Study of Extra Coordination of Bromo-Substituted Porphyrins to Organic Bases

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Abstract—Extra coordination of zinc complexes of bromo-substituted tetraphenylporphyrins was studied by spectrophotometry. It was found that the stability of complexes thus formed markedly increases upon β -bromo-substitution in tetraphenylporphine. The effects of electronic and structural factors on the extra coordination were discussed. The stability constants of complexes formed by zinc porphyrins with organic bases were calculated, and the electronic absorption spectra of porphyrins in toluene and in other organic solvents were studied.

Among the diverse physicochemical properties of porphyrins (H₂P), the additional coordination (extra coordination) of organic molecules (L) to metalloporphyrins (MP) is especially important [1–3]. As a rule, this coordination is a stepwise interaction giving extra complexes (L_nMP) due to the donor–acceptor bonding between the metal atom and the organic base. In addition, porphyrin macrocycles can act as both electron donors and acceptors, depending on the nature of the porphyrin ligand and the metal. Of special interest are porphyrins with an unusual structure resulting from the effect of multiple substitution at the β - and *meso*-positions on the macrocyclic π -system.

In this work, we study the effect of substituents (bromine atoms) in the pyrrole and phenyl fragments of tetraphenylporphine on the physicochemical properties of zinc porphyrins.

EXPERIMENTAL

The study was performed for zinc complexes with 5,10,15,20-tetraphenyl-(2'-tetrabromo)porphyrin (H_2P^1) , 5,10,15,20-tetraphenyl-(3'-tetrabromo)porphyrin (H_2P^2) , 5,10,15,20-tetraphenyl-(3',5'-octabromo)porphyrin (H₂P³), 5,10,15,20-tetraphenyl-(4'-tetrabromo)porphyrin (H₂P⁴), and 2,7,12,17-tetrabromo-5,10,15,20-tetraphenylporphyrin (H_2P^5) and with organic bases (L): pyridine (Py), piperidine (Pip), and dimethyl sulfoxide (DMSO). The porphyrins $H_2P^1-H_2P^4$ were prepared by condensation of substituted pyrroles with benzaldehyde and purified by a reported procedure [4]; H_2P^5 was synthesized by a known procedure [5]. The porphyrins and their complexes were identified using electronic absorption and IR spectra [4, 5]. The organic bases L and toluene were dried and purified by known procedures [6]. The water content in organic solvents was checked using Fischer titration.



Zinc complexes were prepared as reported previously [3] by refluxing porphyrins in DMF with analytical grade $Zn(Ac)_2$ taken in a 1 : 5 molar ratio for 40 min (for $H_2P^1-H_2P^4$) or 10 min (for H_2P^5).

The formation of zinc porphyrins was monitored by electronic absorption spectra, the reactions being stopped when the absorption bands for free porphyrins disappeared from the spectra. After the synthesis, the mixture was cooled and the metalloporphyrin was extracted with chloroform. The chloroform solution of zinc porphyrin was washed with water to remove excess salt and DMF and purified by chromatography on alumina (activity II) or on Silufol plates. Chloroform was used for elution and visualization.

The extra coordination was studied in toluene. This was done by the isothermal saturation method. A series of solutions (12 to 15) with equal metalloporphyrin concentrations (10^{-5} mol/l) and with specified concentrations of organic bases L were prepared. The electronic absorption spectra of solutions in hermetically sealed quartz cells were recorded on Specord M40 and Hitachi U-2000 spectrophotometers in a chamber maintained at a constant temperature. An increase in the L concentration for an invariable metalloporphyrin concentration brought about changes in the electronic absorption spectra (Figs. 1, 2). The optical density (*A*) was measured at wavelengths where the difference between the electronic absorption spectra of ZnP and LZnP is most pronounced.



Fig. 1. Change in the electronic absorption spectrum of the ZnP⁵–Py system in toluene upon the change in c_{Py} from (1) 0 to (8) 3.6×10^{-3} mol/1; $c_{\text{ZnP}^5} = 6.92 \times 10^{-5}$ mol/1, T = 298 K.

The extra coordination of metalloporphyrins to the ligands L in solutions affords both mono- (n = 1) and biligand (n = 2) species:

$$MP + nL \rightleftharpoons L_n MP.$$
(1)

The stability constant for the resulting complexes has the form

$$K_{\rm s} = \frac{[{\rm L}_n {\rm MP}]}{[{\rm MP}][{\rm L}]^n}.$$
 (2)

Under the experimental conditions, all the zinc porphyrins form complexes with one additional ligand (Fig. 3). It was found that n = 0.97 for the reaction of Pip with ZnP² and n = 0.99 for ZnP¹ and ZnP³–ZnP⁵.

