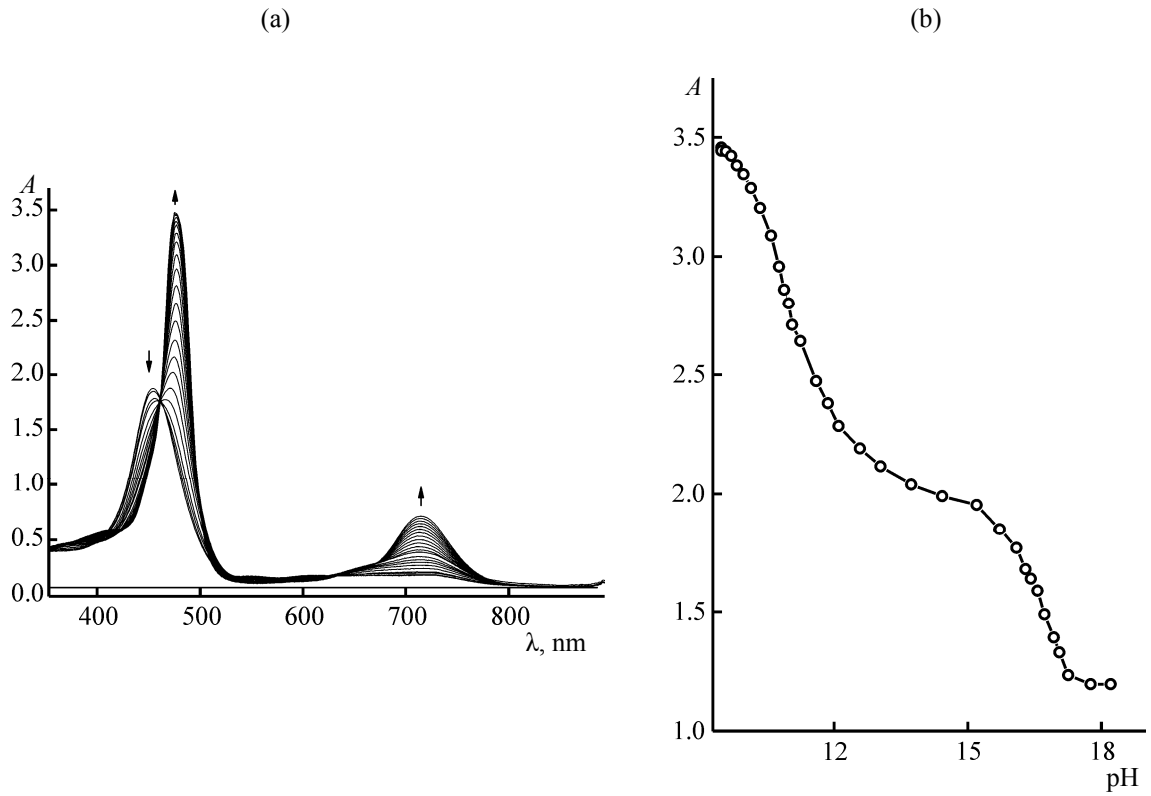


Fig. 3. (a) Variation of the electronic absorption spectrum in the titration of porphyrin **I** in acetonitrile with perchloric acid at 298 K and (b) spectrophotometric titration curve (λ 477 nm); $c_{\mathbf{I}} = 1.00 \times 10^{-5}$ M, $c(HClO_4) = 0–3.9 \times 10^{-5}$ M.

The acid–base properties of porphyrin **I** (H_2P) were studied by spectrophotometric titration with perchloric acid in acetonitrile at 298 K. Protonation of the inner nitrogen atoms in **I** is a two-step process, as follows from the presence of two families of spectral curves and the corresponding isosbestic points in the titration plots (Fig. 3, Table 2). The protonation equilibria may be represented by schemes (6) and (7):

$$H_2P + H^+ \xrightarrow{k_1} H_3P^+, \quad (6)$$

$$H_3P^+ + H^+ \xrightarrow{k_2} H_4P^{2+}. \quad (7)$$

Here, H_2P, H_3P^+, and H_4P^{2+} are, respectively, the free base, monocation, and dication of **I**.

