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Regularities of Extra Coordination of Nitrogen-containing Ligands with an Anthracenyl-capped Zinc Porphyrin

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Abstract — 3,3'-Dibutyl-4,4'-dimethylpyrrolylmethane was reacted with 9,10-bis(2-formylphenyloxymethyl)-anthracene to synthesize a capped porphyrin, and its zinc complex was prepared. The coordination properties of the capped zinc porphyrin in extra coordination with *N*-methylimidazole, imidazole, pyridine, 3,5-dimethylpyrazole, and dimethylformamide in *o*-xylene were studied. A correlation of the stability of the extra complexes and the basicity of the extra ligands was established. A correlation between the stability of the extra complexes and the shifts of their principal electronic absorption bands with respect to those of the zinc porphyrin was found. Deformations of the porphyrin ligand were noted to affect the strengyh of the metal–extra ligand σ bond. The geometric and energetic characteristics of the fivecoordinate zinc porphyrin were obtained by quantum-chemical calculations. A correlation between the calculated energy of interaction of the central metal atom with the nitrogen atom of the extra ligand and the stability of the extra complexes of the capped Zn porphyrin was revealed.

The present work deals with the coordination properties of sterically strained metal porphyrin complexes. A capped porphyrin and its Zn complex (ZnP) were synthesized and regularities of extra coordination of the latter with nitrogen-containing ligands (L) were studied by means of spectrophotometric titration [1] and computer simulation [2–4].

The sterically strained zinc porphyrin ZnP was synthesized by the following scheme.

First we performed chloromethylation of anthracene (**I**) to obtain compound **II** which was reacted with salicylaldehyde to synthesize dialdehyde **III**. 5,5'-Unsubstituted dipyrrolylmethane **V** was obtained by refluxing diester **IV** in a strongly alkaline solution under argon. Condensation of compounds **III** and **V** in acetonitrile in the presence of trichloroacetic acid gave porphyrin **VI**. The zinc complex of porphyrin **VI** was prepared by refluxing the latter with excess zinc acetate in benzene.

The formation of extra complexes (L)ZnP due to drawing the metal atom out of the plane of the porphyrin ligand and the formation of a metal–extra ligand σ bond ($Zn–N_L$) weakens the metal–porphyrin bond ($Zn–N_P$) in the macroring, thereby weakening the σ effect in the electronic absorption spectra and shifting red principal absorption bands of the chromophore (Fig. 1). This allows the extra coordination to be explored by spectral methods.

The observation of a smoothly descending titration curved of ZnP with imidazole suggests that the extra coordination is a one-step reaction (Fig. 2). As found by the Bent–French method [1], the capped zinc porphyrin takes up by one molecule of *N*-methylimidazole (MeIm), imidazole (Im), 3,5-dimethylpyrazole (DMP), pyridine (Py), and dimethylformamide (DMF) (Fig. 3). The experimental stability constants (K_{st}) and calculated geometric and energetic characteristics of the zinc complexes are listed in Tables 1 and 2.

From data in Table 1 we estimated the strength of bonding of the extra ligands with ZnP and deduced the following stability order of the complexes: (Im)ZnP > (MeIm)ZnP > (Py)ZnP > (DMP)ZnP > (DMF)ZnP. The fact that the Zn–L bond strength in the extra complexes decreases in going from imidazole to DMF (Table 2) can be explained in terms of decreasing basicity of the extra ligand (pK_{BH^+}). An exception is MeIm. Apparently, coordination of this nitrogenous base with the metal porphyrin is hindered by steric reasons.

