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Synthesis and Spectral and Coordination Properties of *meso*-Tetraarylporphyrins

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Abstract—5,10,15,20-Tetrakis(3,5-dibromophenyl)porphyrin and 5,10,15,20-tetrakis(3-bromo-4-methoxyphenyl)porphyrin have been synthesized, and their complexing properties with respect to Pd^{2+} ion in acetonitrile at 308–328 K have been studied by spectrophotometry. The synthesized compounds were characterized by UV-Vis, ^{1}H NMR, and mass spectra. The effect of substituents in the *meso*-phenyl rings of the ligands on their spectral and coordination properties was estimated in comparison to 5,10,15,20-tetraphenylporphyrin.

Keywords: porphyrins, basic properties, metalloporphyrins, coordination properties.

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Porphyrins constitute a huge class of natural and synthetic tetrapyrrole compounds containing a 16-membered aromatic macrocycle. Porphyrins are characterized by thermal and photochemical stability, strong absorption over a wide spectral range, and selective and reversible complexing ability with respect to various substrates [1–14]. Strong luminescence, nonlinear optical, redox, semiconducting, and receptor properties of porphyrins make it possible to use them for selective binding and targeted delivery of biologically active substrates, as well as materials for high-capacity storage units and electrochromic and photovoltaic devices [13–15].

Metalloporphyrins are capable of forming ordered structures in crystal and in solution via extra coordination of neutral or anionic ligands [16]. Until present, porphyrin complexes with almost all metals of the Periodic Table have been obtained. The complexation process can be readily and reliably monitored by spectrophotometry, which contributes to rapid development of studies in this field. Coordination properties of porphyrins with respect to metal salts strongly depend on the nature of substituents present in the porphyrin macrocycle, which largely determine the relation between their coordination and acid–base properties, since protonation of ligands is a competing process with respect to coordination.

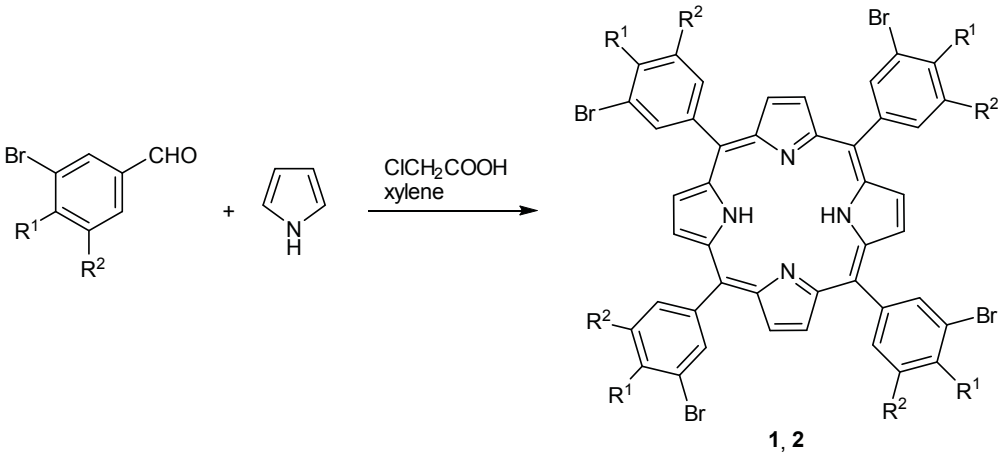
Of particular interest are porphyrin complexes with palladium, which show high absorbance in the electronic spectra and therefore can be used to convert a primary diagnostic response into an analytical optical sensor signal. They also exhibit phosphorescence properties which underlie their use as photosensitizers and markers for time-resolved luminescence immunoassay [17].

