Influence of the Nature of Porphyrin and Extraligand on the Stability of Zinc Extracomplexes

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Abstract: The mutual influence of ligands within the structure of Zn-porphyrins on the thermodynamic stability of the latter was investigated.

**Keywords:** Extracoordination, complex, metalloporphyrins, stability.

Introduction

The influence of the nature of porphyrin and extraligand on the process of formation of extracomplexes of zinc porphyrins in *o*-xylene was studied by a spectrophotometrical titration method and computer simulation. For the research the following metalloporphyrins were used: zinc 5,15-(*para*-butyloxyphenyl)-2,8,12,18-tetramethyl-3,7,13,17-tetraethylporphyrin **ZnP(I)**, zinc 5,15-(*para*-butyl-oxyphenyl)-2,8,12,18-tetramethyl-3,7,13,17-tetrabutylporhyrin **ZnP(II)**, superimposed zinc porphyrin **ZnP(III)** and zinc tetraphenylporphyrin **ZnP(IV)**. N-methylimidazole (MeIm), imidazole (Im), pyridine (Py), 3,5-dimethylpyrazole (DMP) and dimethylformamide (DMF) were used as extraligands (L). The strength of Zn-L bonding was noted to be lower within the series of extracomplex stuctures: **ZnP(IV)** > **ZnP(I)** > **ZnP(II)** > **ZnP(III)**. The stability constant ($\lg K_S$) in the case of sterically unhindered complexes was found to increase linearly with the increase of basisity of the extraligand ($\lg K_{BH}+$). For sterically hindered **ZnP(I), ZnP(II)** and **ZnP(III)** the values of $\lg K_S$ and $\lg K_{BH}+$ and also $\lg K_S$ and $\Delta\lambda$ var-

ied non-linearly. Geometrical structures was computed by quantum - chemical methods and the energy characteristics of pentacoordinated zincporphyrin complexes were obtained. Correlations were found between calculated values of the interaction energy of the central metal atom with extraligand molecules and the stability of Zn-porphyrin extracomplexes.
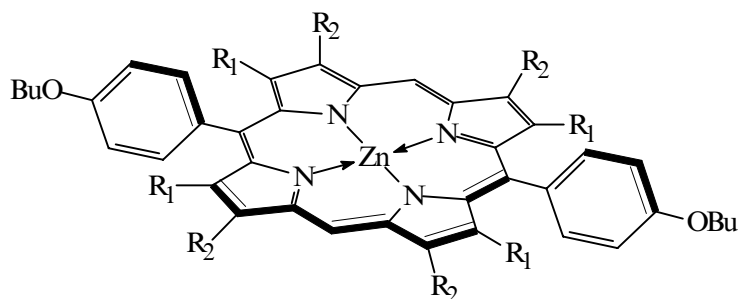
ZnP(I) R_1 = Et, R_2 = Me; **ZnP(II)** R_1 = Bu, R_2 = Me
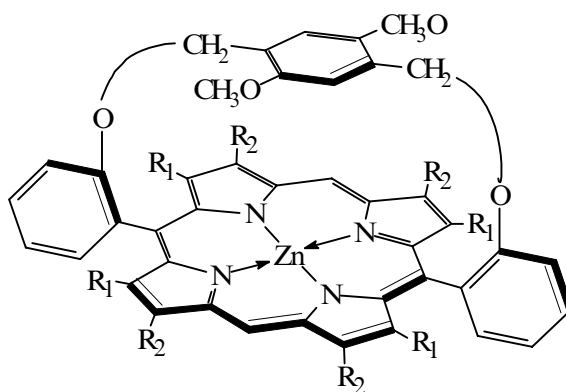
ZnP(III) R_1 = Me, R_2 = Bu
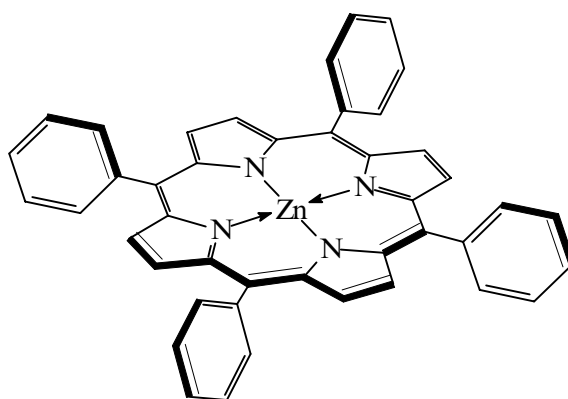
ZnP(IV)

Figure 1.