Unlike the sterically unhindered Zn tetraphenylporphine (ZnTPP) extra complexes [5] whose $\log K_{st}$ vary linearly with pK_{BH^+}, the $\log K_{st}$–pK_{BH^+} correla-

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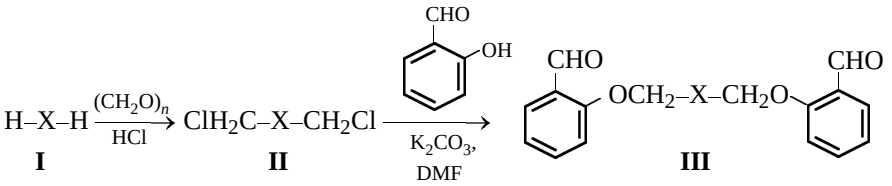
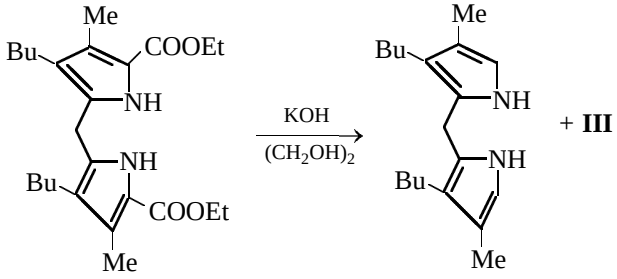
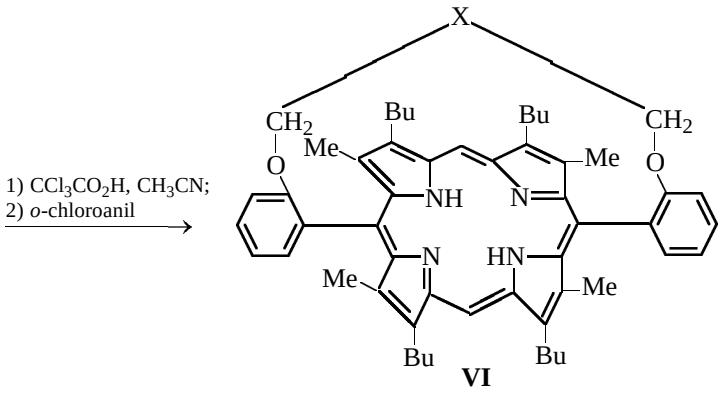


I **II** **III**

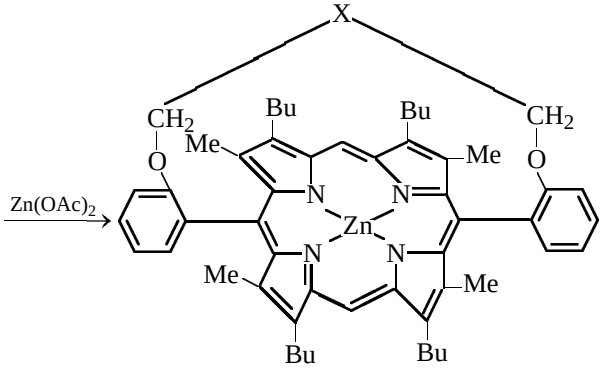


+ **III**

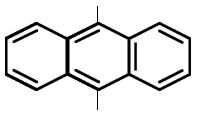
IV **V**



VI



ZnP

X =  .

tion for anthracenyl-capped zinc porphyrins is not linear and has the following equation (Fig 4a).

$$\log K_{st} = 0.0314(pK_{BH^+})^2 - 0.0146(pK_{BH^+}) + 1.9585;$$

$$r\ 0.9928.$$

This finding can be explained by an effect of the nature of the porphyrin ligand on extra coordination. In ZnTPP, the electron density is displaced from the zinc atom to the phenyl substituents; as a result, the effective positive charge on Zn is increased, and the Zn–L bond becomes stronger. In the capped zinc porphyrin that contains less phenyl substituents and whose porphyrin macroring bears β-alkyl substituents, the

