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Coordination of *N*-Substituted Porphyrins with Simple and Chelate Zinc Salts in DMSO

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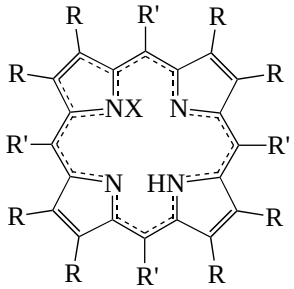
Abstract—The effect of peripheral substitution in the porphyrin macrocycle (H_2OEtP, H_2TPP) of the nature of the *N*-substituent (X = Me, Ph) and of the anion in the salt solvate (A = Ac^-, NO_3^-, $Acac^-$) on the complexation of the *N*-substituted porphyrins with zinc salts in DMSO is studied. The positions of the bands in the electronic absorption spectrum of the (A)M(N-X)P metal complex were found to depend only slightly on the nature of the A anion in the composition of the coordination sphere of the complex. An inhibition of coordination of the *N*-substituted H_2TPP derivatives by zinc nitrate was discovered that is not typical of porphyrins proper. The type of hybridization of the substituted nitrogen atom in the porphyrin molecule is discussed. A mixed type of hybridization is suggested: the sp^2- and p^3-forms in the ligands and an almost complete transition to the p^3-form in the *N*-substituted metal complexes.

As distinct from the porphyrins proper (**I**, **II**), those in which the proton is replaced by the hydrocarbon radical in the coordination site N_4H_2 (H(N-X)P, **III**–**V**) [1] exhibit biological activity in the processes of reversible inhibition of the ferrochelatase enzyme [2], destruction of the blood pigments [3], reversible migration of the *N* substituent from nitrogen to metal, and the formation of σ-metal complexes from porphyrins with the carbon–metal bond [4]. Therefore, the range of the investigated porphyrins wherein the coordination site is modified by the *N*-substituents has been extended over the last two to three decades. Porphyrins with a different type (Alk, Bz, CH_2=CH, Ph, R–Ph, N≡C) [1] and number (from 1 to 4) of the *N*-substitutents [5, 6], as well as bridged *N*,*N'*-compounds [1, 7], have been obtained.



(H_2P)

I: R = Et; R' = X = H
II: R = H; R' = Ph; X = H
III: R = Et; R' = H; X = Me
IV: R = H; R' = Ph; X = Me
V: R = H; R' = X = Ph

In recent years, porphyrins with a doubly modified structure, for example, strongly distorted *N*-dodecasubstituted porphyrins [6], *N*-substituted corrols [8], chlorins [9], and phlorins [10], *N*-substituted porphyrins with an inverted coordination site [11], and *N*-substituted monoazaporphyrins [12], have been synthesized and studied. It has been shown that the rigid macrocycles (tetraazaporphyrins) or the macrocycles with a reduced electron density in the macrocycle (bacteriochlorins) do not undergo transannular *N*-substitution [9, 13]. However, the transannular *N*-substitution in the coordination site of the H_2P molecule is already accompanied by a change in both the electronic and steric properties of the porphyrin molecule [1, 14].

The molecular structure of the *N*-substituted porphyrins has several specific features. First, the hydrocarbon fragment introduced directly into the molecular center produces a strong polarizing effect on the porphyrin macrocycle (the ±*I*- and/or ±*C*-effects). Second, the *N*-substitution is one of the characteristic types of induced distortion of H_2P, since the introduction of the bulky *N*-substituent into a narrow macrocycle cavity results in a substantial violation of its planar structure [6, 14, 15] and causes the electron density to be redistributed a second time. Third, the molecular distortion can lead to a change in the nitrogen atom hybridization (from the sp^2- to p^3-state) [1, 16] and to a local increase in the electron density in the *N*-substituted pyrrole ring. As a result of rehybridization, the substituted nitrogen atom acquires an electron pair, which is not involved in the conjugation, and amine properties.