Results and Discussion

The binding of ligands L with Zn-porphyrins in all cases is accompanied by bathocromic shifts and with changes of intensity of the chromophore basic absorption bands (Figure 2). It is our point of view that this is due to the increase of electron density at the zinc cation and at the porphyrin nitrogen atoms. The growth of a fractional negative charge at N atoms establishes the destabilisation of the a_{2u} molecular orbital at a_{1u}. constant level. As a result the configuration interaction of the E_u-type excited state decreases, and that is sufficient reason for amplification of the first band in the electronic absorption spectra (EAS) of Zn-porphyrins. The bathochromic shift, probably, is caused by the increase in energy of the a_{2u} - type MO.
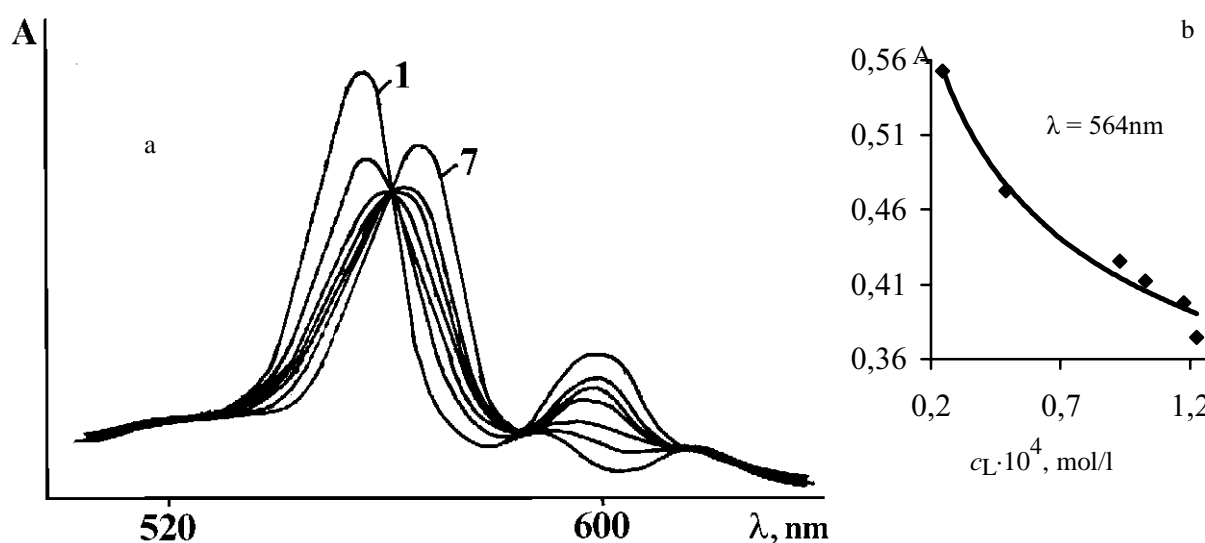

Figure 2. EAS of ZnP(IV) with imidazole in *o*-xylene; 1-7 - ZnP(IV) with concentration Im $0 \div 0.1 \cdot 10^{-3}$ mol/l (a) and corresponding titration curve (b).

