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Spectrophotometric Study of 2,3,12,13-Tetrabromo-5,10,15,20-tetraphenylporphyrin in the System 1,8-Diazabicyclo[5.4.0]undec-7-ene–Acetonitrile at 298 K. Deprotonation of the Pyrrole Rings and Complex Formation with $Zn(OAc)_2$

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Abstract—Acid–base and complexing properties of 2,3,12,13-tetrabromo-5,10,15,20-tetraphenylporphyrin in the system 1,8-diazabicyclo[5.4.0]undec-7-ene–acetonitrile were studied at 298 K by spectrophotometric titration. The titration of 2,3,12,13-tetrabromo-5,10,15,20-tetraphenylporphyrin with 1,8-diazabicyclo[5.4.0]-undec-7-ene was accompanied by successive deprotonation of the pyrrole nitrogen atoms with formation of the corresponding mono- and dianions, and the acid dissociation constants were determined. Complex formation of doubly deprotonated 2,3,12,13-tetrabromo-5,10,15,20-tetraphenylporphyrin with zinc acetate was studied.

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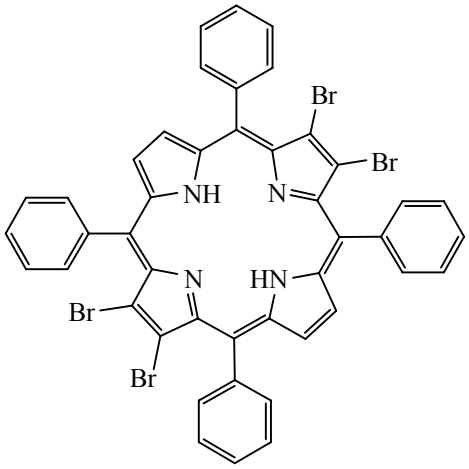
Tetrapyrrole compounds play an exceptionally important role in nature; they mediate a number of key processes in photosynthesis and human and animal life activity. Therefore, the structure and properties of tetrapyrrole derivatives attract increasing interest as subjects for study by different methods. One of the most important interdisciplinary problems of natural sciences is elucidation of the mechanisms of action of tetrapyrrole compounds in natural systems with a view to create their artificial analogs [1–5]. In the past decade, a new impetus to research in this field was given by the substantiation of possible application of various tetrapyrrole compounds in large-scale catalytic processes, medical diagnostics and therapy, light-harvesting systems, and optical data storage and processing systems [6–9].

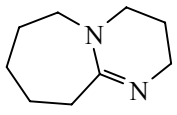
Analysis of published data shows that complex formation of tetrapyrrole macrocycles with metal ions may follow both molecular and ionic mechanisms [5]. In the first case, reactions with metal salts involve tetrapyrrole compounds as free bases (molecular form), and in the second case, their deprotonated forms. As a rule, attention was given primarily to the reactions following the molecular mechanism, whereas ionic complex formation remained beyond the scope of studies. Complex formation of tetraazaporphyrins with magnesium acetate in pyridine and pyridine–surfactant mixture was studied in [10–12]. It was found that tetraazaporphyrins are capable of reacting not only as neutral ligands but also as monoanion or dianion H-associate. In a binary medium, solvation effects on the rate of complex formation may be stronger than electronic effects of substituents [10].

With a view to develop new methods for the preparation of metal complexes and create new highly efficient molecular sensors for metal ions, in the present work we examined complex formation of metal ions with deprotonated macrocyclic ligands. In particular, acid–base properties of 2,3,12,13-tetrabromo-5,10,15,20-tetraphenylporphyrin (H_2TPPBr_4) and complexation of its dianion with zinc acetate in the system of 1,8-diazabicyclo[5.4.0]undec-7-ene–acetonitrile at 298 K were studied by spectrophotometry.

Figure 1 shows variation of the electronic absorption spectra of H_2TPPBr_4 in acetonitrile upon titration with a solution of 1,8-diazabicyclo[5.4.0]



H_2TPPBr_4



DBU

undec-7-ene (DBU). As the concentration of DBU increased, two families of absorption curves appeared in the electronic absorption spectrum, and each family was characterized by its own set of isosbestic points. The electronic absorption spectrum of the free base H_2TPPBr_4 (molecular form) had the following parameters, λ, nm (logε): 435 (4.20), 537 (3.25), 693 (3.15). As the concentration of DBU increased to 1.56×10^{-4} M, the electronic absorption spectrum gradually transformed to that of monoanion $HTPPBr_4^-$ [λ 433 (logε 4.08), 676 nm (3.18)], and further raising the DBU concentration from 1.56×10^{-4} to 7.71×10^{-2} M gave rise to doubly deprotonated species $TPPBr_4^{2-}$ [λ 434 (logε 3.93), 471 nm (3.91)].

