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Coordination Properties of Sterically Stressed Zincporphyrins

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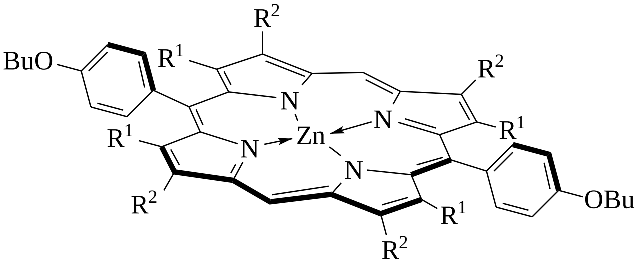
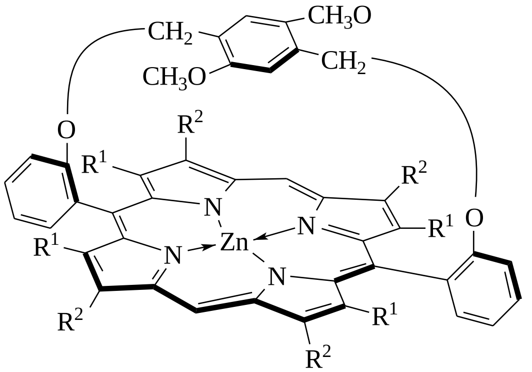
Abstract—Spectrophotometric titration and computer simulation were used to study how the nature of porphyrin and extra ligand affect the formation of extra complexes of zincporphyrins in *o*-xylene. The compounds under study were zincporphyrins (ZnP) with different substituents and phenyl radicals in *meso*-positions (zinc-5,15-(*p*-butyloxyphenyl)-2,8,12,18-tetramethyl-3,7,13,17-tetraethylporphyrin (ZnP^1), zinc-5,15-(*p*-butyloxyphenyl)-2,8,12,18-tetramethyl-3,7,13,17-tetrabutylporphyrin (ZnP^2), zinctetraphenylporphine (ZnP^3), and zinc complexes with overlapped porphyrin (ZnP^4). *N*-Methylimidazole, imidazole, pyridine, 3,5-dimethylpyrazole, and dimethylformamide were used as extra ligands (L). The strength of Zn–L bonding was found to decrease in extra complexes (L)ZnP in the series of ZnP as follows: $ZnP^4 > ZnP^1 > ZnP^2 > ZnP^3$. It was established that the stability constant ($\log K_{st}$) for sterically nonstressed complexes $(L)ZnP^4$ linearly increases with growth in the extra ligand basicity ($\log K_{BH^+}$) and is proportional to the shift of the main absorption bands ($\Delta\lambda$) in the electronic spectra of extra complexes of zinctetraphenylporphine. For spatially distorted $(L)ZnP^1$, $(L)ZnP^2$, and $(L)ZnP^3$, the values of $\log K_{st}$ and $\log K_{BH^+}$, as well as $\log K_{st}$ and $\Delta\lambda$, change symbatically. The geometric structure and energy characteristics of pentacoordinated zincporphyrins were calculated by quantum-chemical methods. Correlations were established between the calculated values of the energy of the interaction of the central metal atom with the extra ligand molecule and the stability of the extra complexes of zincporphyrins.

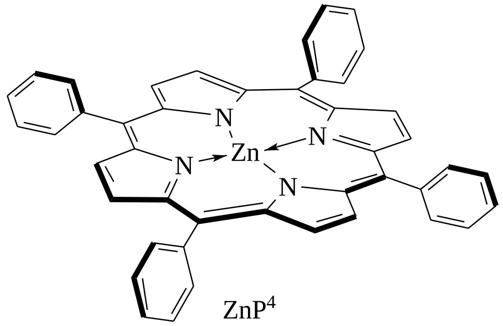
The aim of this work was a systematic study of the regularities of extracoordination of metalloporphyrins, namely, of the effect of porphyrin and extra ligand nature on the formation of sterically stressed extra complexes. We studied the coordinating properties of zinc complexes with porphyrins of different structures (ZnP).



ZnP^1: R^1 = Et, R^2 = Me; ZnP^2: R^1 = Bu, R^2 = Me



ZnP^3: R^1 = Me, R^2 = Bu



ZnP^4

Spectrophotometric titration [1] and computer simulation [2–4] were used to investigate extracoordination. It was established, on the basis of experimental and calculated data, how the strength of a bond between zinc and an additional molecular extra ligand L depends on the porphyrin nature and basicity of L.