During the study complexes **ZnP(I)**, **ZnP(II)**, **ZnP(III)** were found to have the property of attaching one molecule of MeIm, Im, DMP, Py, DMF. For **ZnP(IV)** the coordination of two molecules of extra-ligand is observed only in the case of DMF. K_S values obtained, calculated characteristics of geometric structure and energy parameters of molecules of Zn-porphyrins are presented in Tables 1 and 2. The comparison of the data in Table 1 enables us to estimate the strength of additional ligand binding with Zn-porphyrins and to establish a series for their stability. In the case of formation of extracomplexes of Zn-porphyrins with MeIm and Im the series is: **ZnP(IV)** > **ZnP(II)** $\approx$ **ZnP(I)** > **ZnP(III)**. This is explained by the influence of porphyrin ligand nature on the extracoordination process. In the case of **ZnP(IV)**, the electron density withdrawal from the zinc atom by phenyl rings increases its partial positive charge. Hence, the Zn-L bonding becomes stronger. The decrease of the number of phenyl substi-

tutions and the introduction of alkyl-groups in the β-position of the porphyrin macrocycle for **ZnP(I)**, **ZnP(II)**, leads to an increase of electron densities at nitrogen atoms in the coordination center and to the decrease of positive charge at the zinc atom that reduces the strength of Zn-L bonding. Thus, extra-complexes **(L)ZnP(I)**, **(L)Zn(II)** are less stable in comparison with **(L)ZnP(IV)**. The low value of the stability constant of extracomplexes **(L)ZnP(III)** in comparison with the remaining members of the se-ries is explained not only by the influence of substituents on the porphyrin macrocycle, but by its distor-tion as a result of steric strain caused by the "cover".

Stability constants of zinc complexes with Py are practically the same (Table 1) and the nature of porphyrin ligand, in this case, has practically no influence on the process of extracoordination. The rea-son of such anomalous behavior of pyridine remains unexplainable.

Table 1. Thermodynamic characteristics of extracoordination reactions of nitrogen-containing ligands by zinc complexes of porphyrins in *o*-xylene.

Complex	Extraligand	$K_S^{298} \cdot 10^{-3}$, mol$^{-1} \cdot$l	E_b Zn-L, kcal/mol	$\Delta\lambda$, nm
ZnP(I)	Me-Im	0.477 ± 0.001	-16.01	5.0
	Im	4.4 ± 0.1	-15.94	12.0
	Py	1.14 ± 0.06	-4.52	9.0
	DMP	1.64 ± 0.03	-12.85	10.0
	DMF	0.019 ± 0.001	0.05	2.5
ZnP(II)	Me-Im	0.56 ± 0.01	-	5.0
	Im	6.7 ± 0.4	-	17.0
	Py	1.8 ± 0.1	-	10.0
	DMP	1.9 ± 0.1	-	10.5
	DMF	0.15 ± 0.02	-	4.0
ZnP(III)	Me-Im	0.46 ± 0.02	-0.0299	4.0
	Im	0.93 ± 0.01	-0.0298	8.0
	Py	0.24 ± 0.02	-0.0256	3.0
	DMF	0.042 ± 0.003	-0.0097	2.0
ZnP(IV)	Me-Im	110 ± 8	-290.21	15.5
	Im	15 ± 2	-152.77	14.5
	Py	1.8 ± 0.1	-147.73	11.0
	DMP	1.5 ± 0.2	-145..36	10.0
	DMF	0.6 ± 0.01	1.90	15.0

The nature of the extraligand has an effect on the stability of Zn-porphyrin extracomplexes. The

strength of Zn-L bonds (Table 2) increases and the K_S values of complexes raise (Table 1) with the increase of the extraligand basisity. A linear correlation between $\lg K_S$ and pK_{BH+} values with the regression equation $\lg K_S = 0.2564 \cdot pK_{BH+} + 2.4589$ and a correlation coefficient $r = 0.963$, is observed for the sterically non-strained **ZnP(IV)** complex (Figure 3). In the case of **ZnP(I)** and **ZnP(II)**, where distortions of the porphyrin macrocycle are observed, at extracoordination, the function of $\lg K_S$ from pK_{BH+} became non-linear and is described by equations:

$$\text{for } \textbf{(L)ZnP(I)} \; \lg K_s = -0.038 \, pK_{BH+}^2 + 0.558 \cdot pK_{BH+} + 1.741; \; (r = 0.984),$$

$$\text{for } \textbf{(L)ZnP(II)} \; \lg K_s = -0.069 \cdot pK_{BH+}^2 + 0.936 \cdot pK_{BH+} + 0.536; \; (r = 0.979).$$

Table 2. Some geometric characteristics of pentacoordinated Zn-porphyrins.