The experimental spectrophotometric titration curve (Fig. 2) indicates that the reaction of DBU with H_2TPPBr_4 includes two steps (1) and (2):

$$H_2TPPBr_4 \overset{K_1}{\leftrightarrow} HTPPBr_4^- + H^+, \quad (1)$$

$$HTPPBr_4^- \overset{K_2}{\leftrightarrow} TPPBr_4^{2-} + H^+. \quad (2)$$

The coordinate of the inflection point on the titration curve (Fig. 2), i.e., the corresponding DBU concentration, defines the DBU concentration ranges for equilibria (1) and (2). The first and second acid ionization constants were calculated by Eq. (3).

$$\log K_a = \log I + n \log c_{DBU}. \quad (3)$$

Here, K_a is the acidity constant of H_2TPPBr_4 at the first (K_1) or second step (K_2), I is the indicator ratio $HTPPBr_4^-/H_2TPPBr_4$ (first step) or $TPPBr_4^{2-}/HTPPBr_4^-$ (second step), c_{DBU} is the concentration of DBU in solution, M, and $n = 1$ is the number of protons bound by DBU. The ionization constants K_1 and K_2 of H_2TPPBr_4 in acetonitrile at 298 K were thus estimated at 8.32×10^{-2} and 6.16×10^{-5}, respectively.

With account taken of equilibria (1) and (2) and material balance equation (4), simple calculations showed that at a DBU concentration of 3.5×10^{-2} M almost all H_2TPPBr_4 molecules exist as dianions. The calculation procedure was described in detail in [13].

$$c_0 = c(H_2TPPBr_4) + c(HTPPBr_4^-) + c(TPPBr_4^{2-}). \quad (4)$$

The complexation of deprotonated macrocyclic ligands with metal ions was studied by direct titration of doubly deprotonated form $TPPBr_4^{2-}$ with zinc acetate in acetonitrile in the presence of DBU at 298 K (Fig. 3). As the concentration of $Zn(OAc)_2$ increased {$c[Zn(OAc)_2]$ = 0–6.78×10^{-5} M}, the electronic

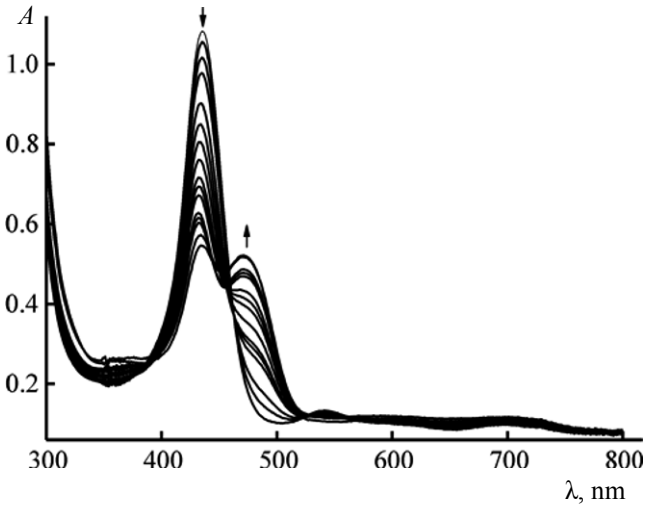


Fig. 1. Electronic absorption spectra of H_2TPPBr_4 (c_{porph} = 6.84×10^{-5} M) in acetonitrile containing 0 to 7.71×10^{-2} mol/l of DBU at 298 K.