In this work we synthesized 5,10,15,20-tetrakis(3,5-dibromophenyl)porphyrin [**1**, H_2(3,5-BrPh)P] and 5,10,15,20-tetrakis(3-bromo-4-methoxyphenyl)porphyrin [**2**, H_2(3-Br-4-MeOPh)P] and studied their complexation with palladium(II) ions in acetonitrile at 308–328 K by spectrophotometry. The effect of substituents in the *meso*-phenyl rings on the spectral and coordination properties of porphyrins **1** and **2** was examined using 5,10,15,20-tetraphenylporphyrin (**3**, H_2TPP) as reference.

Porphyrins **1** and **2** were synthesized in 16.5 and 23.5% yield, respectively, by condensation of the corresponding substituted benzaldehydes with pyrrole in xylene in the presence of chloroacetic acid on exposure to air (Scheme 1; see Experimental). The products were characterized by electronic absorption, ^{1}H NMR, and mass spectra.

It is known that the nature and position of substituents in the macrocycle strongly affect acid–base properties of porphyrins. As we showed previously [18], introduction of bromine atoms and methoxy group into the *meso*-phenyl rings reduce the basicity of the tetrapyrrole macrocycle in the series: H_2TPP <

Scheme 1.



1, R^1 = H, R^2 = Br; **2**, R^1 = OMe, R^2 = H.

H_2(3-Br-4-MeOPh)P < H_2(3,5-BrPh)P. Due to negative inductive (–*I*) and weak mesomeric (+*M*) effects of bromine atoms, the basicity of H_2(3-Br-4-MeOPh)P is lower by more than an order of magnitude than the basicity of H_2TPP [19]; in the case of H_2(3,5-BrPh)P, the difference is more than two orders of magnitude. Geometry optimization of porphyrins **1**–**3** by the PM3 quantum chemical method (HyperChem, version 7.02) showed that their molecules have almost planar structure with a slight puckering [18]. The dissociation constants of protonated porphyrins agree well with the classical views on the substituent effects [17].

The kinetics of the complex formation of porphyrins **1**–**3** with palladium in acetonitrile were studied by spectrophotometry [18–20], taking into account significant differences in the electronic absorption spectra of the free ligands and their complexes. The complexation of porphyrins with palladium(II) acetate in a pure solvent follows Eq. (1):

$$H_2P + [Pd(OAc)_2(Solv)_{n-2}] \rightarrow PdP + 2AcOH + (n-2)Solv,$$

where H_2P stands for porphyrin **1**–**3**, Solv is a solvent molecule, and *n* is the metal coordination number.

In all cases, spectrophotometric monitoring of the complex formation process showed distinct isosbestic points, and the reactions were of first order with respect to porphyrin **1**–**3**, as evidenced by the linear plots of $\log(c^0_{H_2P}/c_{H_2P})$ versus time τ (s) (Figs. 1–3). The rates

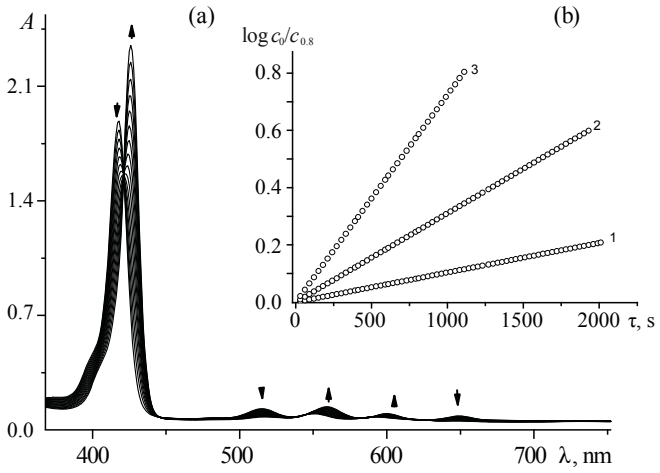


Fig. 1. (a) Variation of the electronic absorption spectrum and (b) $\log(c_0/c)$—τ plot (λ 417 nm) for the complexation of 5,10,15,20-tetrakis(3-bromo-4-methoxyphenyl)porphyrin (**1**) with palladium(II) acetate in acetonitrile; $c_1 = 1.8\times10^{-5}$ M; $c_{Pd} = 4.5\times10^{-3}$ M; temperature, K: (*1*) 308, (2) 318, (3) 328.