A change in the organic base concentration or in the temperature makes it possible to shift the equilibrium (1) toward either the formation or dissociation of the L_n MP complex. The complex concentration was calculated from the optical densities of the solution using the relation for a mixture of two colored substances:

$$c_{\rm LMP} = c_{\rm MP}^0 \frac{A_{\rm eq} - A_{\infty}}{A_0 - A_{\infty}},$$
 (3)

where c_{LMP} is the concentration of the extra complex formed, c_{MP}^0 is the initial concentration of the metalloporphyrin, A_0 is the initial optical density of the met-



Fig. 2. Dependence of *A* on $\log c_{\rm L}$ for the formation of the LZnTPP(β -Br)₄ complexes in toluene (*T* = 298 K) for L = (*I*) Pip, (*2*) DMSO, (*3*) Py ($\lambda_{\rm max}$ = 568 nm).



Fig. 3. $\log c_{\rm L}$ vs. $\log \frac{A_0 - A_{\rm eq}}{A_{\rm eq} - A_{\infty}}$ for the formation of PipZnP extra complexes in toluene for P = (1) P², (2) P³, (3) P¹, (4) P⁴, and (5) P⁵; T = 298 K.

alloporphyrin solution, and A_{eq} and A_{∞} are the optical densities of the equilibrium mixture with L and the mixture with the highest content of L. The concentration of free L in the solution, with allowance for the extra coordination, was determined using the equation

$$c_{\rm L} = c_{\rm L}^0 - c_{\rm MP}^0 \left(1 - \frac{A_{\rm eq} - A_{\infty}}{A_0 - A_{\infty}} \right),$$
 (4)

where $c_{\rm L}^0$ is the initial ligand concentration.

2002

No. 9

Vol. 28

Equations (3) and (4) were used to calculate the stability constants; the resulting values for different temperatures were employed to calculate the changes in

ZnP	L	$K_{\rm s}$, l mol ⁻¹				ΔU^0 1.1/m ol	$\Delta S_{\rm c}^0 U(mol V)$
		288 K	298 K	308 K	318 K	– <i>(</i> 1 /17), KJ /11101	, J/(ΠΙΟΙ Κ)
ZnTPP [3]	Ру	10600 ± 200	5800 ± 200	3600 ± 100	2000 ± 200	43 ± 2	72 ± 4
	Pip	146000 ± 12000	80900 ± 6500	45400 ± 2100	7200 ± 500	44 ± 1	52 ± 2
ZnP ¹	Ру	4996 ± 375	3823 ± 250	2957 ± 245	2332 ± 125	21 ± 1	38 ± 2
	Pip	16330 ± 1125	14030 ± 995	12125 ± 600	10570 ± 750	12 ± 1	15 ± 1
	DMSO	1418 ± 100	865 ± 45	610 ± 27	460 ± 33	30 ± 2	75 ± 4
ZnP ²	Ру	6545 ± 490	5380 ± 300	4495 ± 350	3750 ± 300	15 ± 1	18 ± 1
	Pip	54000 ± 300	43610 ± 580	32820 ± 1000	25705 ± 750	20 ± 1	29 ± 2
	DMSO	1734 ± 250	1200 ± 180	835 ± 50	589 ± 25	29 ± 1	71 ± 3
ZnP ³	Ру	8235 ± 450	7200 ± 400	6376 ± 380	5558 ± 350	11 ± 1	30 ± 2
	Pip	89720 ± 8125	63030 ± 3500	45145 ± 3000	33010 ± 3000	27 ± 1	49 ± 2
	DMSO	2748 ± 200	2205 ± 150	1753 ± 100	1410 ± 50	18 ± 1	32 ± 2
ZnP ⁴	Ру	3440 ± 180	2010 ± 100	1260 ± 85	870 ± 40	37 ± 2	95 ± 5
	Pip	8375 ± 530	5880 ± 480	4465 ± 300	3810 ± 150	21 ± 2	39 ± 2
	DMSO	1617 ± 60	1096 ± 55	679 ± 24	462 ± 21	34 ± 2	88 ± 4
ZnP ⁵	Ру	46177 ± 2035	28360 ± 110	17238 ± 1200	10625 ± 8501	40 ± 1	95 ± 5
	Pip	645480 ± 30560	446245 ± 31105	293736 ± 30000	198532 ± 27050	32 ± 2	60 ± 4
	DMSO	5820 ± 300	4396 ± 250	3164 ± 180	2460 ± 140	24 ± 1	48 ± 3