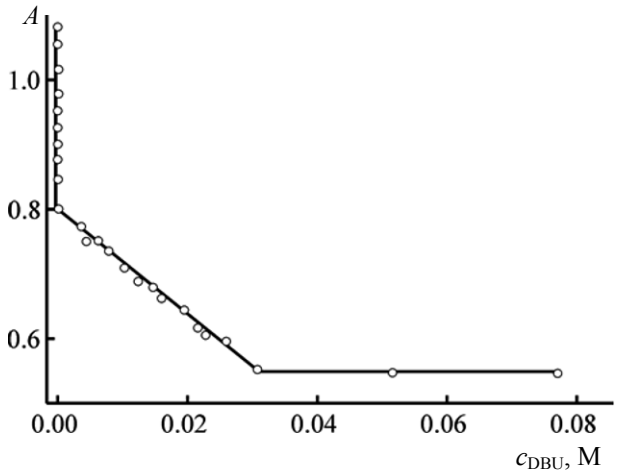


Fig. 2. Spectrophotometric titration curve of H_2TPPBr_4 (c_{porph} = 6.84×10^{-5} M) in acetonitrile with DBU at 298 K; λ 435 nm.

Electronic absorption spectra of $ZnTPPBr_4$ in organic solvents at 298 K

Solvent	λ_{Soret}, nm	λ_{0-1}, nm	λ_{0-0}, nm	$ZnTPPBr_4$:L
Toluene	435	561	601	1:0
Toluene–pyridine	439; asym.	572; –	616, 642 sh	1:1; 1:2
Tetrahydrofuran	432	568	610	1:1
Acetonitrile	432	568	611	1:1
Acetonitrile–DBU	442	582	631	1:2
Acetonitrile–DBU–$Zn(OAc)_2$	442	581	631	1:2

absorption spectrum of the dianion $TPPBr_4^{2-}$ gradually transformed into the spectrum of the coordination compound [λ 442 (logε 4.14), 581 (3.25), 631 nm (3.23)]. The electronic absorption spectra of the specially synthesized zinc complex $ZnTPPBr_4$ in acetonitrile displayed similarity to the spectrum of the titration product, but the absorption maxima of the former were displaced toward shorter wavelengths, λ, nm (logε): 432 (5.47), 568 (4.11), 611 (3.86). It should be noted that the absorption spectrum of $ZnTPPBr_4$ in tetrahydrofuran given in [14] [λ, nm (logε): 432 (5.32), 568 (4.08), 610 (3.94)] differs only slightly from the spectrum in acetonitrile measured in the present work.

The spectrophotometric titration curve (λ 442 nm) of the dianion $TPPBr_4^{2-}$ with $Zn(OAc)_2$ (Fig. 4) and similarity of the absorption spectra (see above) unambiguously indicates formation of the $ZnTPPBr_4$ complex as a result of titration. The different positions of the absorption maxima of $ZnTPPBr_4$ in acetonitrile–DBU and THF may be rationalized by extra coordination of DBU, which is typical of nitrogen bases such as pyridine, piperidine, and imidazole. The electronic spectra of porphyrin metal complexes with extra ligands are characterized by long-wave shift of the absorption maxima, whose magnitude depends on the metal–extra ligand bond strength [15].

In order to verify the above assumption we measured the electronic absorption spectra of $ZnTPPBr_4$ in some coordinating and non-coordinating solvents, as well as in the presence of liganding co-solvents (see table). For comparison, the spectral parameters of the complex obtained by titration of $TPPBr_4^{2-}$ with $Zn(OAc)_2$ in acetonitrile–DBU are also given. It is seen that the electronic absorption spectrum of $ZnTPPBr_4$ in toluene, which is a non-coordinating solvent, strongly differs from those recorded in other solvents. Presumably, the spectrum in toluene corresponds to the structure with no extra ligand. Addition of pyridine as coordinating solvent leads to extra coordination with formation of complexes with mixed stoichiometry; most part of the complexes have the composition 1:1, while 1:2 complexes are minor. This follows from the asymmetric shape of the Soret band and from the appearance of a shoulder on the