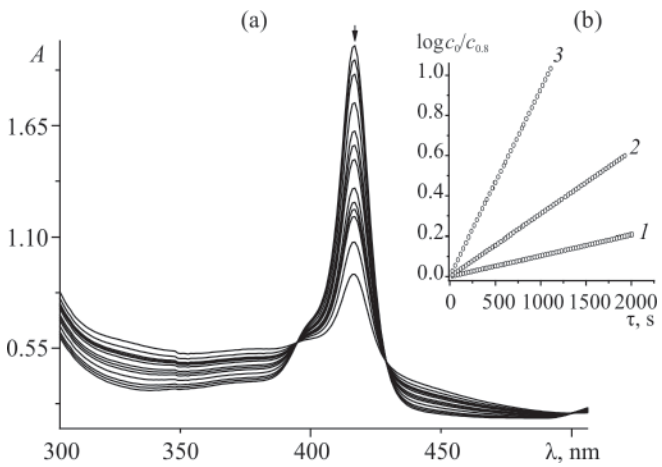


Fig. 2. (a) Variation of the electronic absorption spectrum and (b) $\log(c_0/c)$—τ plot (λ 417 nm) for the complexation of 5,10,15,20-tetrakis(3,5-dibromophenyl)porphyrin (**2**) with palladium(II) acetate in acetonitrile; $c_2 = 1.90\times10^{-5}$ M; $c_{Pd} = 4.5\times10^{-3}$ M; temperature, K: (*1*) 308, (2) 318, (3) 328.

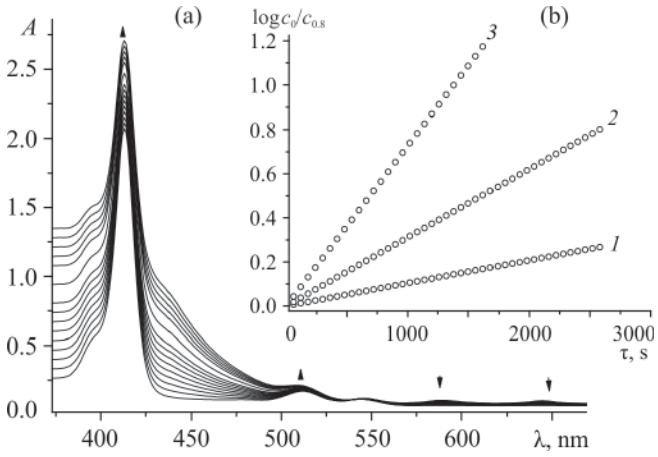


Fig. 3. (a) Variation of the electronic absorption spectrum and (b) log(c_0/c)—τ plot (λ 413 nm) for the complexation of 5,10,15,20-tetraphenylporphyrin (**3**) with palladium(II) acetate in acetonitrile; $c_3 = 1.97\times10^{-5}$ M; $c_{Pd} = 4.5\times10^{-3}$ M; temperature, K: (*1*) 308, (2) 318, (3) 328.

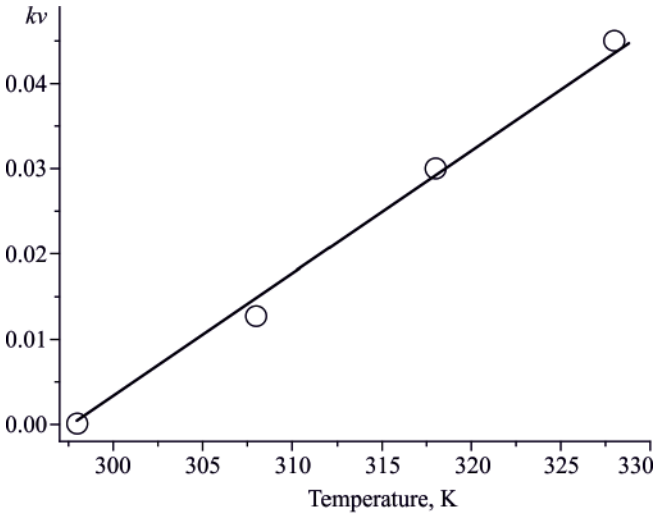


Fig. 4. Temperature dependence of the rate constant of complex formation for porphyrin 1.