The authors of [1, 16] suggested partial rehybridization of the substituted nitrogen atom in the coordination site of the molecule H(N-X)P; however, the mechanism of this process remains unclear. The aforementioned nitrogen atom in *N*-substituted porphyrins can exist, most likely, in two electronic states, namely, in the sp^2-and p^3-states. Obviously, the ratio of these structures will depend on the nature of H_2P. The content of the rehybridized p^3-form participating in the chemical coordination is likely to increase as the H_2P molecule and the salt solvate approach each other, and this

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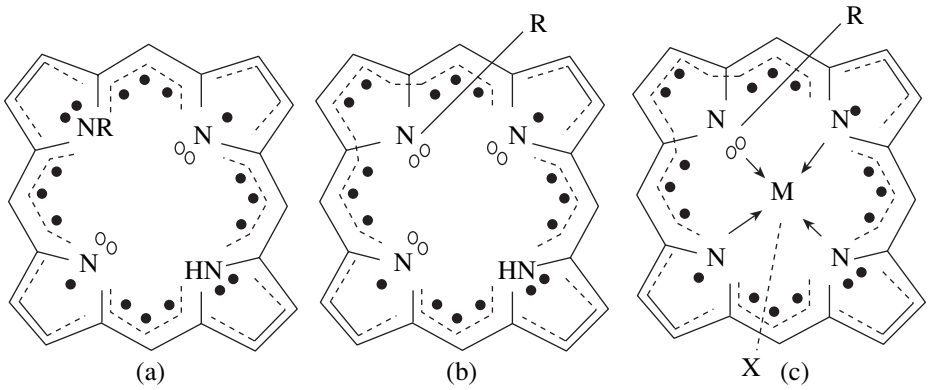
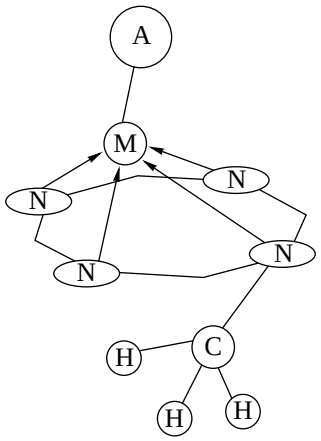


Fig 1. The electronic structures of (a) the sp^2- and (b, c) p^3-forms of (a, b) the *N*-substituted porphyrins H(N-X)P and (c) their complexes (A)M(N-X)P (● are the *p* electrons in the composition of the main conjugation contour, $_{\circ}^{\circ}$ are the *p* electrons outside the main conjugation contour).

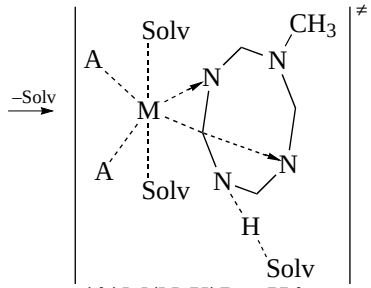
form prevails in the *N*-substituted metal complex where the weak pseudocoordination (X)-N ⟶ M bond can form only due to a free electron pair of the substituted nitrogen atom. In nonsubstituted porphyrins, this electron pair forms the main conjugation contour of the macrocycle (the sp^2-state) (Fig. 1).

The above factors determine all physicochemical properties of the nonplanar *N*-substituted porphyrins in comparison with the mainly planar non-*N*-substituted H_2P (**I** and **II**), including their complexing properties. For instance, in the complexation with the *N*-substituted molecule, only one proton is removed from the H(N-X)P coordination sphere rather than two protons, as with common H_2P. In this case, the $MX_2(Solv)_{n-2}$ salt solvate is attacked in the course of reaction only on one side of the macrocycle plane, while the metal ion charge in the complex is compensated due to the additional ligand A, namely, the salt anion:



The fact that complexation with the *N*-substituted porphyrins occurs at a significantly higher rate than that with the nonsubstituted H_2P [19] is, in our opinion, more evidence that the general approach to the reaction mechanism developed previously in [20–22] is correct. According to this mechanism, the H_2P coordination with the metal salt solvate occurs as a synchronous donor–acceptor process through the formation of a bimolecular transition state,

$$H(N\text{-}X)P + MA_2(Solv)_{n-2}$$



$$\longrightarrow (A)M(N\text{-}X)P + HA, \qquad (1)$$

with participation of the tertiary nitrogen atoms and a molecule of the partially desolvated salt.

The other approach to the mechanism of the process under study [23] does not take into consideration the bulky solvate sphere of the metal ion but suggests that the event of the chemical interaction involves two metal ions that attack the H_2P molecule on both sides of the macrocycle. It is clear that realization of this mechanism is impossible, since the coordination site of the macrocycle is shielded on one side by the N-substituent. It thus follows that, in the case of the second mechanism, the coordination of the *N*-substituted porphyrins should be slowed down rather than accelerated.