EXPERIMENTAL

The reaction $ZnP + nL = ZnL_nP$ under study was run in *o*-xylene, which does not form stable solvate complexes with metalloporphyrins and is regarded as a neutral solvent.

The changes in the electronic absorption spectra (EAS) that depend on the extra ligand concentration make it possible to apply the spectral method for studying extracoordination. The details of the experiment and the procedures of calculating the stability constants (K_{st}) for the extra complexes are described in [1, 5–8].

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The quantum-chemical calculations were performed by jointly using the Fletcher–Reeves and the Polak–Raivier methods [9]. A specified gradient 0.04 kJ/mol was used for the count termination.

The investigated porphyrins (5,15-(*p*-butyloxyphenyl)-2,8,12,18-tetramethyl-3,7,13,17-tetraethylporphyrin (H_2P^1), 5,15-(*p*-butyloxyphenyl)-2,8,12,18-tetramethyl-3,7,13,17-tetrabutylporphyrin (H_2P^2) and tetraphenylporphine (H_2P^4)) were synthesized following the procedures in [10–12]. The overlapped porphyrin H_2P^3 was obtained according to [13].

Zincporphyrins ZnP^1, ZnP^2, ZnP^3, and ZnP^4 were synthesized by boiling respective porphyrins with a tenfold excess of zinc acetate in benzene for 40–50 min. The complexes were purified by chromatography on Al_2O_3 of activity degree II (with chloroform used as eluent) and by further recrystallization from chloroform.

Electronic absorption spectra of the complex solutions were recorded on a Specord M400 spectrophotometer. Data on the EAS of synthesized zincporphyrins in benzene (λ, nm (logε)) are given below (except for ZnP^3 spectrum taken in xylene):

Band no.	I	II	III
ZnP^1	570.0(3.98)	534.0(4.31)	407.0(5.18)
ZnP^2	575.0(3.00)	541.0(4.25)	412.0(5.08)
ZnP^3	587.0(4.22)	549.0(4.43)	410.0(5.34)
ZnP^4	590.0(3.49)	550.0(4.23)	422.5(5.57)

The extra ligands used were *N*-methylimidazole (MeIm), imidazole (Im), pyridine (Py), 3,5-dimethylpyrazole (DMP), and dimethylformamide (DMF).

RESULTS AND DISCUSSION

Binding of ligands L with zincporphyrins is accompanied in all cases by a bathochromic shift and by a change in the intensities of the main absorption bands of a chromophore (Fig. 1). We believe that this occurs due to an increase in the electron density on the zinc cation and, respectively, on the porphyrin nitrogen atoms. Growth in the fractional negative charge on the N atoms leads to destabilization of the a_{2u} MO with an unchanged position of the a_{1u} level. As a result, the configurational interaction of the excited state of the E_u type decreases, which is a substantial reason for increasing the intensity of the first band in the EAS of zincporphyrins. The bathochromic shift probably occurs due to an increase in the a_{2u} energy.

It was found that the ZnP^1, ZnP^2, and ZnP^3 complexes can each add one molecule of MeIm, Im, DMP, Py, or DMF. In the case of ZnP^4, coordination of two DMF molecules occurs.