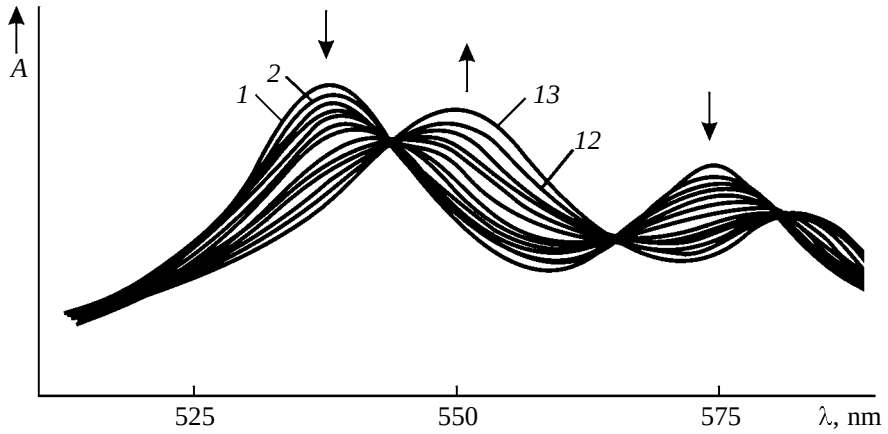


Fig. 1. Electronic absorption spectra of *o*-xylene solutions of capped zinc porphyrin ZnP with (*1*) no imidazole added, (*2–12*) intermediate concentrations of imidazole, and (*13*) excess imidazole. (*1*) c_{ZnP} 4×10^{-6} M and (*2–12*) c_{ZnP} 4×10^{-6} M and c_{Im} 1.15×10^{-4}–5.5×10^{-3} M.

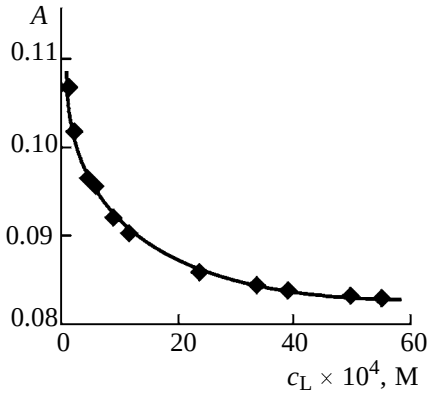


Fig. 2. Titration curve of capped zinc porphyrin ZnP with imidazole at c_{Im} 10^{-4}–5.5×10^{-3} M.

electron density on the nitrogen atoms of the coordination center is increased and the positive charge on Zn is decreased. The cap enhances distortions of the macroring and thus contributes into its electron density redistribution. Together the above factors operate to weaken the Zn–N_L bond. The same pattern we earlier observed in the extra complexes of 2,5-dimethoxyphenylene-capped zinc porphyrins [5].

It should be noted that the stability of the extra complexes of the capped zinc porphyrin (L)ZnP correlates with the shift of their principal electronic absorption bands $\Delta\lambda_{max}$ (Table 1). The fact that this is not a linear correlation (Fig. 4b), as is the case with ZnTPP [5], provides further evidence for our assumption that extra coordination enhances steric strain in ZnP. The observed correlation is described by the following equation.

$$\log K_{st} = 1.1245\ln(\Delta\lambda_{max}) + 0.3961;\ r\ 0.9993.$$

From the magnitude of the red shift we can draw qualitative conclusions concerning the strength of the Zn–L bond and, consequently, estimate the deviation of the metal atom from the plane of the coordination center.

Considering the stabilities of the extra complexes of the anthracenyl-capped zinc porphyrin (Table 1), its unhindered analogs, and ZnTPP [5], we can conclude that enhancing deformation strain of the porphyrin ligand decreases aromaticity of sterically distorted complexes and increases their basicity. As a result, the strength of the metal–ligand σ bond and the K_{st} value decrease. The decreased stability of the capped