Although there is a great number of publications devoted to the chemistry of the *N*-substituted porphyrins, this field lacks systematic physicochemical studies. For example, data on the effect of the nature of the metal on the complexing properties are available only for H(N-Me)TPP, but even they can be compared very infrequently due to the experimental conditions being different [16, 19, 24]. On the other hand, the influence of the composition and properties of the complex solvate (the nature of the solvent and the salt anion), as well as the effect of the porphyrin structure (the nature

of the *N*- and peripheral substitution) in comparable conditions were not almost studied. Therefore, we decided to systematically study the effect of some of the above factors on the kinetics of the complex formation and the spectral properties of the *N*-substituted porphyrins and their metal complexes.

EXPERIMENTAL

We studied the kinetics of complexation of the *N*-methyltetraphenylporphine (H(N-Me)TPP, **IV**), *N*-phenyltetraphenylporphine (H(N-Ph)TPP, **V**), and *N*-methyloctaethylporphine (H(N-Me)OEtP, **III**) with zinc acetate ($ZnAc_2$), nitrate ($Zn(NO_3)_2$), and acetylacetonate ($Zn(Acac)_2$) in DMSO in the temperature interval 298–328 K. In order to compare the reactivity, the reaction of complexation with tetraphenylporphine (H_2TPP, **II**) and octaethylporphine (H_2OEtP, **I**) (358 K) was also studied.

Accurately measured volumes of the solutions (porphyrin and zinc salt in DMSO) with known concentration preliminarily thermostatically controlled for at least 15 min were poured into a cell. The reaction mixture was thoroughly stirred, and its optical density (D_i) was measured at equal intervals of time (τ).

The process of complex formation was monitored spectrophotometrically (using Hitachi U-2000 and Specord M40 spectrophotometers) at the wave length corresponding to the maximum of the first absorption band of the Zn complex (575, 610, and 680 nm for **III**, **IV**, and **V**, respectively).

With significant salt excess ($c_{ZnA_2} = 2 \times 10^{-3}$, $c_{H_2P} = 4 \times 10^{-5}$ mol/l), the reaction was always the first-order reaction in porphyrin (linear dependence ($c^0_{H_2P}/c_{H_2P}$) = $f(\tau)$), which indicates that the general stoichiometric mechanism of the reaction of complex formation suggested for H_2P in [20] (reaction (1)) can also be applied to the *N*-substituted porphyrins. In connection with this, the salt concentration in the reaction course was regarded to be unchanged and the effective constant (k_{eff}) was calculated as

$$k_{eff} = \frac{1}{\tau}\ln\frac{c^0_{H_2P}}{c_{MP}} = \frac{1}{\tau}\ln\frac{D_\infty - D_0}{D_\infty - D_\tau}. \quad (2)$$

The values of the true rate constant of complex formation (k_v) were found from the formula

$$k_v = k_{eff}/c_{ZnA_2}. \quad (3)$$

Porphyrins were prepared according to procedures described in [1, 12, 25, 26]. The reagent grade DMSO was purified from impurities and water by vacuum distillation, but it was kept previously over BaO for a day. The reagent grade zinc acetate and nitrate were additionally purified by recrystallization. Zinc acetylacetonate (reagent grade) was recrystallized from benzene.

Table 1. The rate constants of complexation of the planar porphyrins with $ZnAc_2$ and $Zn(NO_3)_2$ in DMSO at 358 K ($c_{H_2P} = 2 \times 10^{-5}$ mol/l; $c_{ZnA_2} = 2 \times 10^{-3}$ mol/l)

System	k_v, s^{-1} mol^{-1} l*
$H_2OEtP + Zn(NO_3)_2$	0.42
$H_2OEtP + ZnAc_2$	Very slowly
$H_2TPP + Zn(NO_3)_2$	0.64
$H_2TPP + ZnAc_2$	0.11

* The error in determining k_v does not exceed 10%.

RESULTS AND DISCUSSION

Effect of *N*-substitution and of the nature of the *N*-substituent. The reactions of complexation with mainly planar porphyrins H_2OEtP and H_2TPP occur in DMSO very slowly as compared to other organic solvents, such as EtOH, HAc, $CHCl_3$, etc [27]. Therefore, the rates of their coordination by $Zn(Ac)_2$ and $Zn(Acac)_2$ were only measured at 358 K (Table 1). The low rate of the process in DMSO is explained by the high stability of the solvate shell of the salt molecule in this solvent [28].