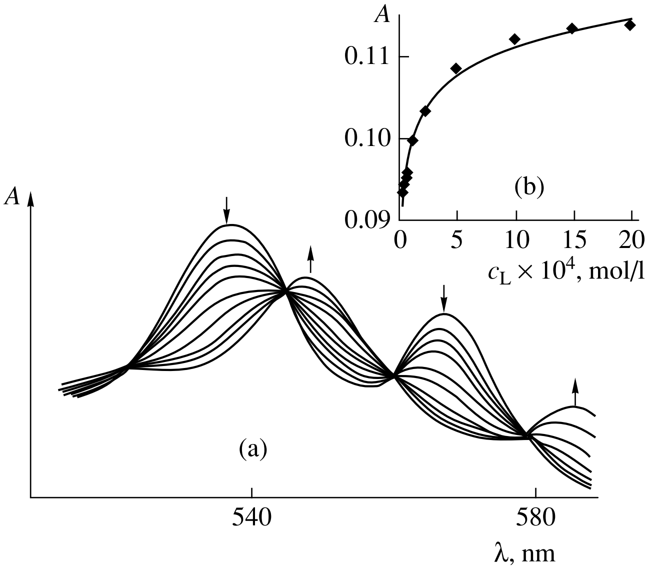

Fig. 1. (a) Changes in EAS of solutions of ZnP^1 in *o*-xylene in the presence of L with a change in c_L from 0 to 1.9×10^{-3} mol/l, $c^0_{ZnP^1} = 0.9 \times 10^{-5}$ mol/l and (b) the corresponding curve of spectrophotometric titration at λ = 550 nm.

Tables 1 and 2 present K_{st} for (L)ZnP complexes that were obtained on the basis of EAS data, as well as some geometric and energy characteristics of these complexes as calculated by quantum-chemical methods. Data in Table 1 make it possible to estimate the strength of bonding of the additional ligand with zincporphyrin and to obtain stability series for the extra complexes. The stability of the extra complexes with MeIm and Im drop in the series of ZnP as follows: $ZnP^4 > ZnP^2 > ZnP^1 > ZnP^3$. This can be explained by the influence of the porphyrin ligand nature on the extracoordination process. In the case of ZnP^4, the phenyl rings draw the electron density from the zinc atom and thus increase its fractional positive charge. Accordingly, the Zn–L bond becomes stronger. A decrease in the number of phenyl substituents and introduction of alkyl groups in the β-position of a porphyrin macrocycle in ZnP^1 and ZnP^2 result in an increase in the electron density on the nitrogen atoms in the coordination center and in a decrease in the positive charge on the zinc atom, which in turn weakens the strength of the Zn–L bond. Thus it becomes clear that the extra complexes $(L)ZnP^1$ and $(L)ZnP^2$ are less stable than $(L)ZnP^4$. The low stability constant of the $(L)ZnP^3$ as compared to those of the remaining members of the series is explained by the substantial distortion of the porphyrin macrocycle as a result of the steric stresses caused by a “cap” rather than by the effect of substituents in the porphyrin macrocycle. In the case of the extra complexes of zincporphyrins with DMF, the series is as follows: $ZnP^4 > ZnP^2 > ZnP^3 > ZnP^1$. The stability constants for ZnP complexes with Py are nearly equal (except for $(L)ZnP^3$) (Table 1); i.e., the nature of the porphyrin ligand in this case produces almost no effect on the extracoordination pro-

Table 1. Thermodynamic characteristics of extracoordination of nitrogen-containing ligands by zincporphyrins in *o*-xylene

Complex	Extra ligand	$K_{st}^{298} \times 10^{-3}$, mol/l	E_b, Zn–L, kcal/mol^{-1}	Δλ, nm
ZnP^1	MeIm	0.477 ± 0.001	–16.01	5.0
	Im	4.4 ± 0.1	–15.94	12.0
	Py	1.14 ± 0.06	–4.524	9.0
	DMP	1.64 ± 0.03	–12.85	10.0
	DMF	0.019 ± 0.001	0.049	2.5
ZnP^2	MeIm	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^3	MeIm	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^4	MeIm	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

cess. The reason for such a behavior of zincporphyrin remains unclear.

The stability of extra complexes of zincporphyrins is also influenced by the nature of the extra ligand. A growth in its basicity (Table 3) makes the Zn–L bond stronger (Table 2) and the K_{st} of the complexes increase (Table 1). Thus, for sterically nonstressed complexes ZnP^4, extra complexes with MeIm and Im are the most stable. Linear dependence can be observed between the values of $\log K_{st}$ for (L)ZnP^4 and $\mathrm{p}K_{BH^+}$ for extra ligand L:

$$\log K_{st} = 0.2564\,\mathrm{p}K_{BH^+} + 2.4589$$

with correlation factor $r = 0.963$ (Fig. 2). Despite the high basic properties of MeIm, complexes ZnP^1, ZnP^2, and ZnP^3 react with it with difficulty. This can most probably be explained by steric hindrances and by distortion of the porphyrin macrocycle during extracoordination. The values of $\log K_{st}$ for (L)ZnP^1 and (L)ZnP^2 and of $\mathrm{p}K_{BH^+}$ change symbatically and are related by the equations

$$\log K_{st} = -0.038\,\mathrm{p}K^2_{BH^+} + 0.558\,\mathrm{p}K_{BH^+} + 1.741,$$
$$r = 0.984;$$

$$\log K_{st} = -0.069\,\mathrm{p}K^2_{BH^+} + 0.936\,\mathrm{p}K_{BH^+} + 0.536,$$
$$r = 0.979,$$