Table 1. Stability constants and thermodynamic parameters for extra coordination of the ZnP^1 – ZnP^5 complexes (H_2P^1 – H_2P^5 are bromo-substituted porphyrins)

enthalpy (ΔH) and entropy (ΔS) from known chemical thermodynamics relations:

$$\Delta H = 2.3R \frac{T_1 T_2}{T_2 - T_1} \log \frac{K_2}{K_1},\tag{5}$$

$$\Delta G = -RT\ln K,\tag{6}$$

$$\Delta S = \frac{\Delta H - \Delta G}{T}.$$
 (7)

The results of calculations are summarized in Table 1.

RESULTS AND DISCUSSION

The porphyrins studied in this work are intermediate between classical porphyrins with a planar aromatic π -system in the macrocycle and an inert NH bond (tetraphenylporphine, octaalkyl- and octapseudoalkylporphyrins, etc. [7–9]) and nonclassical porphyrins with nonplanar structures (dodeca-substituted porphyrins) and reactive, highly polarized NH bond (tetraazaporphyrins, phthalocyanine).

The replacement of H atoms in the tetraphenylporphine (H_2 TPP) by strongly polarizing bromine atoms markedly distorts the planar structure of the macrocycle [10–12] if the Br atoms enter the *ortho*-positions in the benzene rings, for example, in H₂TPP(*o*-Br)₄ (H₂P¹), or β -positions of each pyrrole ring, for example, H₂TPP(β -Br)₄ (H₂P⁵). It follows from the electronic absorption spectra of the tetraphenylporphine dications H₄TPP²⁺ that the accumulation of positive charge at the reaction site (H₃N₄⁺, H₄N₄²⁺, and M^{\sigma+}) is favorable for partial conjugation of electrons of the phenyl groups with electrons of the substituted C₆H₄X groups, where X is a σ -or π -electron donor.

The bromine atoms in the $H_2P^1-H_2P^5$ porphyrins exhibit a strong inductive effect (-*I*), irrespective of their positions in the macrocycle, as in any other organic molecule [13]. In addition, the bromine atom has a nonbonding orbital occupied by a pair of $4p_z$ electrons, which can be conjugated with various π -bonds, benzene rings, and π -systems of nonbenzene aromatic molecules.

The electrons of bromine atoms in the ZnP^1-ZnP^5 molecules can, in principle, be conjugated with the macrocycle π -system. However, the nonorthogonal arrangement of the macrocycle π -system and C_6H_4Br (or $C_6H_3Br_2$) precludes pronounced $\pi-\pi$ interaction in the case of ZnP^1-ZnP^4 . In the $ZnTPP(\beta-Br)_4$ (ZnP^5) molecule, the bromine atoms are located in the plane of

ZnD	Solvent		1)* nm			
ZIIF	Solvent	Band I	Band II	Soret	$\neg \Delta \lambda_{\rm I}$, min	
ZnTPP	Toluene	588(3.44)	549(4.28)	423(5.68)		
	Ру	606(3.98)	566(4.27)	431(5.81)	18	
	Pip	610(4.01)	568(4.27)	432(5.72)	22	
ZnP ¹	Toluene	596(3.55)	551(4.30)	423(5.67)		
	Ру	602(3.65)	563(4.27)	430(5.84)	6	
	Pip	603(3.69)	564(4.29)	431(5.85)	7	
	DMSO	597(3.62)	560(4.29)	429(5.83)	1	
ZnP ²	Toluene	588(3.67)	549(4.69)	420(5.64)		
	Ру	601(4.18)	562(4.66)	427(5.85)	13	
	Pip	602(4.29)	565(4.67)	431(5.89)	14	
	DMSO	597(3.95)	558(4.42)	427(5.80)	9	
ZnP ³	Toluene	588(3.88)	549(4.64)	422(5.02)		
	Ру	603(4.32)	563(4.63)	428(5.07)	15	
	Pip	605(4.33)	565(4.63)	429(5.08)	17	
	DMSO	598(4.24)	559(4.63)	426(5.09)	10	
ZnP ⁴	Toluene	589(3.57)	550(4.30)	423(5.32)		
	Ру	601(4.00)	562(4.26)	429(5.60)	12	
	Pip	603(4.07)	565(4.28)	430(5.76)	14	
	DMSO	599(4.03)	559(4.29)	428(5.64)	10	
ZnP ⁵	Toluene	609(3.85)	568(4.14)	429(5.12)		
	Ру	618(3.97)	575(4.16)	437(5.29)	9	
	Pip	618(4.11)	576(4.31)	441(5.68)	9	
	DMSO	617(3.95)	572(4.18)	430(5.20)	8	