The introduction of the *N*-substituent into the porphyrin molecule sharply increases the rate of complex formation (almost by five orders in DMSO) [19]. One of the reasons for this phenomenon lies in violation of the macrocyclic effect, namely, of its structural component [14] during the *N*-substitution, which makes the transannular reaction centers (RC) of the porphyrin molecule more accessible for the RC of the reagents.

X-ray diffraction data [1, 15, 16] point to a substantial distortion of the *N*-substituted porphyrins in the crystal, which appears, first of all, as a change in the bond length and angles of the substituted pyrrole ring and its deviation from the mean plane of the nonsubstituted macrocycle (28° for H(N-Me)T(4-Br)PP [15] and 29° for H(N-CN)TPP) [1]. The *N*-susbtituent also extends from the plane of the substituted pyrrole ring and makes an angle of 120° and 150° with it for H(N-Me)T(4-Br)PP and H(N-CN)TPP, respectively.

Distortion of the planar structure of the molecule is likely to also occur in the complexes with *N*-substituted porhyrins. According to X-ray diffraction data [29], the (Cl)Zn(N-Me)TPP complex has the shape of a distorted pyramid. Zinc in the complex forms four bonds with the nitrogen atoms and one bond with the Cl^- anion, the bond between zinc atom and the methylated nitrogen atom being the least stable (2.530 Å) and that between the nitrogen atom in the *trans*-position with respect to the methylated nitrogen atom and Zn being the most stable (2.018 Å). This fact indicates that the hybridization of the *N*-substituted nitrogen atom of the complex changes to p^3. A similar structure is also typical of other *N*-substituted metalloporphyrins [29].

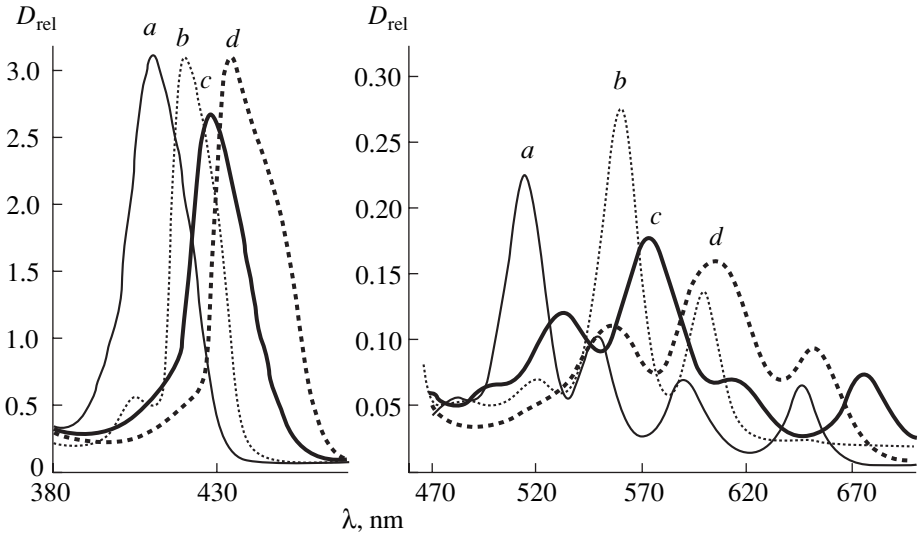


Fig. 2. The electronic absorption spectra of (*a*) H_2TPP, (*b*) ZnTPP, (*c*) H(N-Me)TPP, and (*d*) (Ac)Zn(N-Me)TPP in DMSO.

Other evidence of rehybridization is the change in the chromophore properties of these compounds. The general pattern of the electronic absorption spectrum of porphyrin remains almost unchanged in the course of the *N*-substitution (four bands in the visible region and the Soret band (see Fig. 2, spectra *a*, *c*)), whereas in the visible region of the spectrum of the *N*-substituted metal complex, one can observe three more diffuse bands with lower intensity (see Fig. 2, spectrum *d*) instead of the two-band pattern typical of MP (symmetry D_{4h}, Fig. 2, spectrum *b*). This can be explained by the reduction in the symmetry of the coordinated porphyrin and by the change in conjugation contour in the molecule. The change in the contour consists in the greater involvement of the π-electrons of the β-carbon atoms of the substituted pyrrole ring into the main chromophore (see Fig. 1).