Table 2. Bond lengths (Å) and characteristics of coordination core in (L)ZnP extra complexes

Complex	Zn–N(1)	Zn–N(2)	Zn–N(3)	Zn–N(4)	Zn–N$_L$	Ct*–Zn	N(1)–Ct	N(3)–Ct	N(1)–N(3)
ZnP^1	2.025	2.055	2.074	2.064		0.049	2.024	2.073	4.097
ZnP^1 + MeIm	2.126	2.109	2.086	2.115	2.100	0.387	2.091	2.049	4.141
ZnP^1 + Im	2.125	2.108	2.086	2.115	2.099	0.459	2.075	2.064	4.139
ZnP^1 + Py	2.121	2.107	2.085	2.112	2.124	0.385	2.085	2.051	4.137
ZnP^1 + DMP	2.088	2.087	2.103	2.101	2.100	0.408	2.048	2.063	4.111
ZnP^1 + DMF	2.069	2.058	2.021	2.049	6.871	0.097	2.066	2.018	4.085
ZnP^3	2.019	2.383	2.019	2.376		0	0	0	4.038
ZnP^3 + MeIm	2.035	2.538	2.037	2.474	1.980	0.855	1.847	1.849	3.696
ZnP^3 + Im	2.032	2.522	2.033	2.484	1.978	0.834	1.853	1.854	3.707
ZnP^3 + Py	2.033	2.519	2.034	2.486	1.990	0.839	1.851	1.853	3.705
ZnP^3 + DMF	2.030	2.497	2.029	2.498	2.016	0.825	1.855	1.855	3.709
ZnP^4	2.055	2.043	2.011	2.043		0.002	2.055	2.011	4.066
ZnP^4 + MeIm	2.070	2.101	2.105	2.096	2.095	0.408	2.029	2.065	4.094
ZnP^4 + Im	2.101	2.105	2.096	2.069	2.096	0.404	2.062	2.056	4.118
ZnP^4 + Py	2.069	2.095	2.101	2.100	2.119	0.400	2.031	2.062	4.093
ZnP^4 + DMP	2.085	2.104	2.095	2.053	2.203	0.429	2.040	2.051	4.091
ZnP^4 + DMF	2.055	2.043	2.011	2.042	7.324	0.006	2.055	2.011	4.066
ZnP^4 + 2DMF	2.011	2.045	2.055	2.040	7.919 7.621	0	2.011	2.055	4.066

* Ct is the center of the coordination cavity of a porphyrin macrocycle.

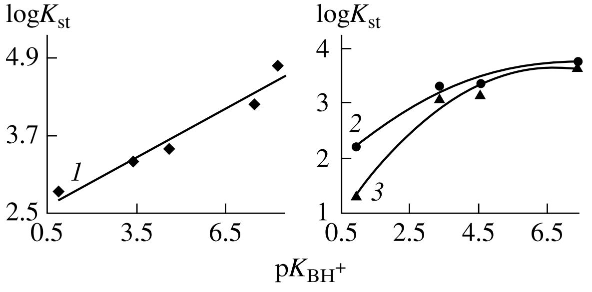

Fig. 2. Plot of $\log K_{st}$ vs basicity of extra ligand L for extracomplex (*1*) $(L)ZnP^4$, (*2*) $(L)ZnP^2$, and (*3*) $(L)ZnP^1$.

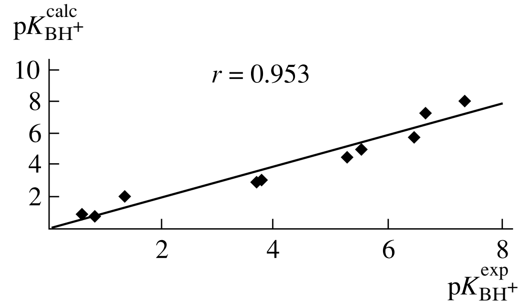

Fig. 4. Correlation between calculated and experimental pK_{BH^+} for nitrogen-containing ligands.