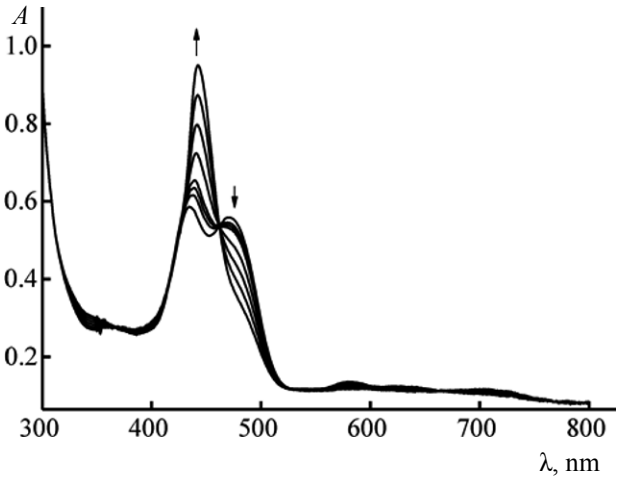


Fig. 3. Electronic absorption spectra of $TPPBr_4^{2-}$ (c_{porph} = 6.84×10^{-5} M) in acetonitrile–DBU in the presence of $Zn(OAc)_2$ (0 to 6.78×10^{-5} M) at 298 K.

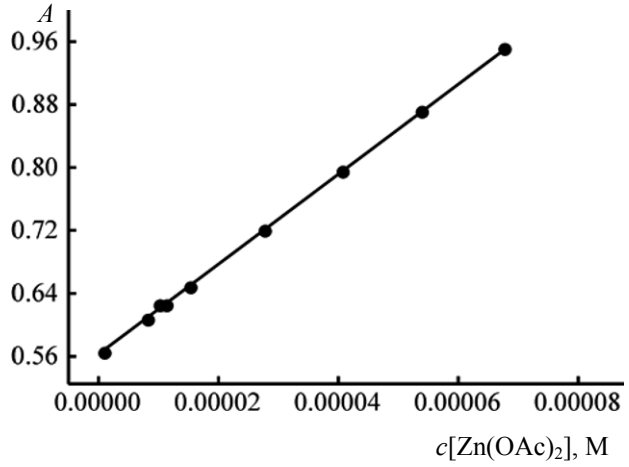


Fig. 4. Spectrophotometric titration curve of $TPPBr_4^{2-}$ (c_{porph} = 6.84×10^{-5} M) with $Zn(OAc)_2$ in acetonitrile–DBU at 298 K; λ 442 nm.

long-wave side of the 0–0 bond. Tetrahydrofuran and acetonitrile molecules are also capable of acting as extra ligands toward porphyrin metal complexes [15], and 1 : 1 complexes are formed in these solvents. However, addition of DBU to a solution of $ZnTPPBr_4$ in acetonitrile changes the absorption pattern, which may be caused by the following two factors. First, DBU is a stronger ligand, and it can replace acetonitrile in the 1 : 1 complex. Second, DBU can add as the second extra ligand to produce 1 : 2 complex. Thus, $ZnTPPBr_4$ can exist in solution as both conventional zinc porphyrin complex and that including one or two extra ligands. The electronic absorption spectrum of $ZnTPPBr_4$ in acetonitrile in the presence of DBU was identical to the spectrum of the complex obtained by titration of $TPPBr_4^{2-}$ with zinc acetate in acetonitrile–DBU. This means that the resulting complex contains two DBU molecules as extra ligands.

Analysis of the obtained results led us to conclude that DBU and pyridine molecules as stronger bases are included as extra ligands into the complex $ZnTPPBr_4$ in the systems acetonitrile–DBU and acetonitrile–pyridine. Therefore, the mechanism of complex formation of 2,3,12,13-tetrabromo-5,10,15,20-tetraphenylporphyrin with zinc acetate in organic solvents may be considered with account taken of solvation effects, which is important from the viewpoint of prediction of results of chemical syntheses. The concentration of zinc acetate required for the complexation with H_2TPPBr_4 (free base) [4, 5] is higher by a factor of 4 than that necessary for the complexation according to the ionic mechanism (with $TPPBr_4^{2-}$) provided that the initial concentrations of the porphyrin ligand are equal.

EXPERIMENTAL

2,3,12,13-Tetrabromo-5,10,15,20-tetraphenylporphyrin was synthesized according to the procedure described in [14]. Spectrophotometric titration with DBU in acetonitrile was performed using a Varian Cary 100 spectrophotometer. The experimental and data processing procedures were analogous to those reported in [16, 17]. The error in the determination of the acidity constants was ±(3–5)%.

Ultrapure acetonitrile (water content less than 0.03%) was used as dipolar aprotic solvent where the initial porphyrin was in the neutral (molecular) form. 1,8-Diazabicyclo[5.4.0]undec-7-ene (DBU), pK_a = 13.2 [18] as deprotonating agent is more advantageous than alkalies due to its solubility in organic solvents.

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