The bathochromic shift of bands in the electronic absorption spectra of the metal complexes with *N*-substituted porphyrins, as compared with their positions in the spectra of the respective complexes with nonsubstituted H_2P, also indicates that the metal complexes AM(N-X)P also contain a distorted macrocycle [6, 14]. Thus, in the electronic absorption spectrum of ZnTPP in DMSO, the first absorption band is observed at 599 nm, while in the spectrum of (Ac)Zn(N-Me)TPP, it lies at 653 nm (Table 2). In this case, $\Delta\lambda^I = \lambda^I_{H_2P} - \lambda^I_{MP}$ for the first complex is equal to –46 nm, while for the second complex, it is equal to –22 nm. The more significant shift of the first band in the electronic absorption spectrum of the Zn complexes with nondistorted porphyrins (H_2OEtP, H_2TPP) (the spectral criterion of the complex stability [20]) agrees with their higher kinetic stabilities in proton–donor media as compared with the corresponding complexes of the *N*-substituted porphyrins [30].

As compared with porphyrins proper, the activation energy in the reaction of complex formation with the *N*-substituted H_2P decreases almost by half [31]. The activation entropy also decreases, which suggests an increase in the solvation of the transition state [20]. During complex formation, the H(N-X)P reactivity increases still more (by 3–35 times, depending on the nature of the salt) when going from porphyrins with X = Me to derivatives with X = Ph (Table 3) due to both the higher distortion of the macrocycle (the bulky substituent) and the electron-acceptor properties of the *N*-Ph group.

According to X-ray diffraction data, H(N-Ph)TPP (**V**) is only slightly more nonplanar than H(N-Me)TPP (**IV**). For example, the *N*-substituted pyrrole ring deviates from the mean plane of the macrocycle by 42° and 38.5° for **V** and **IV**, respectively. The effect of the peripheral substituents (R and R') in the molecule on its distortion in the crystal was found to be also negligible [33, 34].

The above data allow one to suggest that the substantial differences in the reactivity of H_2P with different peripheral and *N*-substituents are due to electronic factors rather than structural factors. For instance, the reduction of the *N*-methylporphyrins always affords a respective chlorin [9], whereas the reduction of the *N*-phenyl derivative (with the electron density in the *meso*-positions reduced owing to the two above-mentioned reasons) results in the destruction of the conjugation contour and the formation of an unusually stable phlorin structure [10]. Therefore, the electronic factor is the most important in the change of the properties of the *N*-substituted porphyrins. As was previously shown for other nonplanar porphyrins (in particularly, for dodeca-substituted porphyrins) [14], the transfer of the electronic effects does not weaken upon distortion, while the distortion of the porphyrin molecule even

Table 2. The electronic absorption spectra of porphyrins and their metal complexes in DMSO

Porphyrin (metalloporphyrin)	λ, nm (D_{rel})					$\Delta\lambda^I$, nm
	Soret	**IV**	**III**	**II**	**I**	
H_2OEtP	394.5(21.2)	495.5(2.1)	528.5(1.6)	564.5(1.3)	618.0(1.0)	
ZnOEtP (from $Zn(NO_3)_2$)	408.5(15.9)			537.5(1.0)	574.0(1.0)	−44.0
ZnOEtP (from $ZnAc_2$)	408.0(4.4)			530.0(1.1)	572.5(1.0)	−45.5
H_2TPP	416.0(35.4)	513.0(2.0)	548.0(1.2)	558.0(1.0)	645.0(1.0)	
ZnTPP (from $Zn(NO_3)_2$)	426.0(31.7)			559.0(1.5)	599.0(1.0)	−46.0
ZnTPP (from $ZnAc_2$)	426.0(13.7)			558.5(1.3)	599.0(1.0)	−46.0
H(N-Me)OEtP	407.5(20.5)	503.0(2.6)	533.5(1.4)	583.5(1.2)	640.5(1.0)	
					613.5(0.68)	
(Ac)Zn(N-Me)OEtP	416.0(23.1)		513.0(2.0)	581.0(2.5)	616.5(1.0)	−24.0
	424.0(20.0)					
(NO_3)Zn(N-Me)OEtP	413.0(33.9)		533.5(2.2)	582.0(2.8)	615.0(1.0)	−25.5
(Acac)Zn(N-Me)OEtP	412.5(30.5)		533.5(2.2)	583.0(2.5)	615.0(1.0)	−25.5
	425.0(21.4)					
H(N-Ph)TPP	438.0(30.9)	557sh(1.4)	596.5(3.1)	634sh(1.4)	704.0(1.0)	
(Ac)Zn(N-Ph)TPP	447.5(15.4)		567.5(1.0)	628.0(1.3)	681.5(1.0)	−22.5
	457.0(13.6)					
(NO_3)Zn(N-Ph)TPP	445.0(15.1)		566.5(0.9)	624.0(1.4)	678.0(1.0)	−26.0
	455.0(13.0)					
(Acac)Zn(N-Ph)TPP	445.0(22.2)		567.0(0.9)	627.5(1.4)	681.0(1.0)	−23.0
	454.0(19.0)					
H(N-Me)TPP	429.0(34.0)	531.5(1.5)	573.0(2.0)	612.0(0.9)	675.0(1.0)	
(Ac)Zn(N-Me)TPP	438.0(16.1)		558.5(1.2)	607.5(1.3)	653.0(1.0)	−22.0
	446.0(14.3)					
(NO_3)Zn(N-Me)TPP	435.0(22.5)		558.0(1.1)	606.5(1.5)	652.0(1.0)	−23.0
	444.0(18.91)					
(Acac)Zn(N-Me)TPP	434.5(26.6)		562.5(1.3)	609.5(1.5)	654.5(1.0)	−20.5
	444.0(21.8)					