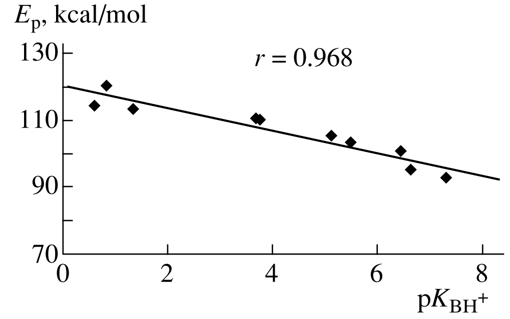

Fig. 3. Energy of protonation of nitrogen-containing molecules vs their basicity.

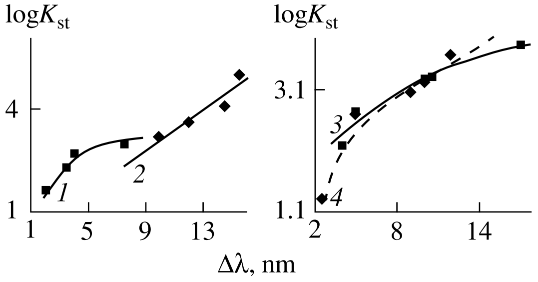

Fig. 5. Dependence of $\log K_{st}$ for (*1*) ZnP^3, (*2*) ZnP^4, (*3*) ZnP^1, and (*4*) ZnP^2 on a shift of band II in the EAS of these extra complexes.

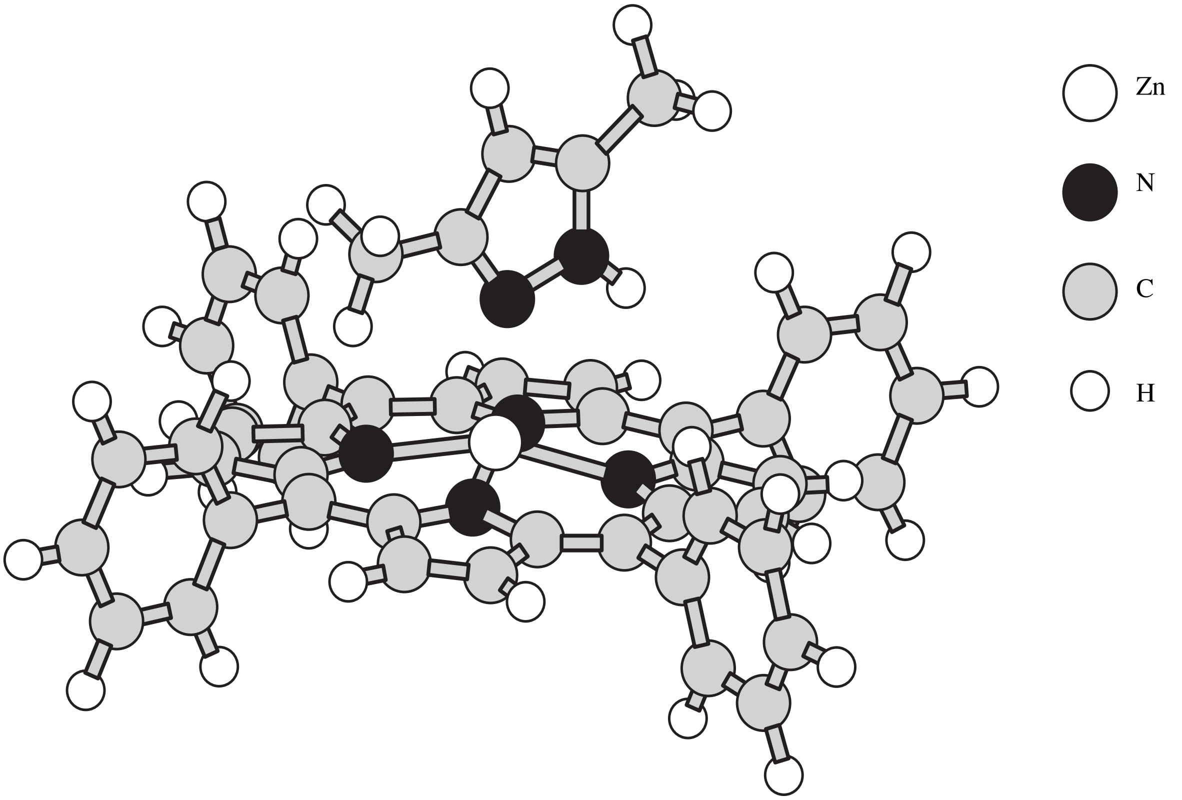

Fig. 6. Structure of ZnP^4 extra complex with DMF calculated by the quantum-chemical method.