of formation of palladium complexes were low even at elevated temperature (308–318 K); therefore, the rate constant at standard temperature was determined by extrapolation (an example is shown in Fig. 4.). The order of reactions with respect to the metal salt was determined as the slope of the $\log k_{ef}$—$\log c_{Zn(OAc)_2}$ dependence (an example is shown in Fig. 5). Tables 1 and 2 contain characteristics of the electronic absorption spectra of porphyrins **1**–**3** and their palladium complexes, as well as the kinetic parameters of the complexation reaction. It is seen that substitution in the *meso*-phenyl rings affects the coordination and acid–base properties of porphyrins, obviously due to electronic effects of the substituents and deformation of the macrocycle. The activity of ligands in such systems is also determined by the structure of acid–base complexes formed in solution, whose ionizing ability depends on the degree of proton transfer from the acid to the base molecule (solvent). The complexation rate constant may also depend on the nature of the central metal ion. Analysis of the data in Table 2 and our previous data on the formation of zinc complexes of the same porphyrins [18] shows that the rates of formation of palladium complexes with unsubstituted tetraphenylporphyrin **3** and octabromo derivative **2** are more than 500 times lower than the rates of formation

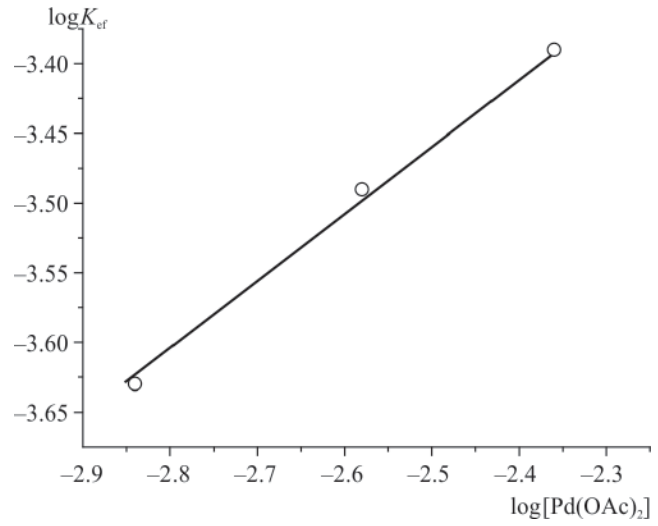


Fig. 5. Correlation between $\log k_{ef}$ and $\log c_{Pd(OAc)_2}$ for the complexation of paladium(II) acetate with porphyrin **2** in acetonitrile at 328 K; slope 1.1, correlation coefficient 0.999.

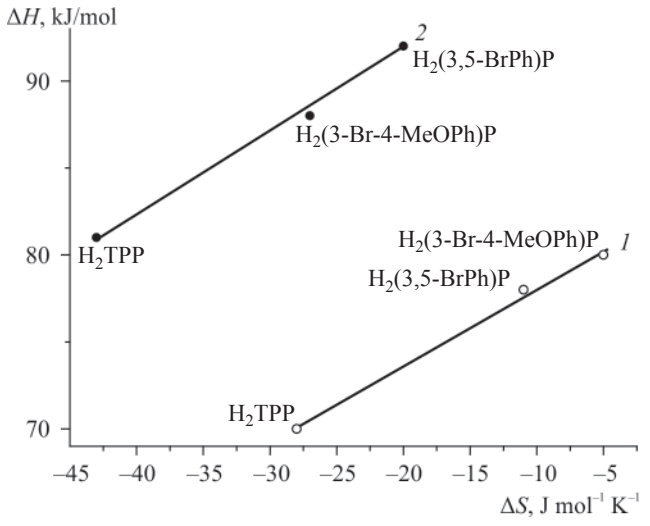


Fig. 6. Correlations between ΔH and ΔS for the complexation of tetraphenylporphyrins **1**–**3** with (*1*) Zn^{2+} and (*2*) Pd^{2+}.