Table 1. Thermodynamic characteristics of capped zinc porphyrin complexes

Complex	$K_{st}^{298\ K}\times10^{-3}$, mol^{-1} l	$-E_b(M-N_L)$, kJ/mol	$\Delta\lambda_{max}$, nm
(MeIm)ZnP	0.793 ± 0.008	–76.84	8
(Im)ZnP	1.955 ± 0.055	–76.52	13
(Py)ZnP	0.439 ± 0.021	–65.40	7.5
(DMP)ZnP	0.212 ± 0.022	–31.80	5.5
(DMF)ZnP	0.091 ± 0.008	–14.28	4
(Im)ZnTPP[a]	15 ± 2	–611.08	
(Py)ZnTPP[a]	1.8 ± 0.1	–590.92	
(Im)ZnP®h[a]	0.93 ± 0.01	–0.119	
(Py)ZnP®h[a]	0.24 ± 0.02	–0.102	

[a] Data of [5]; ZnPrh is a 2,5-dimethoxyphenylene-capped porphyrin.

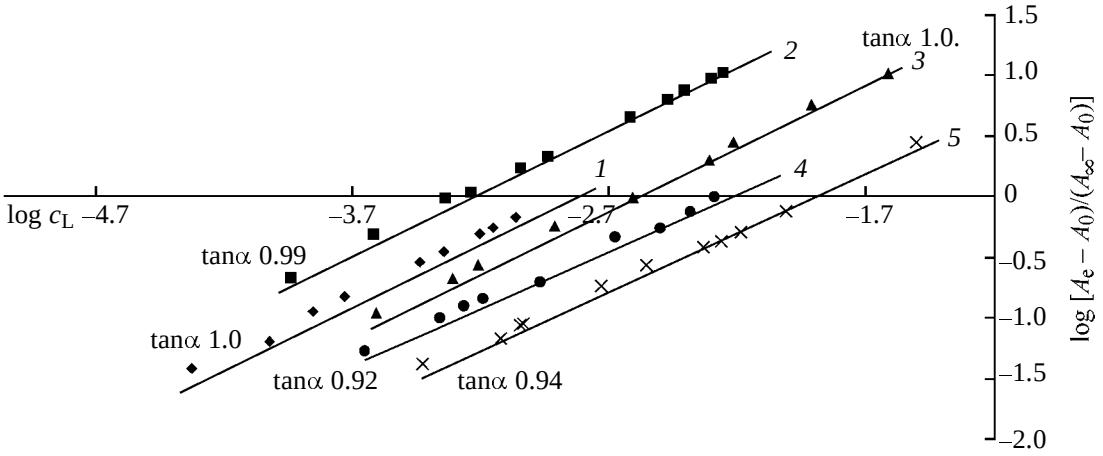


Fig. 3. log [(A_e – A_0)/(A_∞ – A_0)]–log c_L correlations for extra coordination of ZnP with (*1*) *N*-methylimidazole, (*2*) imidazole, (*3*) pyridine, (*4*) 3,5-dimethylpyrazole, and (*5*) dimethylformamide (A_0, A_e, A_∞ are the optical densities of the solutions at the wavelengths of metal porphyrin and equilibrium mixture of ligand and extra complex).

zinc porphyrin complexes is associated with the entropy factor, since the anthracenyl cap hinders extra coordination. The coordination properties of capped zinc porphyrins depend on the nature of the cap. Thus, a porphyrin complex with an anthracenyl cap instead of 2,5-dimethoxyphenylene [5] features less pronounced distortions of the macrocyclic ligand due to less strained O(CH_2) tethers and smaller angles of inclination of the phenyl groups to the cap (Fig. 5). In this case, more stable extra complexes are formed (Table 1). It thus can be concluded that the coordination properties of sterically strained zinc porphyrins depend on the degree of distortion of the macroring.

