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Spectral and Complex-Forming Properties of β-Bromo-Substituted Porphyrins in *N,N*-Dimethylformamide

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Abstract—Contributions of structural and electronic effects to the reactivity and chromophore properties of tetrapyrrole macrocycles modified by bromine atoms were revealed on the basis of the kinetic data on the complex formation of 2-bromo-5,10,15,20-tetraphenylporphyrin, 2,3,12,13-tetrabromo-5,10,15,20-tetraphenylporphyrin, and 2,3,7,8,12,13,17,18-octabromo-5,10,15,20-tetraphenylporphyrin with zinc(II) and copper(II) acetates in *N,N*-dimethylformamide, and also by measuring spectral characteristics of porphyrin ligands and zinc and copper porphyrinates.

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Formation and decomposition of metal porphyrynates defining their ability to existence in live systems and to functioning as industrial catalysts, coloring agents, photo and thermal stabilizers of polymers have been studied within many decades [1–10].

Salts of two-charge transition metal ions, i.e. cations of metals with sizes corresponding to a macrocycle cavity size, react most readily with porphyrins. However, the formation of metal porphyrynates with these salts proceeds extremely slowly. A full completion of the reactions often requires heating or a long time. It is connected first of all with the fact that the limiting stage of the reactions of macrocycles with cations is the stage of the transition state formation [1]. In perch-type complexes, where a cation-guest remains on the apex of a binding cavity of a host, the destructtion of a cation solvate shell is rather insignificant, whereas in capsular complexes, such as porphyrinates, it is maximal. In a transition state of the complex formation the cation should be desolvated, this process being energy unprofitable and leading to a high-energy transition state. As a result the following rule is valid: the more rigidly a ligand is preorganized for cation binding, the lower is the process rate. Rigid aromatic porphyrin molecules react with metal cations at low rates.

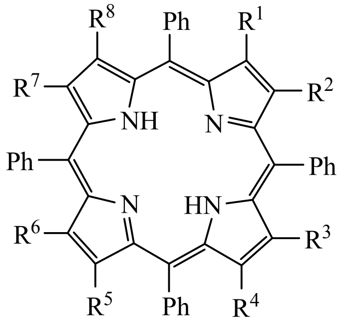
The aim of the present work was to determine the effects of a macrocycle deformation and electronic and structural contributions of substituents on the variation of spectral and complex-forming properties of tetraphenylporphin in the course of sequential chemical modification of β-pyrrole positions of a macrocycle by bromine atoms. It was found that changes in the molecular structure of tetraphenylporphyrin H_2TPP (**I**), for example, on passing to 2-bromo-5,10,15,20-tetraphenylporphyrin $H_2TPP(\beta\text{-Br})$ (**II**), 2,3,12,13-tetrabromo-5,10,15,20-tetraphenylporphyrin $H_2TPP(\beta\text{-Br})_4$ (**III**), and 2,3,7,8,12,13,17,18-octabromo-5,10,15,20-tetraphenylporphyrin $H_2TPP(\beta\text{-Br})_8$ **IV**, strongly affect the rate and mechanism of the complex formation:

$$H_2TPP(X)_m + [MA_2(Solv)_{m-2}] \rightarrow MTPP(X)_m + 2HA.$$

Here $MA_2(Solv)_{m-2}$ is a metal salt solvate with a coordination number m in a solvent medium ($M = Zn^{2+}$, Cu^{2+}), A is the salt anion, and X is an electron-donor or electron-acceptor substituent.

The features of the chemical behavior of substituted porphyrins is caused mainly by a complicated branched macrocycle, a strong conjugation of a π-electronic system [1], and a macrocyclic effect, i.e. a spatial macrocycle distortion and a steric screening of reaction centers by substituents. β-Substituted por-phyrins are of special interest, as in this case, accord-ing to the published data and our own results, the electronic influence of a substituent on the macrocycle π-electronic system is maximal as compared to *meso*-substituents [1–6, 10].

