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Spectrophotometric Study of the Complexing Properties of 2,3,7,8,12,13,17,18-Octaethyl-5,10,15-trinitroporphyrin and Its Dianion toward $Zn(OAc)_2$ in Acetonitrile

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Abstract—Complexing properties of 2,3,7,8,12,13,17,18-octaethyl-5,10,15-trinitroporphyrin and its dianionic form in the systems acetonitrile–$Zn(OAc)_2$ and 1,8-diazabicyclo[5.4.0]undec-7-ene–acetonitrile–$Zn(OAc)_2$ have been studied by spectrophotometric titration. Zinc complexes of 2,3,7,8,12,13,17,18-octaethyl-5,10,15-trinitroporphyrin have been characterized by spectral data, and kinetic parameters of the complex formation according to the molecular and ionic mechanisms have been analyzed.

Keywords: porphyrin, metal complex, kinetics, deprotonation

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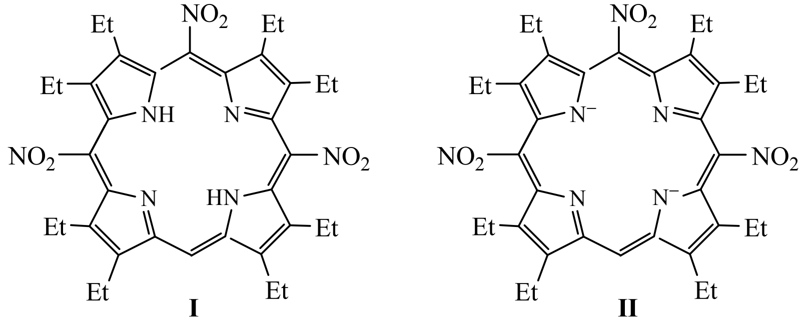
Modification of porphyrin structure via introduction of various bulky substituents into the tetrapyrrole molecule has been the subject of a number of publications [1–6]. Introduction of any substituent (electron-donating, electron-withdrawing, hydrophilic, lipophilic, etc.) distorts planar structure of the porphyrin macrocycle, which induces variation of acid–base and complexing properties; in particular, the rate of coordination may decrease or increase [5, 6]. Furthermore, an important factor is the state of the porphyrin molecule during coordination to metal ion: in some systems porphyrins exists as neutral molecules, while in others, as ionized species [7–9]. This factor essentially affects the mechanism and rate of complex formation and relative contributions of the electronic and steric effects of substituents to the kinetic parameters of complex formation. In the present study we compared the molecular and ionic mechanisms of formation of zinc complexes of 2,3,7,8,12,13,17,18-octaethyl-5,10,15-trinitroporphyrin in which the nitro groups occupy *meso* positions of the macrocycle in the systems acetonitrile–$Zn(OAc)_2$ and 1,8-diazabicyclo[5.4.0]undec-7-ene–acetonitrile–$Zn(OAc)_2$.

As we showed previously [8, 9], 2,3,7,8,12,13,17,18-octaethyl-5,10,15-trinitroporphyrin (**I**, H_2P) in acetonitrile in the presence of 1,8-diazabicyclo[5.4.0]-undec-7-ene (DBU) [system (1)] can exist as neutral

Scheme 1.



I **II**

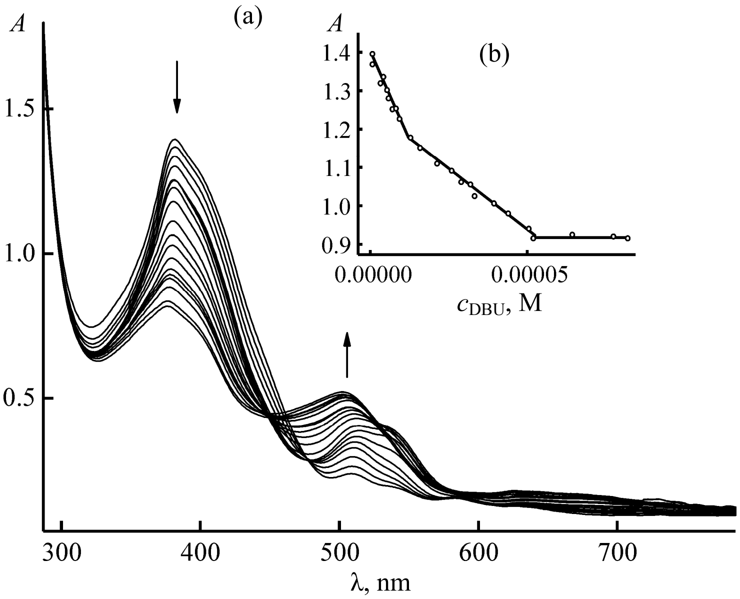


Fig. 1. (a) Variation of the electronic absorption spectrum and (b) titration curve of 2,3,7,8,12,13,17,18-octaethyl-5,10,15-trinitroporphyrin (**I**) [$c(H_2P) = 4.02 \times 10^{-5}$ M, λ = 382 nm] in the system acetonitrile–1,8-diazabicyclo[5.4.0]undec-7-ene (c = 0–8.22×10^{-5} M) at 298 K.