Table 3. Protonation energies and basicity of nitrogen-containing molecules

Extra ligand	pK_{BH^+}		E_p^{calcd}, kcal/mol
	experiment*	calculation	
MeIm	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

* The values of pK_{BH^+} were obtained by the potentiometric method in water at 298 K [13].

respectively, (Fig. 2).

On the basis of quantum-chemical calculations of the electronic structure of the nitrogen-containing ligands, a linear correlation was established between their basicity and energy of protonation (E_p) (Fig. 3). Comparison of the pK_{BH^+} values produced from this correlation with the respective data in the literature [14] shows that the discrepancy does not exceed 10% in most cases (Table 3, Fig. 4). Therefore, we believe that the calculated value of the protonation energy can be used to estimate the basicity of the nitrogen-containing compounds.

Comparison of the stability constants for the extra complexes with an absorption band shift in the EAS of zincporphyrins during extracoordination allowed us to detect the following correlation between these values: an increase in K_{st} is accompanied by an increase in the shift of absorption band II ($\Delta\lambda$) (Table 1).

Linear dependence and regression equation $\log K_{st} = 0.306\Delta\lambda + 0.039$ ($r = 0.971$) are characteristic only for (L)ZnP^4 (Fig. 5). The stability of extra complexes (L)ZnP^1, (L)ZnP^2, and (L)ZnP^3 changes symbatically with $\Delta\lambda$, which, in turn, confirms our suggestion that steric stresses arise in these compounds in the course of extracoordination. The obtained correlations (Fig. 5) are described by the following equations:

$$(\mathrm{L})\mathrm{ZnP}^1\colon \log K_{st} = -0.006\Delta\lambda^2 + 0.2384\Delta\lambda + 1.497,$$

$$r = 0.952;$$

$$(\mathrm{L})\mathrm{ZnP}^2\colon \log K_{st} = -0.020\Delta\lambda^2 + 0.511\Delta\lambda + 0.299,$$

$$r = 0.932;$$

$$(\mathrm{L})\mathrm{ZnP}^3\colon \log K_{st} = -0.069\Delta\lambda^2 + 0.917\Delta\lambda + 0.055,$$

$$r = 0.979.$$

The value of a bathochromic shift can serve as a qualitative characteristic of the Zn–L bond strength. The results of the quantum-chemical calculations make it possible to explain the reasons for the change in the stability of the extra complexes of sterically stressed zincporphyrins depending on the nature of the porphyrin and extra ligand. Calculations show that the energy of the Zn–L bond formation (E_b) for the extra complex changes symbatically with its stability (Table 1). An increase in E_b when changing from (L)ZnP^1 to (L)ZnP^4 points to an increase in the complex stabilities in this series.

Zincporphyrins have a square–pyramidal structure of the coordination core with a metal atom slightly extending from the N_4 plane toward the extra ligand (Fig. 6). Data presented in Table 2 indicate that the metal extension from the macrocycle plane correlates with the Zn–L bond length. It was found that a decrease in the basicity of the nitrogen-containing bases in the series Im > DMP > Py > DMF with increasing strength of the σ bond Zn–N(1–4) is accompanied by a decrease in the Zn–Ct distance (Table 2). In this case, interaction of the zinc atom with the nitrogen atom of ligand L weakens and, as a consequence, the stability of the extra complex drops (Table 1). Thus, a *cis*-position of the ligands incorporated in the composition of the extra complexes of the zincporphyrins produces a significant effect. One should note that an increase in the Zn–L bond strength leads to a growth in the steric stresses in metalloporphyrins (Table 3). Alkyl substituents in ZnP^1 and ZnP^2 and a cap in ZnP^3 also induce a macrocycle deformation, which becomes even greater when going to the extra complexes and, thus, results in their destabilization.

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