| Complex	Zn-N1 Å	Zn-N2 Å	Zn-N3 Å	Zn-N4 Å	Zn-N$_L$ Å	Ct-Zn Å	N1-Ct Å	N3-Ct Å	N1-N3 Å
ZnP(I)	2,025	2,055	2,074	2,064		0,049	2,024	2,073	4,097
ZnP(I)+Me-Im	2,126	2,109	2,086	2,115	2,100	0,387	2,091	2,049	4,141
ZnP(I)+Im	2,125	2,108	2,086	2,115	2,099	0,459	2,075	2,064	4,139
ZnP(I)+Py	2,121	2,107	2,085	2,112	2,124	0,385	2,085	2,051	4,137
ZnP(I)+DMP	2,088	2,087	2,103	2,101	2,100	0,408	2,048	2,063	4,111
ZnP(I)+DMF	2,069	2,058	2,021	2,049	6,871	0,097	2,066	2,018	4,085
ZnP(III)	2.019	2.383	2.019	2.376		0	0	0	4.038
ZnP(III)+Me-Im	2.035	2.538	2.037	2.474	1.980	0.855	1.847	1.849	3.696
ZnP(III)+Im	2.032	2.522	2.033	2.484	1.978	0.834	1.853	1.854	3.707
ZnP(III)+Py	2.033	2.519	2.034	2.486	1.990	0.839	1.851	1.853	3.705
ZnP(III)+DMF	2.030	2.497	2.029	2.498	2.016	0.825	1.855	1.855	3.709
ZnP(IV)	2,055	2,043	2,011	2,043		0,002	2,055	2,011	4,066
ZnP(IV)+Me-Im	2,070	2,101	2,105	2,096	2,095	0,408	2,029	2,065	4,094
ZnP(IV)+Im	2,101	2,105	2,096	2,069	2,096	0,404	2,062	2,056	4,118
ZnP(IV)+Py	2,069	2,095	2,101	2,100	2,119	0,400	2,031	2,062	4,093
ZnP(IV)+DMP	2,085	2,104	2,095	2,053	2,203	0,429	2,040	2,051	4,091
ZnP(IV)+DMF	2,055	2,043	2,011	2,042	7,324	0,006	2,055	2,011	4,066
ZnP(IV)+ 2 DMF	2,011	2,045	2,055	2,040	7,919 7,621	0	2,011	2,055	4,066
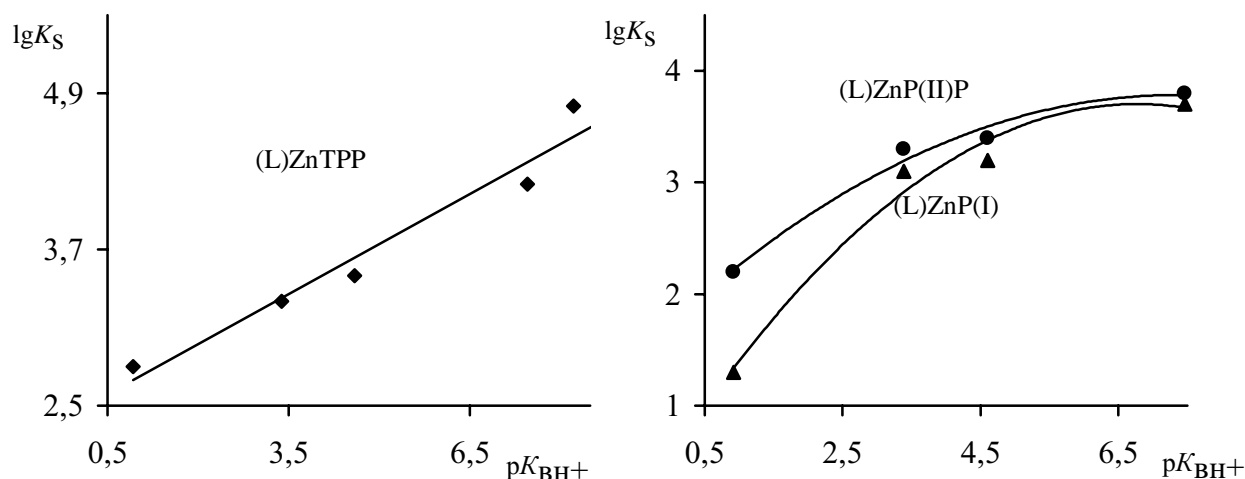
Figure 3. Dependency of extracomplex stabilities of Zn-porphyrins on the basisity of added extraligands.

