Coordination ability of zinc(II) porphyrins with respect to electron-donating ligands. Influence of the structure and solvation effects

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Thermodynamics of the formation of molecular complexes of synthetic and natural zinc(II) porphyrins with *n*-propylamine and glycine methyl ester in benzene was investigated. Study of the π—π complexes of zinc(II) porphyrins with benzene demonstrated that thermodynamic stability of the axial complexes depends on both the structure of the porphyrin macrocycle and the ability of the corresponding metalloporphyrins to form energetically stable π—π complexes with aromatic molecules.

Key words: metalloporphyrins, molecular complexes, thermodynamics, titration calorimetry.

The coordination properties of metalloporphyrins attract continuing interest for several reasons. First, metalloporphyrins are of biological importance. They are known as prosthetic groups of certain proteins, enzymes, and vitamin B_{12}. Iron porphyrins are components of hemoglobins, myoglobins, cytochromes, catalases, and peroxidases.[1] Metalloporphyrins perform virtually all useful biological functions through specific interactions with various ligands. For example, the π system and the peripheral substituents of the iron protoporphyrin molecule in hemoglobin are involved in various specific interactions with aromatic and aliphatic amino-acid residues of the protein and other organic molecules (pharmaceuticals, toxins, *etc.*). The electron density redistribution caused by these interactions affects the coordination properties of the central metal ion.[2] Evidently, elucidation of the significance and degree of influence of a particular interaction in natural macrosystems presents a difficult problem. Because of this, studies aimed at revealing factors affecting the activities of metalloporphyrins are carried out using simplified model systems. Such studies are scarce[3] because of the problems associated with investigation of intermolecular interactions of poorly soluble compounds (solubility of metalloporphyrins in organic solvents is 10^{-7}—10^{-4} mol L^{-1}) and insufficient sensitivity of the majority of physicochemical methods.[4]

Second, the successful use of metalloporphyrins in medical practice (in the design of efficient blood substitutes, pharmaceuticals, and transport agents) calls for information on the influence of the nature of metalloporphyrin on its complexation properties with respect to electron-donating ligands. This problem is of particular importance taking into account that the activity of some pharmaceuticals is enhanced by a factor of 7—10 upon the addition of a zinc protoporphyrin complex.[5] However, the lack of data characterizing intermolecular interactions depending on the structure of the porphyrin macrocycle and solvation effects does not allow one to perform a targeted search for metalloporphyrins as potential pharmaceuticals.

The aim of the present study was to elucidate the influence of the structure of the porphyrin macrocycle, the nature of peripheral functional substituents, and specific π—π interactions of metalloporphyrins with solvent molecules (benzene) on the thermodynamic stabilities of molecular complexes of macrocycles with electron-donating ligands. We studied synthetic zinc(II) tetraphenylporphyrin (ZnTPhP) (**1**) and natural zinc(II) porphyrins of the proto group, *viz.*, zinc(II) hematoporphyrin IX t.m.e. (ZnHP) (**2**), zinc(II) deuteroporphyrin IX d.m.e. (ZnDP) (**3**), and zinc(II) protoporphyrin IX d.m.e. (ZnPP) (**4**).*

Zinc porphyrin complexes were chosen for the study because zinc is a biogenic d metal and has no counterions (unlike Fe^{3+}), which makes the interpretation of the results much easier.

Blood-group porphyrins were chosen as subjects of investigation because of differing unsymmetrical peripheral substitutions, which enabled us to study the influ-

* Zinc(II) hematoporphyrin IX tetramethyl ester-ether. Zinc(II) deuteroporphyrin IX dimethyl ester. Zinc(II) protoporphyrin IX dimethyl ester.

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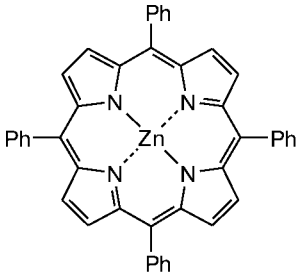
ence of the structure of the porphyrin macrocycle and the nature of peripheral functional substituents.

n-Propylamine (**5**) and glycine methyl ester (**6**) served as electron-donating ligands.