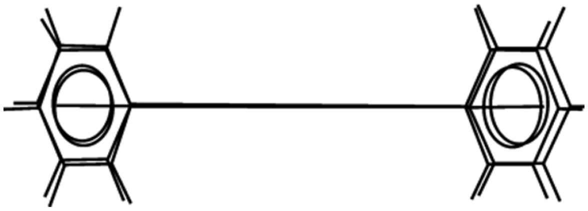
When bromine atoms are introduced in β-positions of pyrrole fragments, the number of π-electrons in the



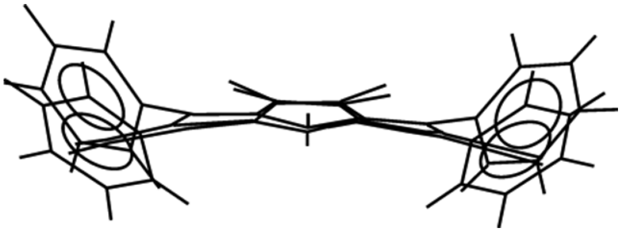
I, H_2TPP, R^1–R^8 = H; **II**, $H_2TPP(\beta\text{-Br})$, R^1 = Br; R^2–R^8 = H; $R^1 = R^2 = R^5 = R^6$ = Br; **III**, $H_2TPP(\beta\text{-Br})_4$, $R^3 = R^4 = R^7 = R^8$ = H; **IV**, $H_2TPP(\beta\text{-Br})_8$, R^1–R^8 = Br.

conjugated system of a macrocycle increases, which results in a greater aromaticity of β-bromo-substituted tetraphenylporphyrins in comparison with the initial state. According to [11], $H_2TPP(\beta\text{-Br})_4$ retains its planar structure (the deviation of pyrrole rings modified by bromine atoms from the macrocycle plane is 4.8°). Benzene rings, as well as in the H_2TPP molecule, are arranged perpendicularly to the N_4H_2 planes, the C^β–C^β bond lengths decrease [1.33 and 1.34 Å for $H_2TPP(\beta\text{-Br})_4$ and H_2TPP, respectively], and the coordination cavity size decreases [4.2 and 4.10 Å for H_2TPP and $H_2TPP(\beta\text{-Br})_4$, respectively].

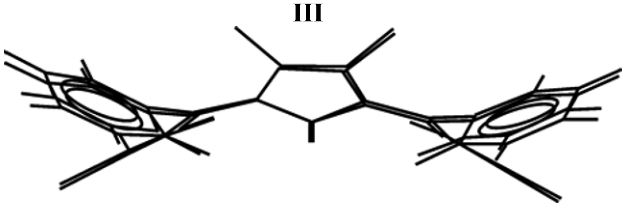
Crystallographic data for the octabromo derivative $H_2TPP(\beta\text{-Br})_8[CF_3COO]_2\cdot 0.5CHCl_3\}$ are given in [12]. According to these data, all phenyl fragments are arranged in the same plane, and the macrocycle takes a saddle-like conformation. Bromine atoms of two adjacent pyrrole rings in compound **IV** are lifted above their planes by 0.170–0.461 Å, and those of two others are located under planes of pyrrole rings. In compound **III** all four bromine atoms are in the same plane. It was shown by the ^{1}H NMR method [13] that the distorted structures of compounds **III, IV** are also retained in solutions.



II



III



IV

A red shift of the Soret band is observed in the electronic spectra of porphyrin **IV** solutions in electron-donor solvents, and bands in the long wavelength region become low-intensive and diffuse as compared with tetraphenylporphin **I**.