Table 2. Band positions and intensities of the electronic absorption spectra of solutions of ZnP^1 – ZnP^5 complexes in organic solvents

* $\Delta \lambda_I = \lambda_I (LZnP) - \lambda_I (ZnP).$

the macrocycle π -system; in this case, the $p_{\pi}(Br)-p_{\pi}(P)$ interaction becomes quite possible. The possibility of this interaction can be evaluated, to a certain extent, from the electronic absorption spectra and the stability constants of the complexes formed by ZnP with electron-donating Py, Pip, and DMSO molecules (Table 2).

Analysis of the data presented in Table 2 leads to the following conclusions. The extra coordination of Py and Pip causes a bathochromic shift of all three bands in the electronic absorption spectrum of ZnTPP. Similar shifts, although less pronounced, occur in the spectra of similar complexes formed by bromoporphyrins. The compound Zn(TPP)(m-Br₂)₄ (ZnP³), in which the -I effect of the eight bromine atoms results in the lowest electron density on Zn, is close to ZnTPP in its $\Delta\lambda_1$ value. Since all the bromine atoms in ZnP³ occur in the *meta*-positions of the benzene rings, they cannot be

involved in the π - π conjugation with either the benzene ring or the macrocycle π -system. The *meta*-dibromosubstitution in H₂TPP is responsible for not only electronic effects in H₂P³ (-*I* effect) but also for the change in the geometric structure of the porphyrin (structural effects).

These two effects act in opposite directions. Therefore, the positions of bands in the electronic absorption spectra of ZnTPP and ZnP³ are close and the molar extinction coefficient (ε) of bands I and II increases upon *meta*-octabromo-substitution.

The introduction of four bromine atoms in the *ortho*-position of the benzene rings induces a bathochromic shift of the λ_I band in the ZnP¹ spectrum in toluene. The energy characteristics and the probabilities of transitions characterized by λ_{II} and λ_{Soret} do not change.

The LZnTPP(o-Br)₄ complexes are 2 to 5 times less stable than the corresponding LZnTPP complexes. The electron-withdrawing effect of the Br atoms is expected to stabilize complexes with organic bases due to the favorable decrease in the electron density on the central Zn atom. However, bromination has the opposite effect on K_s . Thus, there is at least one more factor that influences the properties of the MN₄ coordination unit upon bromination.

It was found previously [14–17] that the introduction of a halogen atom in any position of the benzene rings, especially in the *ortho*-position, markedly stabilizes MTPP complexes (M = Zn, Cu, Ni, Mn) due to steric shielding of the MN_4 reaction site. However, steric restrictions caused by the substituted benzene rings cannot significantly influence the formation and dissociation of extra omplexes with organic bases.

Previously [14–17], on the basis of the activation energy and entropy of dissociation of MTPP(X)₄, a conclusion was drawn that the role of solvation in the dissociation kinetics of MTPP(X)₄ differs appreciably from that for unsubstituted MTPP. The role of solvation, which has not been studied quantitatively in this work, can be clearly traced in the electronic absorption pectra (solvatochromic effect) and in the K_s values of the above-noted complexes (solvato-thermodynamic effect).

The introduction of four bromine atoms in the *meta*positions of the benzene rings (H_2P^2) entails the same changes in the electronic absorption pectra as in the case of ZnP¹, namely, a bathochromic shift of the λ_{II} band with invariable positions of the λ_{II} and λ_{Soret} bands. Among the LZnTPP(*m*-Br)₄ complexes, only the complex with L = Pip is three times more stable than the corresponding complex with the *ortho*-substituted porphyrin (PipZnP²), whereas the stability of the other two complexes (L = Py, DMSO) is equal to that of complexes with H₂P².

The greatest structural-thermodynamic effect is induced by β -tetrabromo-substitution in ZnTPP(β -Br)₄ (ZnP⁵). This shows itself as the greatest bathochromic shifts of all bands in the spectrum observed on passing from ZnTPP to ZnTPP(β -Br)₄, in particular, $\Delta\lambda_I = 21$, $\Delta\lambda_{II} = 19$, and $\Delta\lambda_{Soret} = 6$ nm (Table 2).