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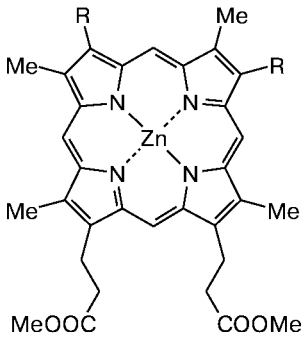

2—4

R = CH(OMe)Me (**2**), H (**3**), $CH=CH_2$ (**4**)

Experimental

Metalloporphyrins were synthesized according to conventional procedures,[4] twice purified by chromatography on Al_2O_3 (Brockmann activity II, Reanal, Hungary), recrystallized from *n*-hexane, and dried to a constant weight *in vacuo* at 343—353 K. The purities of metalloporphyrins were determined by UV-Vis spectroscopy from the extinction of the Soret band. Benzene (Aldrich) was additionally dried using 4 Å molecular sieves followed by distillation.[6] According to the results of gas chromatography, the purity of C_6H_6 was 99.95%. The content of water in benzene (Karl Fischer titration) was no higher than 0.01%. Glycine methyl ester (**6**) was synthesized according to a known procedure.[7]

Calorimetric studies were carried out on a high-precision differential automatic titration calorimeter described earlier.[8] A solution of *n*-propylamine (**5**) or glycine methyl ester (**6**) in benzene (the concentration of the ligand was 0.2—0.3 mol kg^{-1}) was placed into a dispenser, and a solution of zinc(II) porphyrin at a concentration of 10^{-7}—10^{-3} mol kg^{-1} was placed into a cell. The molal concentrations were converted into the molar concentrations using the densities of solutions, which were measured by picnometry at 298.15 K.

Compilation and processing of experimental data were completely computerized.[8] The thermodynamic characteristics of the processes were calculated using the CALORY program,[9] which is based on known procedures.[9,10]

The accuracy of the determination of thermodynamic characteristics was evaluated according to recommendations.[11,12]

The calculated thermodynamic characteristics of the processes under investigation correspond to standard conditions, because all data were obtained for dilute solutions in organic solvents at 298.15 K and these values are independent of the concentrations of metalloporphyrin and the ligand in the concentration ranges used.

Thermogravimetric studies were carried out on a 1000 D derivatograph (MOM, Hungary). Crystal solvates of zinc(II) porphyrins with benzene and amines **5** and **6** were prepared according to a conventional procedure,[13,14] as in differential scanning calorimetry and X-ray diffraction analysis and then placed into platinum crucibles. The weights of the samples were 50—220 mg. To achieve the desired accuracy of the results, we used the following conditions for recording preliminary data: the temperature was recorded in the range of 0—500 °C per 250 mm of the scale of a recording instrument; the sensitivity of a galvanometer for recording the DTG and DTA signals was 1 mV and 250 μV, respectively; the sensitivity of a thermobalance was 200 mg per 250 mm of the scale; the rate of sample heating was 0.6 °C min^{-1}. The accuracy of measurements of the sample temperature in the temperature range used was checked against the characteristic temperatures of reference samples.[15] In the present study, the functional dependence of the evaporation rate on the saturated vapor pressure of the solvent, which is sensitive to the difference in the state of the molecules evaporated, was used as the theoretical base of thermogravimetric investigation.[16,17]

The UV-Vis spectra were recorded on a Specord M40 spectrophotometer.

Results and Discussion

In the present study, we used a complex approach which has been successfully applied earlier in investigations of coordination ability of synthetic metalloporphyrins with respect to electron-donating ligands.[10,18—20] This approach is based on the combined use of titration calorimetry and thermogravimetric analysis of crystal solvates. Titration calorimetry was used for studying three-component systems containing metalloporphyrin, an organic ligand, and a solvent. The thermodynamic characteristics (changes in enthalpy, entropy, and the Gibbs energy) of the reactions of metalloporphyrins with organic ligands in solution, the compositions of the complexes prepared, and their thermodynamic stability (K_c) were determined (Table 1). Earlier, two-component systems, zinc(II) porphyrins—benzene, have been studied by thermogravimetric analysis. The data on the characteristic features of solvation interactions of zinc(II) porphyrins with benzene, the thermal and energy stabilities of the corresponding π—π complexes, and their compositions are necessary for estimating the influence of the structural and solvation factors on the thermodynamic parameters of the processes under study.