It is presumed to originate from two major factors: special features of the molecule distortion under the influence of peripheral substituents and also by the interior chromophore polarization caused by a non-equivalence of β- and *meso*-positions [14–16]. Bromine atoms in a macrocycle are under the influence of two electronic effects: a positive conjugation effect (+*C*) and a negative induction effect (–*I*). The higher occupied molecular orbital of porphyrin (a_{2u} and a_{1u}) is located on pyrrole and *meso* carbon atoms, respec-

Table 1. Position (λ_{max}) and intensity (log ε) of absorption bands (*1*–*5*) in electronic spectra of unsubstituted and β-bromo-substituted tetraarylporphyrins **I–IV**

Comp. no.	Solvent	*1*	*2*	*3*	*4*	*5*	Reference
I	Toluene	652(3.81)	592(3.79)	549(3.95)	515(4.28)	415(5.35)	[19]
	DMF	645(3.86)	591(3.83)	548(3.97)	513(4.28)	411(5.31)	
	Chloroform	642	585	542	508	411	[21]
II	Dichloromethane	649(3.79)	594(3.81)	551(3.78)	518(4.33)	421(5.58)	[16]
	Toluene	653(3.71)	596(3.70)	552(3.64)	519(4.23)	424(5.41)	[19]
	Pyridine	653(3.75)	597(3.74)	553(3.67)	519(4.23)	424(5.40)	″
	DMF	651(3.76)	595(3.75)	552(3.68)	519(4.10)	420(5.31)	″
	Acetic acid	678(4.06)	–	–	–	452(3.75)	
III	Dichloromethane	685(4.02)	612(3.58)	533(4.30)	–	436(5.52)	[13]
	Chloroform	683(3.91)	617(3.58)	535(4.23)	–	437(5.38)	″
	Toluene	680(3.86)	614(3.79)	568(3.97)	–	439(5.36)	[19]
	Pyridine	680(3.85)	613(3.79)	568(3.97)	–	442(5.34)	″
	DMF	696(3.53)	612(3.63)	536(3.90)	–	432(4.68)	
	Acetic acid	711(4.31)	–	–	–	432(5.10)	″
IV	Dichloromethane	743(3.87)	626(4.12)	569(3.96)	469(5.31)	370(4.52)	[14]
	Toluene	738(3.85)	622(4.10)	568(3.95)	470(5.25)	367(4.41)	[19]
	Pyridine	760(3.89)	646(4.08)	–	477(5.10)	371(4.38)	″
	DMF	783(3.63)	627(3.44)	–	473(4.81)	393(4.10)	
	Acetic acid	745(4.17)	–	–	–	–	″

tively. The presence of substituents in β-positions gives rise to perturbations leading to the appearance of a great number of configurations. A possible overlap of bands of Q_y and Q_x transitions for porphyrin **IV** and the appearance of an intensive band (λ_{max} 626 nm, log ε 4.12) for solutions in methylene chloride are presumed. A similar relation of absorption bands is observed in the spectrum of compound **IV** in toluene [17].

Table 1 allows us arranging porphyrins under study in the following series according to increasing red shift of absorption band *1* and the Soret band: H_2TPP < $H_2TPP(\beta\text{-}Br)$ < $H_2TPP(\beta\text{-}Br)_4$ <$H_2TPP(\beta\text{-}Br)_8$.

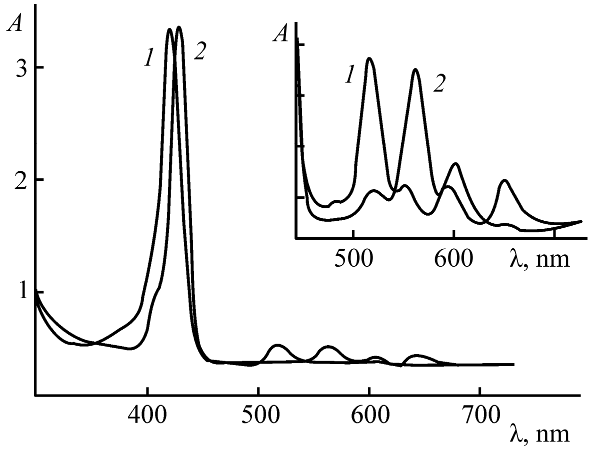


Fig. 1. Electron absorption spectrum of (*1*) $H_2TPP(\beta\text{-}Br)$ and (*2*) its zinc complex in DMF.