[c_{DBU} = 0 M; H_2P, λ_{max}, nm (logε): 382 (4.54), 510 (3.74), 541 (3.63), 584 (3.53)] and dianionic species [$c_{DBU} = 1.22 \times 10^{-4}$ M; P^{2-} (**II**), λ_{max}, nm (logε): 376 (4.31), 502 (4.07)] (Scheme 1). Raising the concentration of DBU from 0 to 1.22×10^{-4} M induces smooth transformation of the four-band electronic absorption spectrum of neutral porphyrin **I** in acetonitrile into two-band spectrum typical of dianion **II** (Fig. 1). The DBU concentration ensuring the maximum concentration of dianion **II** ($c_{DBU} = 6 \times 10^{-5}$ M) was calculated from the known deprotonation constants of 2,3,7,8,12,13,17,18-octaethyl-5,10,15-trinitroporphyrin in system (1) [8, 9]. The mechanism of complexation of porphyrin **I** with $Zn(OAc)_2$ in the systems H_2P–MeCN–$Zn(OAc)_2$ (2) and H_2P–MeCN–$Zn(OAc)_2$–DBU (3; $c_{DBU} = 6 \times 10^{-5}$ M) was studied by spectrophotometry in the temperature range from 298 to 318 K. During the kinetic measurements, the temperature was maintained with an accuracy of ±0.1 K. In all cases, isosbestic points were clearly observed in the electronic absorption spectra (Figs. 2, 3). The spectral parameters of zinc complexes of 2,3,7,8,12,13,17,18-octaethyl-5,10,15-trinitroporphyrin in both systems coincided with published data {λ_{max}, nm (logε): 414 (4.66), 550 (3.81), 583 (3.60) [10]}.

The formation of porphyrin complexes with doubly charged metal cations in nonaqueous solution may be represented by Eqs. (4) and (5).

$$H_2P + [MX_2(Solv)_{n-2}] \rightarrow MP + 2HX + (n-2)Solv; \quad (4)$$

$$P^{2-} + [MX_2(Solv)_{n-2}] \rightarrow MP + 2X^- + (n-2)Solv. \quad (5)$$

Here, X is an anionic ligand, Solv is the solvent molecule, and n is the metal cation coordination number.

The kinetic parameters were calculated according to standard procedure using Eqs. (6)–(11).

$$K_{ef} = (1/\tau)\ln [c^0(H_2P)/c(H_2P)]. \quad (6)$$

Taking into account variation of the optical density, Eq. (6) is transformed into Eq. (7).

$$k_{ef} = (1/\tau)\ln [(A_0 - A_\infty)/(A_\tau - A_\infty)]. \quad (7)$$

Here, τ is the time elapsed from the reaction onset, and A_0, A_τ, and A_∞ are the optical densities of the reaction mixture at the initial moment, at time τ, and by the end of the reaction, respectively. The true rate constant was calculated by formula (8).

$$k_{n+1} = k_{ef}/c^n_{salt}. \quad (8)$$

Here, k_{n+1} is the (n + 1)-order rate constant.

The energy of activation was calculated by the Arrhenius equation from the temperature dependence of the rate constant for complex formation:

$$k = Ae^{-Ea/RT}. \quad (9)$$

$$E = 19.1[T_1T_2/(T_2 - T_1)]\log (k_2/k_1). \quad (10)$$

The entropy of activation $\Delta S^{\neq}$ was calculated by Eq. (11):