All the metalloporphyrins under study form stable molecular complexes with ligands **5** and **6** ($ZnP \cdot nL$). Systems containing ZnPP (**4**) or ZnHP (**2**) give complexes with the composition 1 : 1 and 1 : 2, other metalloporphyrins form 1 : 1 complexes. Solutions of metalloporphyrins in benzene were monitored by UV-Vis spectroscopy before and after calorimetric study, which provided evidence that the interaction of electron-donating ligands involves the central metal atom of metalloporphyrins.[4,21] The largest changes are observed for the first absorption band and the Soret band, which are most

Table 1. Thermodynamic characteristics (ΔH°/kJ mol^{-1}, ΔS°/J mol^{-1} K^{-1}) of interactions of zinc(II) porphyrins with electron-donating ligands

Ligand	Metalloporphyrins	Composition	K_c	$-\Delta H^\circ$	ΔS°	$\beta = K_c^1 \cdot K_c^2$
n-Propylamine	ZnDP(d.m.e.)	1 : 1	93562±10900	8.61±1.00	66±4	
	ZnHP(t.m.e.)	1 : 1	3310±100	49.63±0.02	−99±5	12068260±13000
		1 : 2	3646±130	9.94±0.02	35±2	
	ZnPP(d.m.e.)	1 : 1	5822±110	33.21±0.02	−39±6	45021526±10120
		1 : 2	7733±92	4.57±0.02	59±7	
	ZnTPhP	1 : 1	23602±546	18.03±0.42	23±1	
Glycine methyl ester	ZnDP(d.m.e.)	1 : 1	9970±1270	16.23±2.07	22±4	
	ZnHP(t.m.e.)	1 : 1	51332±360	26.89±0.01	47±4	23356060±50400
		1 : 2	455±140	20.88±0.02	69±3	
	ZnPP(d.m.e.)	1 : 1	9521±112	12.36±0.01	35±6	26420775±6720
		1 : 2	2775±60	16.30±0.01	11±5	
	ZnTPhP	1 : 1	738±54	9.12±0.66	24±2	

sensitive to the state of the aromatic π system of the macrocycle and the central metal ion. For example, the Soret bands of ZnTPhP (**1**) and ZnDP (**3**), which form 1 : 1 complexes with *n*-propylamine, are shifted bathochromically by 15—17 nm. By contrast, the UV-Vis spectra of zinc(II) porphyrins ZnHP (**2**) and ZnPP (**4**), which coordinate two *n*-propylamine molecules each, change to a lesser extent: the Soret band is shifted by 10—14 nm. The results of our study are consistent with the concepts of the theory of UV-Vis spectra of metalloporphyrins. The coordination of the first ligand causes drawing of the central metal ion out of the plane of the macrocycle. Presumably,[4,22] the bathochromic shift is associated with a decrease in the σ electronic effect of coordination and the charge effect, *i.e.*, with two electronic effects of coordination responsible for a short-wavelength shift of the first absorption band in the UV-Vis spectra. After the addition of the second ligand, the metal atom is drawn back in the center of the porphyrin cavity, the σ bond is strengthened, and the Coulomb effect on the nitrogen atoms of porphyrin increases, *i.e.*, the charge effect increases.[21,22] The fact that the spectral changes (Δλ) do not correlate with the thermodynamic characteristics (see Table 1) indicates that the shifts of absorption bands not necessarily provide correct estimates for the coordination ability of metalloporphyrins with respect to electron-donating ligands.[4]

The thermodynamic stability of molecular complexes of zinc(II) porphyrins with ligands **5** and **6** increases in the following series of metalloporphyrins:

ZnTPhP (**1**) < ZnDP (**3**) < ZnHP (**2**) < ZnPP (**4**). (1)