As the concentration of $HClO_4$ increased from 0 to 1.16×10^{-6} M, the electronic absorption spectrum of the free base gradually transformed into the spectrum corresponding to cation H_3P^+, and further raising the titrant concentration to 3.9×10^{-5} M led to the formation of dication H_4P^{2+} (Fig. 3, Table 1). The

Table 1. Kinetic parameters for the complexation of porphyrins **I** and **II** with zinc(II) acetate in acetonitrile

Parameter	**I**	**II** [16, 17]
$c[Zn(OAc)_2]$, M	0.75×10^{-3}	1.50×10^{-3}
k^{298}, L mol^{-1} s^{-1}	986±10	256±7
E_a, kJ/mol	16±2	64±3
$\Delta S^{\neq}$, J mol^{-1} K^{-1}	18±2	8±3

Table 2. Parameters of the electronic absorption spectra of the free bases in acetonitrile and protonated species in $HClO_4$–MeCN (298 K)

Porphyrin	Soret band, λ, nm (log ε)	λ_1, nm (log ε)
H_2P (**I**)	454 (5.27)	717 (4.25)
H_3P^+ (**I**)	473 (5.30)	714 (4.47)
H_4P^{2+} (**I**)	477(5.53)	713 (4.80)
H_2P (**II**) [16, 17]	468 (5.96)	691 (5.16)
H_4P^{2+} (**II**) [16, 17]	470 (6.01)	688 (5.20)

concentration of $HClO_4$ at the inflection point on the titration curve (Fig. 3) was used to distinguish in the electronic absorption spectra two regions corresponding to the first and second protonation steps [reactions (6) and (7)]. The stepwise protonation constants were calculated by Eq. (8).

$$\log k_b = \log Ind + \text{pH}. \quad (8)$$

Here, k_b is the basicity constant of **I** at the first (k_1) or second (k_2) protonation step, and *Ind* is the indicator ratio H_3P^+/H_2P for the first step or H_4P^{2+}/H_3P^+ for the second step. The protonation constants were thus determined as $\log k_1 = 16.65\pm0.03$ and $\log k_2 = 11.25\pm0.05$

The mechanism of formation of metal complexes with porphyrins [1] implies that the main factors determining the rate of reaction (1) are rearrangement and partial decomposition of the coordination sphere of metal solvate, coordination of the metal cation to the porphyrin nitrogen atoms, and stretching and polarization of the N−H bonds in the ligand. Substituents in the porphyrin macrocycle affect in one or another way π-electron density distribution over the latter and hence the degree of solvation of the ground state, as well as the strength of the N–H bonds. The effects of electron-withdrawing and electron-donor substituents on the chemical properties of porphyrins are ambiguous. On the one hand, electron-withdrawing substituents increase the polarity of the N−H bond, which should increase the rate of complex formation. On the other hand, acceptor groups reduce the electron density on the tertiary nitrogen atoms, which does not favor strengthening of N→M coordination in the transition state, so that the reaction rate should decrease. Electron-donating substituents exert the opposite effects.

Porphyrin **I** is characterized by a fairly complex structure. Its molecule contains eight inductively donating methyl groups in the pyrrole rings and four thienyl substituents which also show +*I* effect. According to PM3 calculations, the phenyl fragments in structurally related 5,10,15,20-tetrakis(4-*tert*-butylphenyl)-2,3,7,8,12,13,17,18-octamethylporphyrin (**II**) are turned through an angle of 75°–80° with respect to the macrocycle plane; therefore, they could affect the N_4 moiety only through the σ-bond system [17, 18]. We performed additional studies of the acid–base and complexing properties of porphyrin **II** in the systems $HClO_4$–MeCN (298 K), $Zn(OAc)_2$–MeCN, and MeCN–DBU (1,8-diazabicyclo[5.4.0]undec-7-ene)

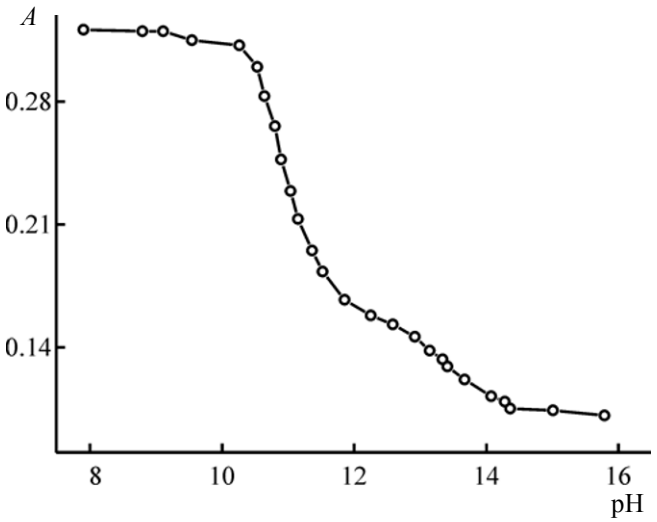


Fig. 4. Spectrophotometric titration curve (λ = 691 nm) of porphyrin **II** in acetonitrile at 298 K; $c_{\mathbf{II}} = 6.60 \times 10^{-6}$ M, $c(HClO_4) = 0–2.8\times10^{-5}$ M.