Quantum-chemical calculations allow one to gain insight into the reasons for the variation in the stability of the extra complexes of the capped zinc porphyrin with the porphyrin and extra ligand. As follows from the calculation results, the metal porphyrin in hand has a dome-shaped structure with outward-protruding tertiary nitrogen atoms (Fig. 5). A characteristic feature of this compound is that its phenyl substituents together with the methylene bridges of the porphyrin moiety are inclined to the anthracenyl cap, thus imparting a saddle-like shape to the porphyring macroring (Fig. 5). The cap is slightly inclined with respect to the porphyrin plane. The metal porphyrin has a strained and distorted structure. Extra coordination enhances axial distortions of the macroring, thus rendering it less aromatic and increasing the electron density on the nitrogen atoms.

The calculated Zn–N_L bond energies (E_b) and stabilities of the extra complexes vary in the same direction (Table 1). The fact that E_b increases in the order (DMF)ZnP > (DMP)ZnP > (Py)ZnP > (MeIm)ZnP > (Im)ZnP suggests stabilization of the complexes in going from dimethylformamide to imidazole. The energy of the metal–extra ligand bond depends on the nature of the porphyrin. Thus, the E_b values for the zinc complexes decrease in the order (L)ZnTPP > (L)ZnP >(L)ZnPph (Table 1). The same

Table 2. Bond lengths (*l*) and deviations of the metal from the plane (Zn–Ct) in capped zinc porphyrin extra complexes

Complex	*l*, Å							Zn–Ct, Å
	Zn–N^1	Zn–N^2	Zn–N^3	Zn–N^4	N^1–N^3	N^2–N^4	Zn–N_L	
ZnP	2.0488	2.0112	2.0263	2.0479	4.0646	4.0698		0.1465
(MeIm)ZnP	2.0847	2.1059	2.1106	2.0827	4.0870	4.1411	2.0736	0.4733
(Im)ZnP	2.0844	2.1059	2.1110	2.0817	4.0871	4.1413	2.0734	0.4735
(Py)ZnP	2.0825	2.1097	2.1077	2.0801	4.0834	4.1368	2.0970	0.4700
(DMP)ZnP	2.0604	2.1145	2.1111	2.0739	4.0769	4.1242	2.1755	0.4415
(DMF)ZnP	2.0862	2.1228	2.1161	2.0794	4.0738	4.1381	2.2064	0.5156

trend is characteristic of the stability of these compounds.

As seen from data in Tables 1 and 2, the K_{st} values correlate with the Zn–N_L bond length. As the strength of the Zn–N_L σ bond increases in the order Im > DMP > Py > DMF, the stability of the extra complexes increases. At the same time, no correlation between the deviation of the metal atom from the N^4 plane and the Zn–N_L bond strength was found (Table 2). Metal–extra ligand interaction weakens the Zn–N_P bond (Table 2). Thus, a farly strong *cis* effect is observed. Finally, a certain correlation between the degree of macroring distortion, i.e. the size of the coordination cavity, and the Zn–N_L bond length is worth noting. Enhancing Zn–N_L bond strength enhances steric strain in the metal porphyrin (Table 2).

EXPERIMENTAL

The electronic absorption spectra of ZnP with various extra ligands were recorded on a Specord M-400 spectrometer at 298 K. The ^{1}H NMR spectra were obtained on a Bruker-200 instrument in CDCl, internal reference HMDS.

Thin-layer chromatography was performed on Silufol plates.

The reactions of ZnP and L were performed in *o*-xylene. The procedures of measurement and calculation of the stability constants of extra complexes were described in detail in [1, 6–9]. The optical densities of solutions with a constant concentration of metal porphyrin and various concentrations of extra ligand were measured at 537 [(MIm)ZnP, (Im)ZnP, (DMP)ZnP, and (DMF)ZnP] and 535 nm [(Py)ZnP].

Quantum-chemical calculations were performed by the PM3 semiempirical method by combining the Fletcher–Reeves and Pollack–Ribiere conjugate gradient methods [10]. The calculations were terminated at a gradient of 0.04 kJ/mol.