On the basis of quantum - chemical calculations for N-containing extraligand structures the linear correlation between their basisity and the energy of protonation E_p (Figure 4) is obtained.
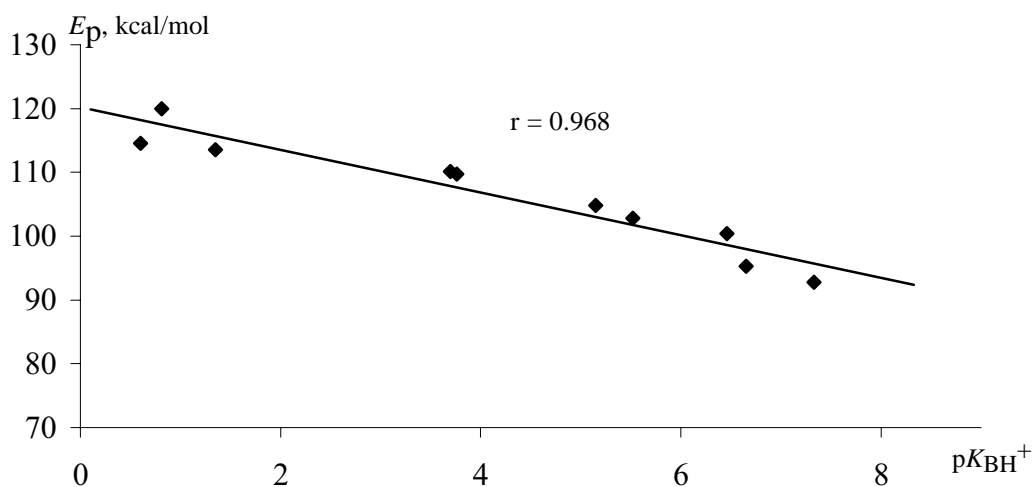

Figure 4. The dependence of protonation energy of nitrogen-containing molecules on their basisity.

Calculated $pK_{BH}+$ values compared with data from literature [14] in most cases is notedto be not more than 10% higher than values of $pK_{BH}+$ (calcul) and $pK_{BH}+^{*}$ (Table 3, Figure 5). In our opinion it allows us to use calculated energy of protonation for the evaluation of the basisity of nitrogen-containing compounds.

Table 3. Calculated values of protonation energy and basisity of nitrogen-containing molecules.

Extraligand	pK_{BH^+}*	$pK_{BH^+(calc.)}$	E_p, kcal/mol
Me-Im	7.33	8.22	92.73
Im	6.65	7.46	95.27
Py	5.29	4.60	104.8
3,4-dimethylpyridine	6.46	5.93	100.38
3-methylpyridine	5.52	5.21	102.79
2-formylpyridine	3.76	3.13	109.74
3- formylpyridine	3.7	3.01	110.14
3-cyanopyridine	1.35	1.99	113.56
2-nitropyridine	0.81	0.73	119.96
pyrazine	0.6	0.8	114.55
DMP	4.27	3.99	108.85
DMF	-	0.92	123.3