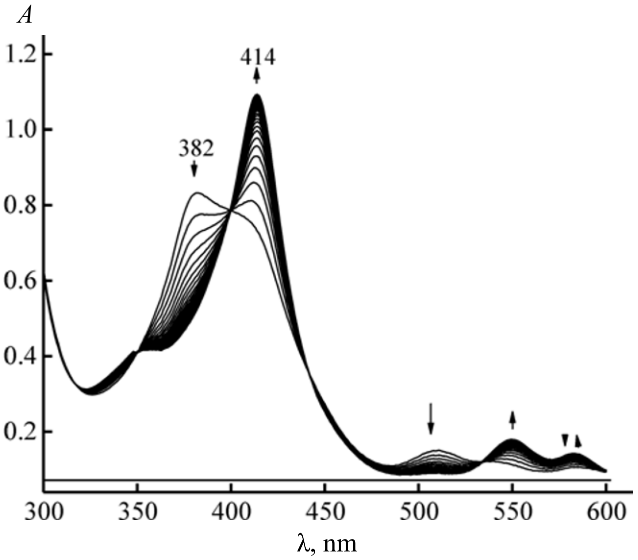


Fig. 2. Variation of the electronic absorption spectrum in the course of the complexation of 2,3,7,8,12,13,17,18-octaethyl-5,10,15-trinitroporphyrin with zinc(II) acetate in acetonitrile [system (2)] at 298 K.

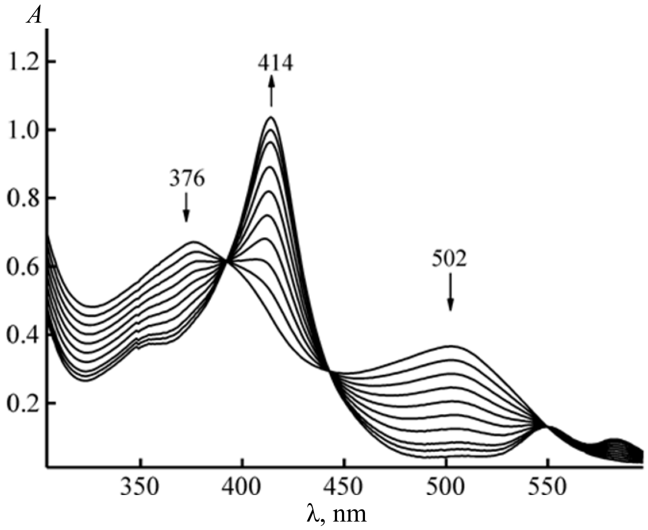


Fig. 3. Variation of the electronic absorption spectrum in the course of the complexation of 2,3,7,8,12,13,17,18-octaethyl-5,10,15-trinitroporphyrin with zinc(II) acetate in acetonitrile [system (3)] at 298 K.

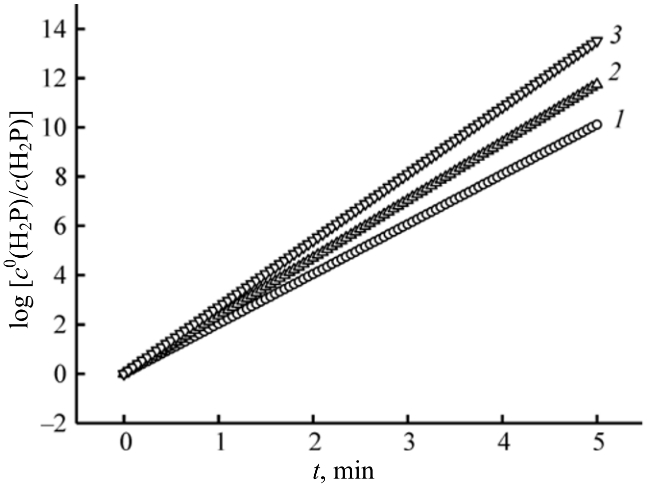


Fig. 4. Plot of log $[c^0(H_2P)/c(H_2P)]$ vs. time (τ) for the formation of the zinc complex of 2,3,7,8,12,13,17,18-octaethyl-5,10,15-trinitroporphyrin in system (3) at (*1*) 298, (*2*) 308, and (*3*) 318 K; $c_{H2P} = 2.30 \times 10^{-5}$ M, $c[Zn(OAc)_2] = 2.35 \times 10^{-3}$ M.