These shifts are due to the strong polarization of the chromophore by the substituents and redistribution of the π -electron density between the macrocyclic (C₁₂N₄) and benzene (C₆H₅) chromophores and the C_β=C_β double bonds [10, 11]. In the ZnP⁵ molecule, the electron-withdrawing action of the Br atom on the ZnN⁴ reaction site (-*I* effect) is so pronounced that K_s of the PyZnTPP(β-Br)₄ complex (T = 298 K) increases by 4.8 times with respect to that of PyZnTPP, while K_s of

PipZnTPP(β -Br)₄ reaches a value of 4.46 × 10⁵ mol⁻¹ 1 (this is the most stable extra complex known to date [2]).

On the basis of the obtained results, one should expect some violation of the planar structure of $H_2TPP(\beta-Br)_4$ in solutions, substantial polarization of the NH bond, an increase in the acid dissociation constant, and an increase in the complexation rate of $H_2TPP(\beta-Br)_4$ with *d*-metal salts.

REFERENCES

- 1. Berezin, B.D., *Koordinatsionnye soedineniya porfirinov i ftalotsianina* (Coordination Compounds of Porphyrines and Phthalocyanine), Moscow: Nauka, 1978.
- 2. Berezin, B.D. and Enikolopyan, N.S., *Metalloporfiriny* (Metalloporphyrins), Moscow: Nauka, 1988, p. 159.
- Karmanova, T.V., Koifman, O.I., and Berezin, B.D., *Koord. Khim.*, 1983, vol. 9, no. 6, p. 772.
- 4. Semeikin, A.S., *Doctoral (Chem.) Dissertation,* Ivanovo: Inst. of Chemistry of Nonaqueous Solutions, Russ. Acad. Sci., 1995.
- 5. Callot, H.J., Bull. Soc. Chim. Fr., 1974, vol. 8, p. 1492.
- 6. Techniques of Organic Chemistry, Weissberger, A. and Proskauer, E.S., Eds., New York: Interscience, 1955. Translated under the title Organicheskie rastvoriteli. Fizicheskie svoistva i metody ochistki, Moscow: Inostrannaya Literatura, 1958.
- Vinogradova, T.V., Karmanova, T.V., Semeikin, A.S., and Berezin, B.D., Abstracts of Papers, XII Vserossiiskoe Chugaevskoe soveshchanie po khimii kompleksnykh soedinenii (XII All-Russia Chugaev Conf. on Chemistry of Complex Compounds), Ivanovo, 1999, p. 113.
- Berezin, B.D., Zh. Prikl. Spektrosk., 1999, vol. 66, no. 4, p. 483.
- Berezin, B.D. and Berezin, D.B., Uspekhi khimii porfirinov (Advances in Chemistry of Porphyrins), Golubchikov, O.A., Ed., St. Petersburg: S.-Peterb. Gos. Univ., 1999, vol. 2, p. 128.
- Hamor, M.J. and Hamor, T.A., J. Am. Chem. Soc., 1964, vol. 86, no. 10, p. 1938.
- 11. Jian-Zhong Zou, Zheng Xu, Ming Li, and Xiao-Zeng You, *Acta. Crystallogr*, 1995, vol. 51, p. 760.
- 12. Knyukshto, V., Zenkevich, E., Sagun, E., et al., Chem. Phys. Lett., 1998, vol. 297, p. 97.
- Berezin, B.D. and Berezin, D.B., *Kurs sovremennoi* organicheskoi khimii (Course of Modern Organic Chemistry), Moscow: Vysshaya Shkola, 1999.
- 14. Tsvetkov, G.A., *Cand. Sci. (Chem.) Dissertation*, Ivanovo: Ivanovo Inst. of Chemical Technology, 1980.
- 15. Berezin, B.D., Shormanova, L.P., and Tsvetkov, G.A., *Zh. Fiz. Khim.*, 1979, vol. 53, no. 11, p. 2716.
- 16. Berezin, B.D., Tsvetkov, G.A., and Shormanova, L.P., *Zh. Neorg. Khim.*, 1980, vol. 25, no. 10, p. 2645.
- Shormanova, L.P., Berezin, B.D., Tsvetkov, G.A., and Artamonova, O.A., *Zh. Fiz. Khim.*, 1984, vol. 58, no. 10, p. 2511.