The complex formation of tetraphenylporphyrins **II–IV** with salts of 3*d*-metals is accompanied by a change in electronic absorption spectra: the spectra of the complexes contain the Soret band and two bands in the visible region (Figs. 1–3), which are caused by electronic transitions. The decrease in the number of bands in the electronic absorption spectra results from a higher molecular symmetry and also from the suppression of vibration states upon the complex formation. The position of absorption bands in the electronic spectra of metal complexes is defined by the nature and strength of M–N chemical bonds.

It was found that the spectral criterion of strength, physical essence of which is described in [18], is applicable to metal complexes. The thermodynamic stability of metal complexes in the series of similar compounds is the greater, the greater is the blue shift of band *1* of a metalloporphyrin compared to band *1* of the ligand, porphyrin H_2P. We can assert on the basis of electronic absorption spectra and kinetic data that the spectral criterion of strength is applicable to complexes of all tetraarylporphyrins under study irrespective of the extent of their macrocycle distortion. Thus band *1* of Cu(II) complexes in the studied series of compounds is always subjected to a blue shift as compared to the λ_I value of less stable Zn(II) complexes, in which an ionic contribution to the M–N bond is more significant (Table 2).

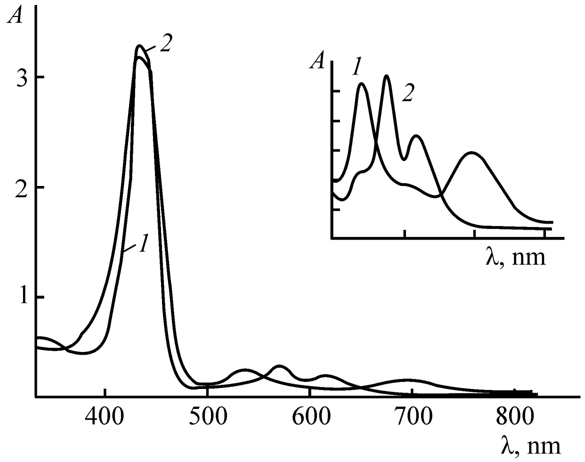


Fig. 2. Electron absorption spectrum of (*1*) $H_2TPP(\beta\text{-}Br)_4$ and (*2*) its zinc complex in DMF.

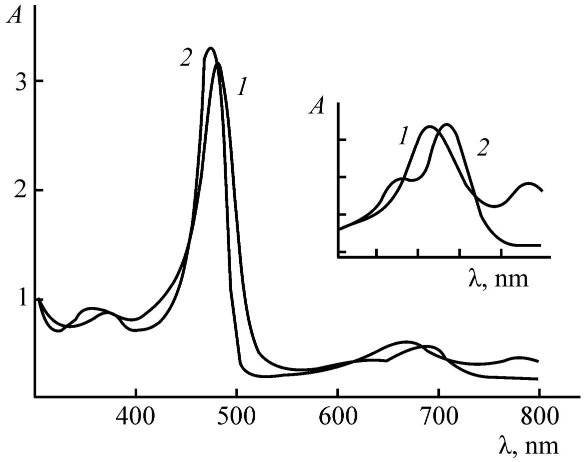


Fig. 3. Electron absorption spectrum of (*1*) $H_2TPP(\beta\text{-}Br)_8$ and (*2*) its zinc complex in DMF.

The effect of bromine substitution in β-positions of compound **I** on its coordination properties in the reactions of $H_2TPP(X)_mC$ with $Zn(OAc)_2$ in toluene, pyridine, and acetic acid was studied in [19, 27]. The reaction of coordination of porphyrins with a low-active N–H bond (weak acids), compound **I** among them, is the fastest in glacial acetic acid and the slowest in pyridine [19]. For NH-active porphyrins (strong acids), like compound **IV**, the reaction rate is maximal in pyridine and minimal in acetic acid.