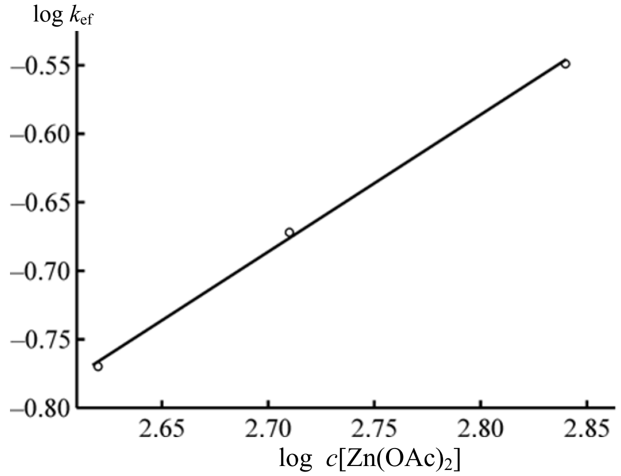


Fig. 5. Plot of log k_{ef} versus log $c[Zn(OAc)_2]$ for the formation of the zinc complex of 2,3,7,8,12,13,17,18-octaethyl-5,10,15-trinitroporphyrin in acetonitrile at 298 K; tan α = 0.999, *r* = 0.9998.

$$\Delta S^{\neq} = 19.1 \ln k^{298} + E/298 - 253. \tag{11}$$

The kinetic measurements were performed in triplicate at three different temperatures. The order of the reaction with respect to porphyrin was determined from the plots of log $[c^0(H_2P)/c(H_2P)]$ versus of time (linear dependence corresponds to first order; Fig. 4) [8, 9]. The order of the reaction in zinc acetate was determined from the slope of the linear dependence – log K_{ef} ot log $c[Zn(OAc)_2]$ (Fig. 5). The kinetic parameters for the formation of porphyrin zinc complexes are given in table.

These data show that the presence of nitro groups in molecule **I** affects the rate of its coordination to zinc cation. Nitro groups as strong electron-withdrawing substituents make the N–H protons more acidic and facilitate the reaction, whereas the effect of donor ethyl groups is the opposite. Therefore, the rate of formation of zinc complexes of porphyrin **I** in systems (2) and (3)

Kinetic parameters for coordination of porphyrins to zinc(II) acetate in systems (2) and (3)

Porphyrin (system)	c[Zn(OAc)$_2$], M	k^{298}, L mol^{-1} s^{-1}	ΔE, kJ/mol	Δ$S^{\neq}$, J mol^{-1} K^{-1}
2,3,7,8,12,13,17,18-Octaethylporphyrin (2) [7, 8]	2.56×10^{-3}	64±2	47±4	–15±1
2,3,7,8,12,13,17,18-Octaethyl-5,10,15,20-tetranitroporphyrin (2) [7, 8]	2.35×10^{-3}	81±3	54±5	12±1
2,3,7,8,12,13,17,18-Octaethyl-5,10,15,20-tetranitroporphyrin dianion (3) [7, 8]	2.35×10^{-3}	1103±9	4±0.4	–104±9
I (2)	2.35×10^{-3}	73±2	50±4	–3±1
II (3)	2.35×10^{-3}	850±6	11±1	–85±3

according to mechanisms (4) and (5), respectively, increases as the number of nitro groups in the porphyrin macrocycle increases. The energy required for the formation of porphyrin zinc complexes in system (2) [from neutral ligand molecule; scheme (4)] is considerably higher than that necessary for the complexation with dianion **II** [system (3); reaction (5)]. The difference is 13.5 times for 2,3,7,8,12,13,17,18-octaethyl-5,10,15,20-tetranitroporphyrin [8] and 4.5 times for trinitro analog **I**, and decrease of Δ$S^{\neq}$ indicates more ordered transition state.

Molecular mechanics calculations of analogous nickel complexes of 5-mono-, 5,15-di-, 5,10-di-, 5,10,15-tri-, and 5,10,15,20-tetranitro derivatives of octaethylporphyrin [11] showed appreciable distortion of the molecular geometry as the number of nitro groups increases (Fig. 6). 2,3,7,8,12,13,17,18-Octaethyl-5,10,15-trinitroporphyrin and 2,3,7,8,12,13,17,18-octaethyl-5,10,15,20-tetranitroporphyrin were characterized by considerable deviation of the pyrrole fragments from coplanar arrangement and variation of bond lengths therein, which reduces the electron