favors its internal polarization in a number of cases [35]. The type of transfer of the electronic effects is monitored in this case by the degree of macrocycle distortion. Thus, as in the nonsubstituted H_2P, the *meso*-phenyl rings in the *N*-substituted H_2P act as electron density buffers and compensate its excess or shortage in the macrocycle in the course of chemical conversions (acid–basic equilibria [5]).

Effect of substituents R and R' in the periphery of the H_2P molecule. The kinetic data in Tables 1 and 3 make it possible to conclude that the change in the rate of complexation in DMSO for both planar and nonplanar porphyrins distorted by the *N*-substitution agrees with the concepts of the electronic effects of the peripheral substituents in them, their transfer to the coordination site of the molecule, and with the concepts on the mechanism of the process under study [20]. Thus, the complexation with H_2TPP in DMSO occurs faster than that with H_2OEtP (Table 1). Similarly, H(N-Me)TPP reacts with $ZnAc_2$ almost 10 times as fast as H(N-Me)OEtP (Table 3). Eight ethyl groups in the β-positions of the H_2P molecule produce the donor effect (+*I*) on the macrocycle and depolarize the N–H bond, thus hampering its dissociation in the transition state.

Although involved in its nature, the mechanism of porphyrin complexation is a synchronous process occurring in one stage; this is why the limiting stage cannot be distinguished. However, it is known [20] that, during the formation of the transition state, the maximum energy is required for the elimination of the NH protons from the coordination site of the macrocyclic ligand, especially, in electron-donor solvents (DMSO, Py) [22].

The *meso*-phenyl substitution produces the opposite electronic effect, and, therefore, the rate of complexation in this case increases. The kinetic (Table 3) and

Table 3. Kinetic parameters of complexation of the *N*-substituted porphyrins in DMSO ($c_{porph} = 4 \times 10^{-5}$ mol/l; $c_{ZnA_2} = 2 \times 10^{-3}$ mol/l)

Porphyrin	Salt	λ_{exp}, nm	*T*, K	k_v^*, l s^{-1} mol^{-1}	E_a, kJ mol^{-1}	$\Delta S^{\#}$, J mol^{-1} K^{-1}
H(N-Me)TPP	$ZnAc_2$	610	298	6.14	33.8	−125.0
			308	10.90		
			318	14.59		
	$Zn(NO_3)_2$		298	0.14	63.6	−56.0
			308	0.30		
			318	0.72		
	$Zn(Acac)_2$		298	0.20**	48.8	−103.0
			308	0.38		
			318	0.64		
			328	1.20		
H(N-Ph)TPP	$ZnAc_2$	680	293	20.18	34.2	−110.0
			298	29.67		
			303	33.00		
	$Zn(NO_3)_2$		298	5.25	41.0	−102.0
			308	8.89		
			318	14.88		
	$Zn(Acac)_2$		298	0.65**	56.0	−69.0
			308	1.26		
			318	2.68		
			328	4.78		
H(N-Me)OEtP	$ZnAc_2$	565	298	0.55	62.4	−48.0
			308	1.29		
			318	2.74		
	$Zn(NO_3)_2$		298	2.69	57.9	−51.0
			308	5.29		
			318	15.27		
	$Zn(Acac)_2$		298	0.11**	64.3	−56.0
			318	0.55		
			328	1.00		
			338	2.29		

* The error in determining k_v does not exceed 10%.
** Calculated from the Arrhenius equation.

calorimetric [18] data show that the electronic effects of the peripheral substituents are also effectively transferred to the reaction center in the course of the porphyrin molecule distortion by the *N*-substituent.