The bromine atom in β-position favors the shift of π-electrons of nitrogen atoms in a macrocycle, the increase in the polarity of the N–H bond, and the change in the complex formation rate as compared to unsubstituted tetraphenylporphyrin [k_v^{298} 7.03× 10^{-2} l mol^{-1} s^{-1} for compound **II** in a mixed toluene-pyridine solvent, whereas for compound **I** k_v^{298} 8.70× 10^{-3} l mol^{-1} s^{-1} in pyridine] [19]. The complex-formation rate in the toluene-pyridine medium is two orders of magnitude less than in the toluene-acetic acid mixed solvent [k_v^{298} 7.03×10^{-2} and 6.08 l mol^{-1} s^{-1}, respectively]. Orders of magnitude of the true kinetic constants in Py, k_v^{298} 0.85 l mol^{-1} s^{-1}, and AcHO, k_v^{298} 3.46 l mol^{-1} s^{-1}, for compound **III** [17] are close to each other, which reflects a partial polarization of the N–H bond under the influence of four bromine atoms. Low values of the activation energy E_a point to the increase in ionization of the N–H bond under the action of an organic base. The complex formation with compound **IV** in pyridine is instantaneous, whereas in acetic acid it does not proceed at all.

The kinetics of $H_2TPP(\beta\text{-}Br)_8$ complex formation with metals (Co, Cu, Zn) in the $CHCl_3$–MeOH (1:1) mixture were studied by the spectrophotometric stopped-flow method [20]. Complex-formation rate constants exceed a corresponding value for tetra-phenylporphyrin by 2–3 orders of magnitude. Bhyrappa et al. attribute this increase not to the increase in the basicity of tertiary nitrogen atoms (bromine atoms as substituents reduce the value of protonation constants pK_3 2.6 and pK_4 1.75 [19]), but to the macroring nonplanar structure.

We have studied the kinetics of the complex formation of porphyrins **I–IV** with $Zn(OAc)_2$ and $Cu(OAc)_2$. We have chosen *N,N*-dimethylformamide

Table 2. Characteristics of electronic spectra (absorption bands *1–5*) of porphyrins **I–IV** and their complexes with Cu(II) and Zn(II) in DMF

Compound	*1*	*2*	*3*	*4*	*5*	$\Delta\lambda_I$[a]
I	645	591	548	513	411	
I(Zn)	598	558			420	–47
I(Cu)	539				412	–106
II	651	595	552	519	420	
II(Zn)	601	562			427	–50
II(Cu)	544				419	–107
III	696	612	536		432	
III(Zn)	613	569			435	–83
III(Cu)	598	557			430	–98
IV	783	627			473	
IV(Zn)	680	624			472	–103
IV(Cu)	642	592			473	–141

[a] $\Delta\lambda_I$ is the shift of absorption band 1 in the electronic spectra of tetraarylporphyrins upon the complex formation ($\Delta\lambda_I = \Delta\lambda_I^{mp} - \Delta\lambda_I^{H2P}$).

Table 3. Kinetic parameters of the complex formation reaction of porphyrins **II–IV** with $Cu(OAc)_2$ and $Zn(OAc)_2$ in DMF[a]

Comp. no.	Salt	T, K	k_v, l mol^{-1} s^{-1}	E_a, kJ mol^{-1}	$\Delta S_a^{\neq}$, J mol^{-1} K^{-1}
II	$Zn(OAc)_2$	298[b]	0.106	75±5	–20±19
		318	0.735		
		328	1.634		
		338	3.920		
	$Cu(OAc)_2$	298	0.495	70±1	–24±3
		308	1.245		
		318	2.906		
III	$Zn(OAc)_2$	298	0.892	69±4	–22±15
		308	2.285		
		318	5.047		
	$Cu(OAc)_2$	288	1.525	67±4	–20±12
		293	2.541		
		298	3.906		
IV	$Zn(OAc)_2$	298	Reaction proceeds instantly		
	$Cu(OAc)_2$	298	The same		

[a] c_{salt} 2.5×10^{-3} M, $c(H_2P)$ 2.5×10^{-5} M. [b] Found by extrapolation.