* Basisity values were obtained by potentiometry in water at 298K [14].
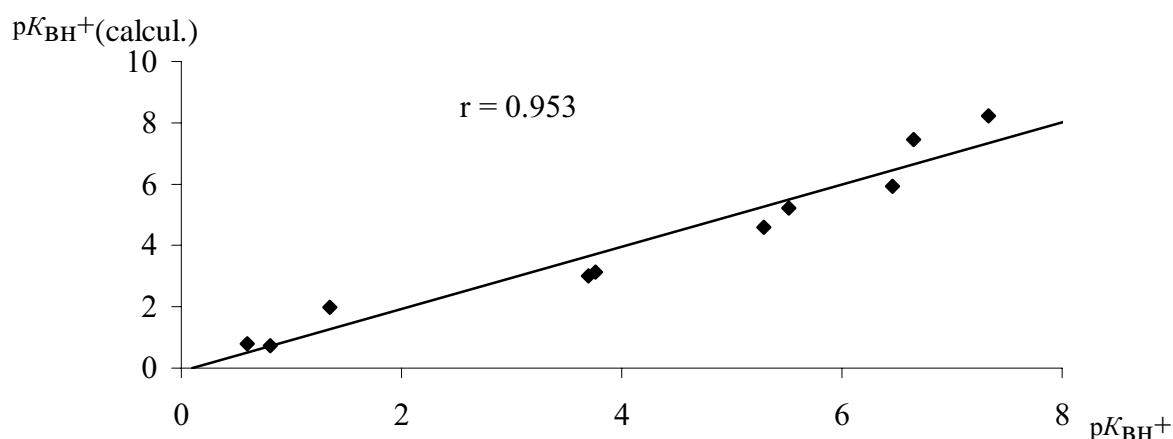
Figure 5. Correlation between calculated and experimental values.

As for **ZnP(IV)**, its complexes with Me-Im and Im are the most stable. In the case of **ZnP(I)**, **ZnP(II)**, **ZnP(III)**, interactions with Me-Im are hindered despite of its high basic properties, probably, because of spatial hindrance and distortion of the porphyrin macrocycle .

With the increase of K_S extracomplex values the magnitude of the shift of basic absorption bands $\Delta\lambda$ (Table. 1) increases. The linear dependence with the regression equation $lgK_S = 0.306 \cdot \Delta\lambda + 0.039$, r = 0.971 is characteristic only for **ZnP(IV)** (Figure 6). Stabilities of **(L)ZnP(I)**, **(L)ZnP(II)**, **(L)ZnP(III)** extracomplexes varies non-linearly against $\Delta\lambda$, values, and that, in turn, confirms our suppositions about steric stresses taking place in these compounds during extracoordination. Correlations obtained (Figure

6), in this case, are described by equations:

for **ZnP(I)** $\lg K_s = -0.006 \cdot \Delta\lambda^2 + 0.2384\,\Delta\lambda + 1.497$, r = 0.952;

for **ZnP(II)** $\lg K_s = -0.020 \cdot \Delta\lambda^2 + 0.511 \cdot \Delta\lambda + 0.299$, r = 0.932;

for **ZnP(III)** $\lg K_s = -0.069 \cdot \Delta\lambda^2 + 0.917 \cdot \Delta\lambda + 0.055$, r = 0.979.
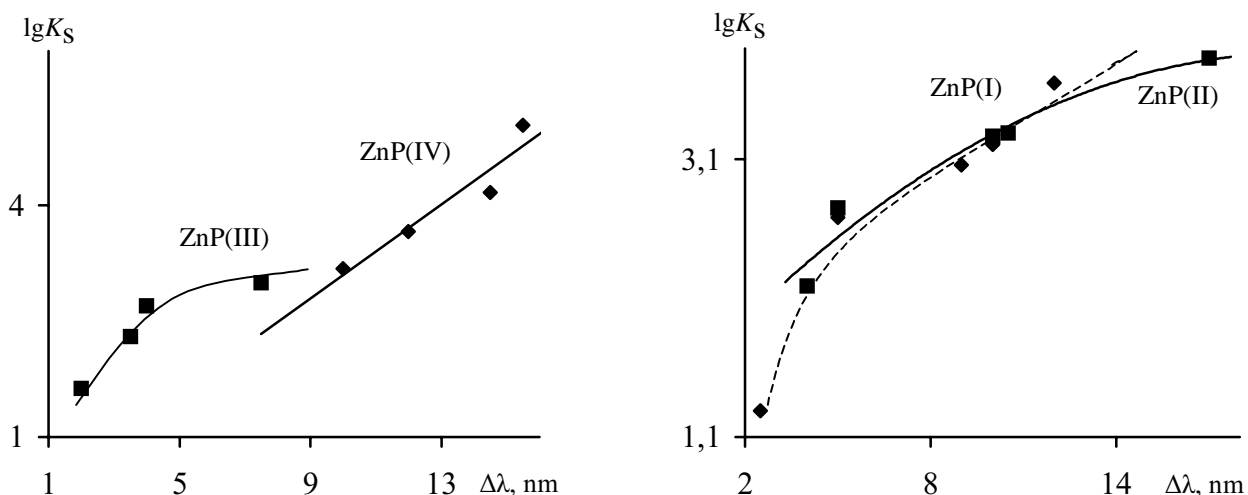