9,10-Bis(chloromethyl)anthracene (II) [11]. Anthracene (**I**), 4.5 g, and 3.5 g of Paraform were added to a mixture of 36 ml of dioxane and 6 ml of hydrochloric acid saturated with gaseous HCl, and the resulting mixture was heated under reflux for 4 h simultaneously passing HCl and then allowed to stand for 12 h. The yellow powder-like precipitate that formed was filtered off, washed with dioxane, dried, and recrystallized from toluene. Yield 4.5 g (60%), mp 258°C (decomp.).

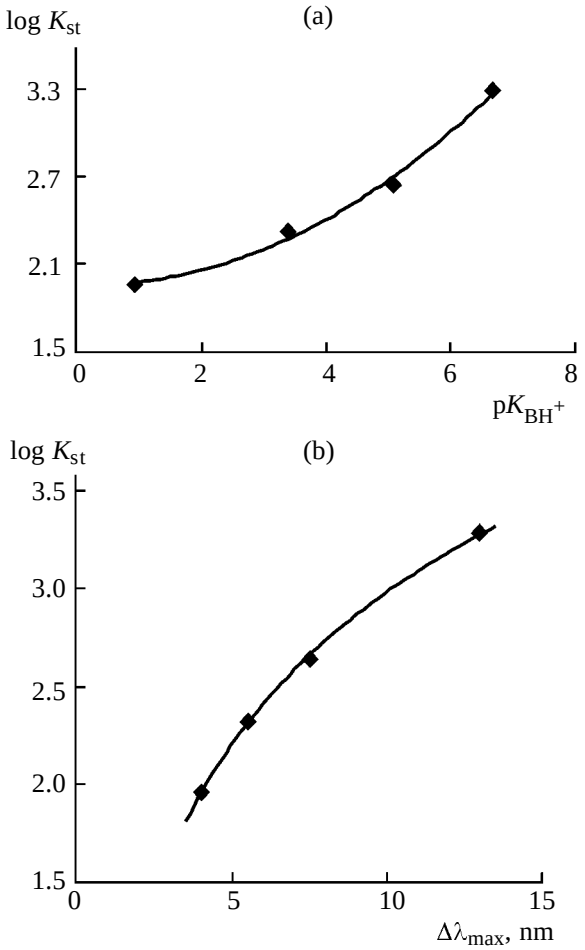


Fig. 4. Correlations of the stability of capped Zn porphyrin extra complexes with (a) the basicity of the ligands and (b) the shifts of principal bands in their electronic absorption spectra.

9,10-Bis(2-formylphenyloxymethyl)anthracene (III). A mixture of 4 g of 9,10-bis(chloromethyl)-anthracene (**II**), 6 g of K_2CO_3, 3 ml of salicylaldehyde, and 50 ml of DMF was stirred at room temperature for 6 h and then poured into water. The precipitate was filtered off, washed with water, dried, and recrystallized from benzene–methanol (1 : 1). Yield 4.6 g (72%), mp 191°C. ^{1}H NMR spectrum, δ, ppm: 9.98 s (1H, CHO), 8.08 m, 7.47 m (8H, X–H), 6.98 m, 7.68 m (8H, Ph–H), 5.28 s (2H, OCH_2).

3,3'-Dibutyl-4,4'-dimethylbis(2-pyrrolylmethane) (V). A mixture of 1.2 g of 3,3'-dibutyl-5,5'-diethoxycarbonyl-4,4'-dimethylbis(2-pyrrolylmethane) (**IV**) [12] and 1.5 g (26.8 mmol) of KOH in 30 ml of ethylene glycol was heated under reflux for 1 h under nitrogen. The solution was poured into water, washed