Table 1. Electronic absorption spectra of tetraphenylporphyrins **1**–**3** and their palladium complexes in acetonitrile and overall protonation constants $pK_{b1,2}$

Compound	λ, nm (log ε)					$pK_{b1,2}$
	Soret band	λ_4	λ_3	λ_2	λ_1	
H_2TPP	413 (5.02)	512 (3.56)	546 (3.12)	589 (2.92)	646 (2.96)	19.8 [19] (18.61)[18]
PdTPP	412 (5.14)		508 (4.06)		544 (3.76)	
H_2(3,5-BrPh)P	417 (5.01)	513 (3.91)	546 (3.67)	588 (3.66)	649 (4.59)	17.50
Pd(3,5-BrPh)P	375 sh (4.43) 416 (4.66)	511 (4.05)		593 (3.97)	654 (3.96)	
H_2(3-Br-4-MeOPh)P	418 (5.03)	515 (3.84)	552 (3.70)	593 (3.62)	651 (3.750	18.09
Pd(3-Br-4-MeOPh)P	426 (5.12)	559 (3.90)	–	–	600 (3.75)	

of the corresponding zinc complexes; furthermore, the complexation with palladium is a more energy-consuming process. In the case of bromomethoxy derivative **1**, the difference in the reaction rates is more than 800 times.

Presumably, the transition state in the examined reaction is more polar than the initial state. This is confirmed by the negative entropies of reaction, as well as by the E_a—$\Delta S^{\neq}$ correlations which showed the kinetic compensation effect due to solvation of the metal salt and N–H coordination site of porphyrin in the transition state [20]. Godd correlations between E_a and $\Delta S^{\neq}$ were observed (Fig. 6) for both zinc and palladium complexes of tetraphenylporphyrins **1**–**3**.

Thus, the results of our study showed that chemical modification of the porphyrin macrocycle alters its acid–base and coordination properties, which may be useful for controlled change of the reactivity of porphyrin ligands for certain purposes.

EXPERIMENTAL

Spectrophotometric titration with solutions of perchloric acid in acetonitrile was performed using Varian Cary 100 and SPEK SSP-715 spectrophotometers. Details of the experimental procedure and data processing were reported in [23, 24]. The kinetic measurements were carried out using cells with ground-joint caps at three temperatures in the range from 308 to 328 K; each experiment was run in triplicate; the temperature was maintained with an accuracy of ±0.1 K. The ^{1}H NMR spectra were recorded on a Bruker AV III-500 spectrometer using TMS as internal standard. The mass spectra were recorded obtained on a Shimadzu Axima Confidence spectrometer (MALDI-TOF). 5,10,15,20-Tetraphenylporphyrin (**3**) was commercial product (Porphychem). Ligands **1** and **2** were purified by chromatography on alumina of Brockmann activity grade III using methylene chloride as eluent [22]. Their purity was checked by TLC on Silufol plates with a sorbent layer thickness of 0.5 mm (Merck) using methylene chloride as eluent. Acetonitrile used as solvent contained less than 0.03% of water.