Figure 6. Dependencies of $\lg K_s$ of Zn-porphyrin extracomplexes and shift values of the basic absorption bands in EAS.

The value of bathochromic shift $\Delta\lambda$, may be used for qualitative characteristic of Zn-L bond strength, and consequently, also of value of metal atom exit from the coordination center plane. The use of quantum - chemical methods for calculations of Zn-porphyrins structures, allows us to explain the reasons of modification in stabilities of their extracomplexes as the function of the porphyrin and extraligand natures. Characteristics calculated show that the energy of Zn-L bonding formation (E_b) of extracomplex varies non-linearly with its stability (Table 1). The increase of E_b in the series **(L)ZnP(I)** to **(L)ZnP(IV)** shows the increase in their stabilities.

Zn-porphyrin extracomplexes have square-pyramidal coordination structures with the metal atom emerging slightly from the N_4 plane towards the extraligand (Figure 7). On the basis the data in Table 2 the correlations between an exit of metal from a plane of macrocycle and length of Zn-L bonding are obtained. We found out that in series of nitrogen-containing bases Im > DMP > Py > DMF the length of Zn-Ct in extracomplexes decreases, the stability of Zn-N bonding increases at coordination center (Table 2), the interaction of zinc atom with nitrogen atom of extraligand weakens and as the consequence, the overall stability of the metalloporphyrin is reduced (Table 1). Thus the cis-effect of ligands within the structure of Zn-porphyrin extracomplexes is shown to be strong. Finally, it is necessary to point out that some dependence is observed between distortion of a macrocycle (i.e. the size of a coordination

cavity) and length of Zn-L bonding. The increase of Zn-L bonding strength causes the increase of steric stresses in the metalloporphyrin (Table 2).
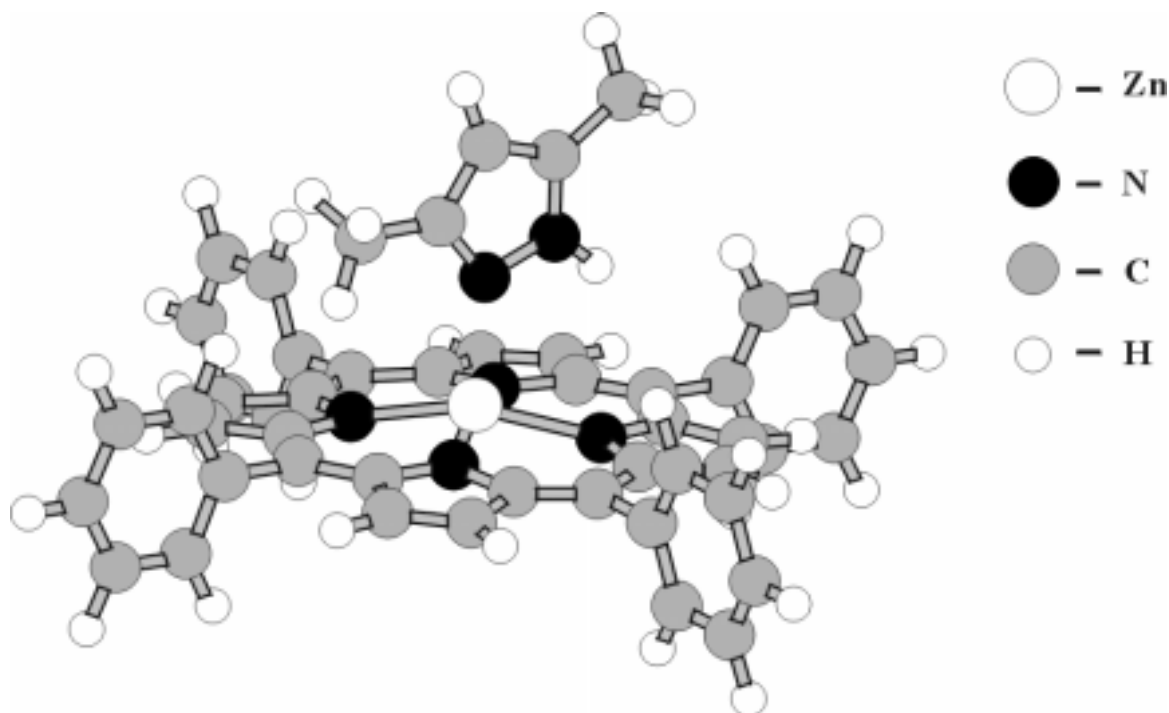