(DMF) as the organic solvent, which has occupied non-bonding φ_N-orbitals and shows σ-donor properties. The 100-fold molar excess of a salt in relation to a porphyrin allows us to describe the reaction by the equation of the pseudo-first order. The linear character of the dependences log $[c^0(H_2P)/c(H_2P)] - f(\tau)$ points to the reaction proceeding according to the first order with respect to porphyrin. The true reaction rate constant [k_v, l/(mol·s)] was calculated as $k_v = K_{ef}/c_s$ (K_{ef} was an effective rate constant of the process, s^{-1}; c_s was a molar concentration of a salt, M).

Sequential β-bromine substitution results in an increase in the complex formation rate for compound **I**, whereas values of activation energy (E_a) and activation entropy ($\Delta S^{\neq}$) remain constant.

Complex formation of compounds **II–IV** (Table 3) has its special features. The comparison of the complex formation ability of $H_2TPP(\beta\text{-}Br)$ and unsubstituted tetraphenylporphyrin in standard conditions (298 K, strongly dilute solutions of a porphyrin and metal salt) shows that k_v for $Zn(OAc)_2$ in DMF increases by the factor of 30 when only one bromine atom is introduced: k_v^{298} 0.0034 l mol^{-1} s^{-1} for H_2TPP [21]; on passing from $H_2TPP(\beta\text{-}Br)$ to $H_2TPP(\beta\text{-}Br)_4$ the rate increases by the factor of 8.5, and with H_2TPP $(\beta\text{-}Br)_8$ the reaction proceeds instantly.

On passing from $H_2TPP(Br)_1$ to $H_2TPP(Br)_4$ the dependence of the complex-formation rate on the metal nature becomes weaker. The ratio $k_v[Cu(OAc)_2]/k_v[Zn(OAc)_2]$ for $H_2TPP(Br)$ in DMF is equal to four, whereas for $H_2TPP(Br)_4$ it is equal to two. The formation of $ZnTPP(Br)_8$ and $CuTPP(Br)_8$ in the same medium at 298 K proceeds instantly. It points to a greater strength of zinc - dimethylformamide solvates as compared with copper solvates and is in agreement with the published data [22]. Complex-forming properties of β-bromo-substituted porphyrins **II–IV** in DMF were studied in our work for the first time.

Thus, according to the data on the kinetics of the complex formation of 2-bromo-5,10,15,20-tetraphenylporphyrin, 2,3,12,13-tetrabromo-5,10,15,20-tetraphenylporphyrin, and 2,3,7,8,12,13,17,18-octabromo-5,10,15,20-tetraphenylporphyrin with zinc(II) and copper(II) acetates in *N,N*-dimethylformamide, and also on the basis of spectral characteristics of porphyrin ligands and zinc and copper porphyrinates, we have revealed structural and electronic effects on the reactivity and chromophore properties of tetrapyrrole macrocycles modified by bromine atoms. Sequential bromo-substitution of pyrrole positions in tetraphenylporphyrin changes the macrocycle electronic structure toward polarization of the N–H bond, which is not suppressed in the DMF medium. These data are of interest for the development of the chemistry of macroheterocyclic compounds capable of selective binding cations of metals various in nature.

EXPERIMENTAL

Porphyrin ligands **II–IV** were synthesized by procedures similar to those in [13, 14, 16]. Synthesized compounds were identified by electronic absorption, ^1H NMR, and IR spectra, which completely corresponded to the characteristics described in the literature. Kinetic measurements were carried out on a Cary 100 spectrophotometer according to the procedure described in [23]. Solvents were purified by the standard procedures [24, 25]. Analytical-grade zinc and copper(II) acetates were recrystallized from glacial AcOH and stored in a desiccator above concentrated H_2SO_4.

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