5,10,15,20-Tetrakis(3,5-dibromophenyl)porphyrin (1). A flask equipped with a reflux condenser and a Dean–Stark trap was charged with a solution of 5.0 g of chloroacetic acid in 150 mL of xylene (isomer mixture). The solution was heated to the boiling point, a solution of 8.7 g (33.0 mmol) of 3,5-dibromobenzaldehyde and 2.3 mL (33.2 mmol) of pyrrole in 50 mL of xylene was gradually added, and the mixture was refluxed for 0.5 h and then for

Table 2. Kinetic parameters of the complex formation of porphyrins **1**–**3** with zinc(II) and palladium(II) acetates in acetonitrile

Porphyrin	$c_{M(OAc)_2}\times10^3$, M	$k^{298}\times10^3$, L mol^{-1} s^{-1}	E_a, kJ/mol	$\Delta S^{\neq}$, J mol^{-1} K^{-1}
M = Zn				
H_2TPP [28]	1.84	302 ± 1	70 ± 2	–28 ± 2
H_2(3,5-BrPh)P	4.5	88 ± 1	78 ± 2	–11 ± 1
H_2(3-Br-4-MeOPh)P	4.5	91 ± 1	80 ± 1	–5 ± 1
M = Pd				
H_2TPP [20]	4.5	56 ± 1	81 ± 2	–43 ± 2
H_2(3,5-BrPh)P	4.5	10 ± 1	92 ± 2	–20 ± 2
H_2(3-Br-4-MeOPhPh)P	4.5	17 ± 2	88 ± 2	–29 ± 2

an additional 1 h while bubbling air. The solvent was removed by steam distillation, and the precipitate was filtered off, washed with water, and air-dried at 70°C. It was dissolved in chloroform, and the product was filtered off. The product was dissolved in chloroform–trifluoroacetic acid (100 : 1 by volume), the solution was filtered, the filtrate was neutralized with diethylamine until its originally green color changed to red, and the precipitate was filtered off, washed with chloroform, and dried to isolate 1.5 g of **1**. The filtrate was combined with the washings and subjected to alumina chromatography. The eluate was concentrated, and the product was precipitated with methanol to isolate an additional 0.2 g of **1**. Overall yield 1.7 g (16.5%), R_f 0.87 (benzene–hexane, 2 : 1). Electronic absorption spectrum, λ, nm (log ε): 648 (3.73), 590 (3.91), 550 (3.93), 516 (4.33), 421 (5.64). ^{1}H NMR spectrum ($CDCl_3$–TFA), δ, ppm: –1.14 s (4H, NH), 8.40 t (4H, 4′-H, J = 1.6 Hz), 8.64 d (8H, 2′-H, 6′-H, J = 1.6 Hz), 8.87 s (8H, β-H). Mass spectrum, m/z (I_{rel}, %): 1167.38 $[M - Br + H]^+$, 1246.64 $[M + H]^+$. $C_{44}H_{22}Br_8N_4$. Calculated: M 1246.96.

5,10,15,20-Tetrakis(3-bromo-4-methoxyphenyl)-porphyrin (2) was synthesized in a similar way from 7.1 g (33 mmol) of 3-bromo-4-methoxybenzaldehyde. Yield 2.0 g (23.5%), R_f 0.63 (benzene). Electronic absorption spectrum ($CHCl_3$), λ, nm (log ε): 651 (3.90), 594 (3.90), 555 (4.10), 519 (4.31), 423 (5.69). ^{1}H NMR spectrum ($CDCl_3$), δ, ppm: –2.84 s (2H, NH), 4.22 s (12H, OCH_3), 7.31 d (4H, 5′-H, J = 8.2 Hz), 8.13 d (4H, 6-H, J = 8.2 Hz), 8.44 s (4H, 2-H), 8.90 s (8H, β-H). ^{1}H NMR spectrum ($CDCl_3$–TFA), δ, ppm: –0.99 s (4H, NH), 4.26 s (12H, OCH_3), 7.57 d (4H, 5-H), 8.41 d (4H, 6-H), 8.77 s (4H, 2-H), 8.64 s (8H, β-H). $C_{48}H_{34}Br_4N_4O_4$ M 1050.44.

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CONFLICT OF INTERESTS

The authors declare the absence of conflict of interests.

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