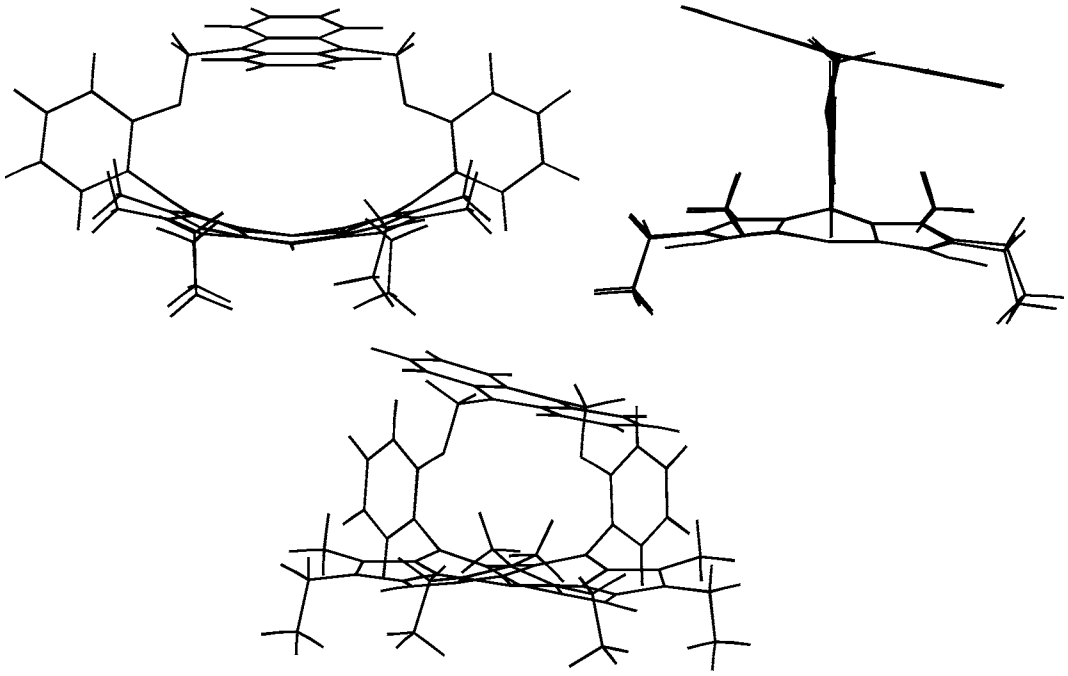


Fig. 5. Structure of the ZnP complex as given by PM3 quantum-chemical calulations.

with water, and dried. Yield 0.66 g (85%); the reaction product was used without further purification.

Capped porphyrin VI. A solution of 0.28 g of chloroacetic acid in 30 ml of acetonitrile was added with stirring under argon to a solution of 0.66 g of compound **V** and 0.51 g of anthracene **III** in 200 ml of acetonitrile. After 4-h stirring in the dark, a solution of 0.85 g of *o*-chloranil in 10 ml of THF was added, and the mixture was allowed to stand for 12 h at room temperature. The acetonitrile was distilled off, the residue was washed with aqueous alkali, water, dried, dissolved in chloroform, and subjected to double chromatography on alumina (Brockmann activity grade II). Porphyrin **VI** was precipitated with chloroform and dried. Yield 0.38 g (34%), R_f 0.36 (eluent chloroform). Electonic absorption spectrum ($CDCl_3$), λ_{max}, nm (log ε): 640 (4.13), 585 (4.21), 554 (4.22), 517 (4.30), 423 (5.08). Found, %: C 83.51; H 7.48; N 5.70. $C_{68}H_{72}N_4O_2$. Calculated, %: C 83.56; H 7.42; N 5.73.

Zinc complex of porphyrin VI. Compound **VI** was heated under reflux in benzene with a tenfold excess of zinc acetate for 40–50 min. The complex was purified by chromatography on Brockmann activity grade II alumina (eluent chloroform), followed by recrystallization from chloroform, R_f 0.80 (elyuent chloroform). Electronic absorption spectrum (*o*-xylene), λ_{max}, nm (log ε): 575 (4.18), 537 (4.46), 413 (5.37). Found, %: C 78.43; H 6.80; N 5.36. $C_{68}\cdot H_{70}N_4O_2Zn$. Calculated, %: C 78.48; H 6.82; N 5.38.

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