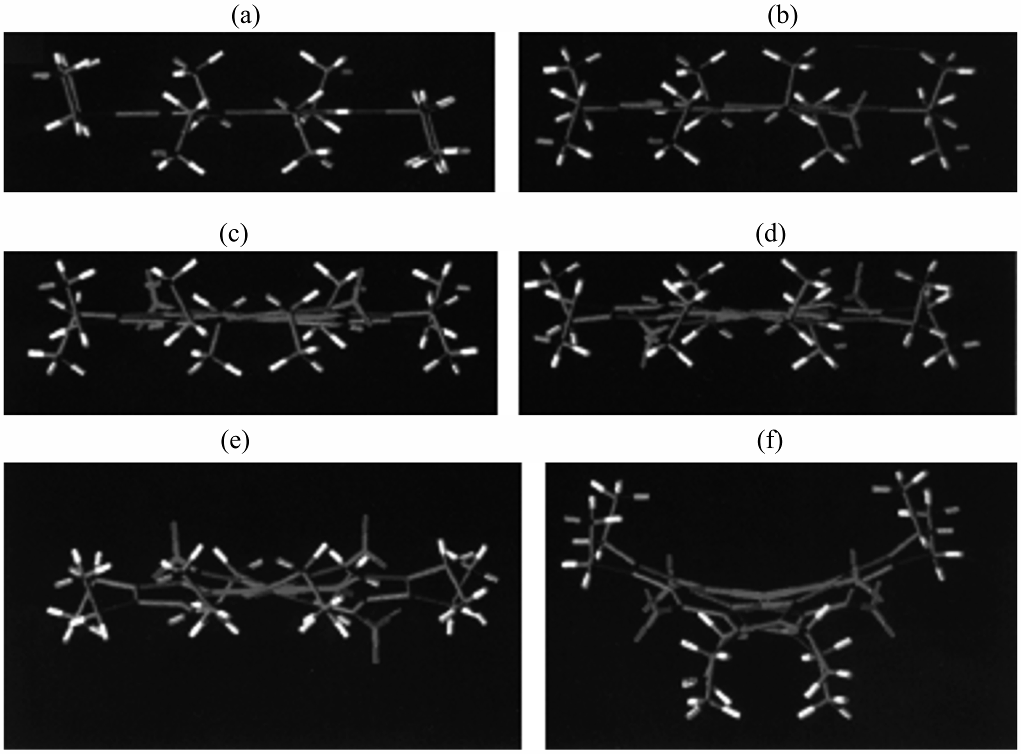


Fig. 6. Structures of the energy-optimized nickel complexes of (a) 2,3,7,8,12,13,17,18-octaethylporphyrin, (b) 2,3,7,8,12,13,17,18-octaethyl-5-nitroporphyrin, (c) 2,3,7,8,12,13,17,18-octaethyl-5,15-dinitroporphyrin, (d) 2,3,7,8,12,13,17,18-octaethyl-5,10-dinitroporphyrin, (e) 2,3,7,8,12,13,17,18-octaethyl-5,10,15-trinitroporphyrin, and (f) 2,3,7,8,12,13,17,18-octaethyl-5,10,15,20-tetranitroporphyrin [11].

affinity and changes chemical reactivity of the porphyrin molecules; in particular the rate of complexation increases due to reduction of the energy of activation. Physicochemical properties of *meso*-nitro-substituted octaethylporphyrins also change as the number of nitro groups increases, and this id reflected in the position of bands in the electronic absorption spectra [11]. Sterically distorted *meso*-nitro octaalkylporphyrins in system (3) (see table) exhibit strong complexing properties as compared to octaethylporphyrin having no nitro groups, which does not form complex with zinc in that system.

Thus, our kinetic study on the complexation of 2,3,7,8,12,13,17,18-octaethyl-5,10,15-trinitroporphyrin (**I**) and its dianion **II** with zinc(II) acetate in acetonitrile showed that the reaction with dianion **II** is considerably faster due to lower energy of activation, which is likely to be related to lower energy requirements for deformation of the ligand molecule and dissociation of the N–H bonds. The rate of formation of zinc complexes by nitro-substituted octaethylporphyrins according to the molecular mechanism is somewhat higher than the rate of formation of the zinc complex of unsubstituted octaethylporphyrin, but the difference does not exceed one order of magnitude. Our experimental data are consistent with the calculations results [11], according to which introduction of nitro groups into the *meso* positions of octaethylporphyrin should enhance the complexing ability.

EXPERIMENTAL

2,3,7,8,12,13,17,18-Octaethyl-5,10,15-trinitroporphyrin was synthesized according to the procedures described in [10, 12]. Spectrophotometric titration with perchloric acid in acetonitrile was performed on a Varian Cary 100 spectrophotometer. The procedures for kinetic measurements and treatment of the experimental data were given in detail in [13, 14]. The electronic absorption spectra were recorded on Shimadzu UV-1800, Hitachi U-2000, and Varian Cary 100 spectrophotometers.

Zinc(II) acetate of analytical grade was purified by recrystallization from aqueous acetic acid and was dried at 380–390 K [15].

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