The observed differences in thermodynamic stability of the complexes under consideration can be primarily attributed to the fact that the electron density distribution in the porphyrin macrocycle and on the nitrogen atoms of the reaction center depends on the nature of peripheral substituents. The ability of the central metal ion in metalloporphyrin to coordinate electron-donating ligands is determined primarily by the residual positive charge on the metal ion, which, in turn, depends on the electron-donating ability of the nitrogen atoms of the reaction center, *i.e.*, on the basicity of the porphyrin macrocycle. For example, the Ph substituents in tetraphenylporphyrin exhibit the $+I$ effect,[10] thus increasing the electron density on the nitrogen atoms of the reaction center and decreasing the residual positive charge on the zinc ion. The higher coordination ability of natural zinc(II) porphyrins compared to ZnTPhP (**1**) (see Table 1) is determined by the fact that natural metalloporphyrins bear peripheral oxygen-containing 6,7-substituents exhibiting the $-F$ electronic effect, which results in a decrease in the electron density on the nitrogen atoms of the reaction center and an increase in the coordination ability of the zinc ion. Porphyrins of the proto groups differ in the nature of 2,4-substituents. Earlier, it has been demonstrated[23,24] that the electronic effect of the complex substituent —CH(OMe)Me in hematoporphyrin is determined by the sum of the electronic effects of the MeO and MeCH= groups; $-I$(MeO) > $+I$(MeCH=). Although possessing both the $+C$ and $-I$ effects, the MeO group in this substituent can exhibit only the $-I$ effect due to the presence of the HC≡ group, which acts as an insulator against conjugation, thus excluding the possibility of conjugation between the p_z electrons of the oxygen atom and the π system of the porphyrin macrocycle. The introduction of the hydrogen atoms possessing the zero electronic effect at positions 2 or 4 of the pyrrole fragments leads to an increase in the electron density in the macrocycle of ZnDP (**3**) compared to that in ZnHP (**2**). It is known that the vinyl group —CH=CH_2 can serve as a conductor of the electronic $+I$ and $\pm C$ effects.[23,24] Therefore, analysis of the electronic effects of the peripheral functional substituents leads us to the conclusion that the coordination

ability of zinc(II) protoporphyrins should increase in the following series:

$$\text{ZnTPhP (}\mathbf{1}\text{)} < \text{ZnPP (}\mathbf{4}\text{)} < \text{ZnDP (}\mathbf{3}\text{)} < \text{ZnHP (}\mathbf{2}\text{).} \quad (2)$$

The series (1) is inconsistent with the series (2), which may be attributed only to the influence of the solvating solvent, *viz.*, benzene. It is well known that metalloporphyrins can form π—π complexes with aromatic solvents. In these complexes specifically solvated by solvent molecules, the latter are located predominantly above and below the *trans*-arranged pyrrole fragments of the porphyrin macrocycle.[13,27] However, in some cases, these solvent molecules can be shifted and sterically block the reaction center of metalloporphyrin.[28]

Earlier, it has been found[23,24,29] that of all known metalloporphyrins, zinc(II) porphyrins ZnTPhP, ZnDP, and ZnHP form energetically and thermally stable complexes with benzene, $ZnP \cdot mS$ ($m = 1$ or 2, S are benzene molecules which specifically solvate ZnP), whereas ZnPP is not specifically solvated by benzene. Consequently, the reactions of ZnPP with *n*-propylamine and glycine methyl ester in benzene proceed according to Eq. (3)

$$ZnP_{solv} + 2\,L_{solv} \overset{K_c^1}{\rightleftharpoons} ZnP \cdot L_{solv} + L_{solv} \rightleftharpoons \overset{K_c^2}{\rightleftharpoons} ZnP \cdot 2L_{solv} + Solv, \quad (3)$$

where K_c is the thermodynamic stability constant of the axial complex formed; L is the axial ligand (*n*-propylamine (**5**) or glycine methyl ester (**6**)); the index "solv" signifies that the complexation proceeds in solution (in benzene); Solv is the solvent (benzene).

In the case of systems containing ZnTPhP, ZnDP, or ZnHP, the process proceeds according to Eq. (4) or (5).

$$ZnP \cdot mS)_{solv} + nL_{solv} \overset{K_c}{\rightleftharpoons} \rightleftharpoons (ZnP \cdot nL)_{solv} + mS_{solv}, \quad (4)$$

$$(ZnP \cdot mS)_{solv} + nL_{solv} \overset{K_c}{\rightleftharpoons} \rightleftharpoons (ZnP \cdot nL \cdot kS)_{solv} + (m - k)S_{solv}, \quad (5)$$

where $ZnP \cdot mS$ is the specific π—π complex of zinc(II) porphyrin with benzene with composition $1 : m$; L = **5** or **6**; m is the number of benzene molecules, which go into solution after decomposition of the $ZnP \cdot mS$ complex; $ZnP \cdot nL \cdot kS$ is the molecular complex of zinc(II) porphyrin with the ligand and benzene of composition $1 : n : k$; $(m - k)$ is the number of benzene molecules, which go into solution after decomposition of the $ZnP \cdot mS$ complex.