[16, 17] in order to compare the effects of different substituents in the *meso* positions on the reactivity of octamethylporphyrin derivatives. Figure 4 shows the spectrophotometric titration curve (λ 691 nm) of porphyrin **II** in MeCN with $HClO_4$ (298 K). The stepwise protonation constants calculated by Eq. (8) were $\log k_1 = 13.54\pm0.03$ and $\log k_2 = 10.81\pm0.04$. It is seen that replacement of *meso*-(4-*tert*-butylphenyl) substituents by 2-thienyl groups increases the basicity by more than three orders of magnitude in the first step and by a factor of 3 in the second step. Analysis of the spectral parameters of porphyrin **I** (Table 1) revealed a considerable growth of the *Q*-band intensity as the acidity of the system H_2P–$HClO_4$–MeCN increased ($\log\varepsilon$ ~0.55 against ~0.04 for porphyrin **II**), the blue shift of that band being the same (~4 nm) [16, 17]. Comparison of the kinetic parameters for the formation of zinc complexes by porphyrins **I** and **II** in the system $Zn(OAc)_2$–MeCN showed increase of the rate of reaction (1) by almost four orders of magnitude in going to the thienyl derivative (Table 1).

Thus, we have found that introduction of four thienyl substituents into the *meso* positions of octamethylporphyrin strongly affects acid–base and coordination properties of the ligand, in particular enhances its coordinating ability in the complexation with zinc in acetonitrile.

EXPERIMENTAL

Zinc(II) acetate of analytical grade was additionally purified by recrystallization from aqueous acetic acid and dried at 380–390 K [18]. The electronic absorption spectra were recorded on a Shimadzu UV-1800 spectrophotometer. The ^{1}H NMR spectrum was obtained on a Bruker 500 spectrometer at 500 MHz using $CDCl_3$ as solvent and TMS as internal reference.

2,3,7,8,12,13,17,18-Octamethyl-5,10,15,20-tetrakis(thiophen-2-yl)porphyrin (I). Concentrated aqueous HBr, 2.0 mL, was added to a mixture of 1.0 g (10.5 mmol) of 3,4-dimethylpyrrole and 1.2 g (10.5 mmol) of thiophene-2-carbaldehyde in 30 mL of methanol under stirring in an argon atmosphere. The mixture was stirred for 1 h, the precipitate (porphyrinogen) was filtered off, washed with methanol, and dissolved in 10 mL of THF, a solution of 1.9 g (7.7 mmol) of chloranil in 20 mL of THF was added, and the mixture was stirred for 24 h at room temperature. The solvent was removed, and the residue was washed with a 5% solution of potassium hydroxide and with water, dried in air at 70°C, and subjected to chromatography on alumina (activity grade III according to Brockmann) using chloroform as eluent. Porphyrin **I** thus isolated was treated with methanol, filtered off, washed with methanol, and dried in air at room temperature. Yield 1.42 g (72%), R_f 0.58 ($CHCl_3$–MeOH, 10 : 2), 0.64 (PhH–MeOH, 5 : 1). ^{1}H NMR spectrum, δ, ppm: 7.88 d (4H, 3′-H, J = 5.1 Hz), 7.60–7.63 m (4H, 4′-H), 7.47–7.50 m (4H, 5′-H), 1.96–1.99 m (24H, CH_3). Electronic absorption spectrum ($CHCl_3$), λ_{max}, nm (logε): 711 (3.79), 615 (4.05), 562 (4.05), 460 (5.26).

Spectrophotometric titration with a solution of perchloric acid in acetonitrile was carried out using a Varian Cary 100 spectrophotometer. The titration and data processing procedures were described in [19–21]. Highly pure acetonitrile containing less than <0.03% of water was used as solvent; compounds **I** and **II** in that solvent existed in the neutral form.

The complexation of porphyrins with zinc(II) acetate was studied by spectrophotometry using temperature-controlled ground-joint cells. The temperature was maintained in the range from 283 to 298 K with an accuracy of ±0.1°C.

The spectrophotometric and ^{1}H NMR studies were performed at the Upper Volga Regional Physicochemical Research Center.

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