Figure 7. The structure of ZnP(IV) extracomplex with DMF, calculated by the PM3 quantum-chemical method.

Conclusions

On the basis of experimental and calculated data the dependence between the stability of extracomplexes Zn(L)P and the nature of porphyrin and the basicity of additional molecular ligands was obtained. Correlations between K_S values, the magnitude of basic absorption band displacements $\Delta\lambda$ in EAS of metalloporphyrins and calculated bonding energy of zinc atom with nitrogen atom of extraligand (E_b) were found.

Experimental

Zinc complexes with various porphyrin structures (**ZnP(I), ZnP(II), ZnP(III), ZnP(IV)**) were investigated to systematically study regularities of extracoordination reactions at metalloporphyrins. **ZnP(IV)** was taken as model compound. The reaction $ZnP + Ln = Zn(L)_nP$ was studied at three temperatures: 298K, 303K and 308K (for **ZnP (IV)**: 298K, 308K and 318K) in *o*-xylene, which was chosen because it forms no strong solvate complexes with metalloporphyrins and it is a neutral solvent. Spectrophotometrical titration [1] and computer simulation [2-4] was used to investigate extra-coordination.

Porphyrins studied (H$_2$TPP, 5,15-(*para*-butyloxyphenyl)-2,8,12,18-tetramethyl-3,7,13,17-tetraethylporphyrin and 5,15-(*para*-butyloxyphenyl)-2,8,12,18-tetramethyl-3,7,13,17-tetrabutylporphyrin) were synthesized by known methods [5-8].

Zn-tetraphenylporphyrin

It was synthesized by boiling tetraphenylporphyrin with a tenfold excess of zinc acetate in benzene during 40-50 min. The zinc complex was purified by chromatography on Al$_2$O$_3$ (activity II) using chloroform as eluent, followed by recrystallization from chloroform. EAS (benzene) λ_{max} nm, (lgϵ): 590.0 (3.49), 550.0 (4.23), 422.5 (5.57).

Zn-5,15-(para-butoxyphenyl)-2,8,12,18-tetramethyl-3,7,13,17-tetraethylporphyrin

It was obtained in the same way. EAS (benzene) λ_{max} nm, (lgϵ):570.0 (3.98), 534.0 (4.31), 407.0 (5.18).

Zn-5,15-(para-butoxyphenyl)-2,8,12,18-tetramethyl-3,7,13,17-tetrabutylporphyrin

It was obtained in the same way. EAS (benzene) λ_{max} nm, (lgϵ):575.0 (3.99), 541.0 (4.25), 412.3 (5.08).

Superimposed Zn-porphyrin

It was obtained in the same way. EAS (*o* - xylene) λ_{max} nm, (lgϵ): 587.0 (4.22), 549.0 (4.43), 410.0 (5.34).

Changes in metalloporphyrin EAS with the concentration of extraligand allowed us to use a spectral method for study of extracoordination. The experimental technique and calculations of stability constants of extracomplexes (K_S) are discussed in more detail in the literature [1, 9-12]. The quantum - chemical calculations were carried out by a combination of conjugated gradient methods [13]. The condition of termination of the optimization was given by a gradient of 0.04 kJ/mol.

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Samples Availability: Available from the authors.