To refine the compositions of the molecular complexes based on ZnTPhP, ZnDP, and ZnHP, which are generated after titration, we studied their crystalline

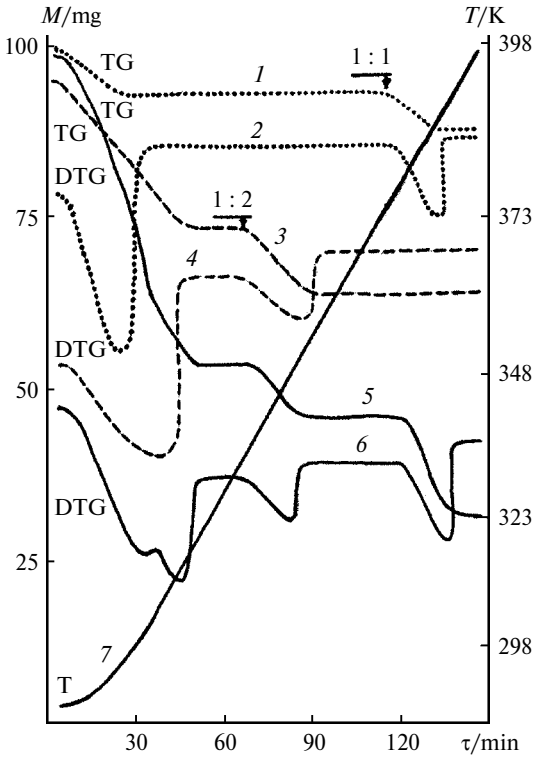

Fig. 1. Derivatograms of crystal solvates of ZnTPhP with organic ligands measured by thermogravimetric analysis (*1*, *3*, *5*) and differential thermogravimetric analysis (*2*, *4*, *6*): *1* and *2*, $ZnTPhP \cdot$Gly-OMe; *3* and *4*, $ZnTPhP \cdot 2C_6H_6$; *5* and *6*, $ZnTPhP \cdot 2C_6H_6 \cdot$Gly-OMe; and the temperature change (*7*).

samples by thermogravimetry. Figure 1 illustrates derivatograms reflecting thermal decomposition of the molecular complexes of ZnTPhP with organic ligands (benzene and glycine methyl ester). Analysis of the derivatograms leads us to conclude that a mixed molecular complex containing zinc(II) porphyrin, the ligand, and benzene is decomposed. Based on the results of our study, it can be suggested that competitive interactions take place in systems containing ZnTPhP, ZnDP, or ZnHP, and coordination of the electron-donating ligands to the above-mentioned ZnP proceeds according to Eq. (5).

The nature of the coordinated ligand has a pronounced effect on the thermodynamic characteristics of the processes under consideration. For systems containing ZnDP or ZnTPhP, the use of glycine methyl ester instead of *n*-propylamine results in a decrease in thermodynamic stability of the resulting complexes by more than an order of magnitude. Besides, coordination of glycine methyl ester proceeds more exothermically than that of *n*-propylamine. Evidently, the presence of oxygen atoms in glycine methyl ester is responsible for a decrease in the electron-donating ability of the nitrogen atom due to the overall $-F$ effect. Hence, the complexes of zinc(II) porphyrins with glycine methyl ester are thermodynamically less stable than the corresponding complexes with

n-propylamine. For ZnPP, the replacement of *n*-propylamine with glycine methyl ester also decreases thermodynamic stability of the complex, the enthalpy component of the interaction being changed only slightly. Another thermodynamic situation is observed for a system containing ZnHP, which forms a thermodynamically more stable complex with glycine methyl ester compared to that with *n*-propylamine. The zinc(II) hematoporphyrin molecule contains two ester groups along with two ether groups, whereas other porphyrins (of the proto group) bear only two ester groups. Based on the structural features of the porphyrin molecule ZnHP, the unexpectedly high thermodynamic stability of the molecular complex of ZnHP with glycine methyl ester can be attributed to coordination of the nitrogen atom of molecule **6** to the Zn^{2+} ion and the formation of attractive hydrogen bonds between the 2,4 substituents of the porphyrin macrocycle and the O atom of the ester group of the coordinated glycine ester.

To summarize, our study demonstrated that stability of the molecular complexes of metalloporphyrins with electron-donating ligands depends on the nature of the compounds involved in the interaction, the presence of attractive interactions, and solvation effects. In some cases, the influence of specific solvation interactions between metalloporphyrins and solvent molecules can have a more pronounced effect on the formation of molecular complexes than structural modifications of the macrocycle.

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