The polarization and depolarization of the N–H bond by the peripheral substituents are also manifested in the kinetic parameters of the complexation process. The complexation with H(N-Me)OEtP requires a higher energy (62 kJ/mol for $ZnAc_2$) than that with H(N-Me)TPP (34 kJ/mol for $ZnAc_2$). The high activation energy is specified by the lower solvation of the transition state which, in the case of H(N-Me)OEtP, is less polarized than in the case of H(N-Me)TPP.

The effect of the salt anion A. When the NO_3^- anion is used in complexation with nondistorted porphyrins (H_2TPP, H_2OEtP), the reaction proceeds at a higher rate than in the case of A = Ac [20, 36]. This is explained by the structure of the complex solvate involved in reaction (1) and by the strength of the M–A and M–Solv bonds in this complex [28]. The Zn–Ac bond is known to be more covalent than the Zn–NO_3 bond, as a result of which more reactive solvates, i.e.,

$[Zn(DMSO)_5Ac]^+Ac^-$ or $[Zn(DMSO)_6]^{2+}Ac_2^-$, cannot form in the DMSO solution. On the contrary, since the $Zn–NO_3$ bond is weaker, $Zn(NO_3)_2$ more readily forms outer-sphere complex solvates such as $[Zn(DMSO)_6]^{2+}(NO_3)_2^-$ [28].

We have discovered that the nitrate anion inhibits the reaction of complex formation. For instance, the rate of the reaction of H(N-Me)TPP (**IV**) with $Zn(NO_3)_2$ is 38 times, while that of H(N-Ph)TPP (**V**) with $Zn(NO_3)_2$ is 5.5 times, as low as that with $ZnAc_2$. At the same time, the complexation with H(N-Me)OEtP (**III**) exhibits no abnormalities and the rate of reaction with $Zn(NO_3)_2$ is 5 times as high as that with $ZnAc_2$. One should note that reaction (1) was always conducted under the same conditions; i.e., the structure of the $Zn(NO_3)_2$ complex solvate remained unchanged. This fact indicates that the mechanism of complexation of the *N*-substituted porphyrins strongly depends not only on the nature of the metal ion, salt anions, the structure of the complex sovate, and on the nature of the solvent, but also on the nature of the substituents on the periphery of the molecule (the sensitivity of the salt solvate to the nature of H_2P). In addition, the types of distortion of molecules **III** and **IV** (their most stable conformations) are likely to differ significantly, while the reaction centers of the $Zn(NO_3)_2$ complex solvate readjust to the reaction centers of porphyrin more easily in the case of **III** than in the case of **IV**.

When a simple Zn^{2+} salt is replaced by a chelate salt, for example, $Zn(Acac)_2$, the mechanism of complexation becomes more involved [31] and, hence, the process slows down. The reaction of complexation of $Zn(Acac)_2$ or other chelate salts (dithizonate, diphenylcarbazonate) with the planar porphyrins in DMSO does not almost occur [31]. All of the three investigated *N*-substituted porphyrins (**III**–**V**) react with $Zn(Acac)_2$ at rates which are 5–30 times lower than those with $ZnAc_2$ and 8–25 times lower than with $Zn(NO_3)_2$ except for (**III**).

The mechanism of H_2P complexation with the chelate salts is complicated by the competition of two ligands, namely, the chelate ligand (Acac) and the macrocyclic ligand (H_2P), for the coordination of the metal ion [14]. The data in Table 3 show that the solvation of the transition state in the reaction of the *N*-substituted porphyrins with $Zn(Acac)_2$ occurs, as a rule, more difficultly than that with the simple salts. The explanation is that the coordination site of the porphyrin molecule is shielded by the bulky acetylacetonate ion.

The data in Table 2 reveal that the nature of the A counterion in the *N*-substituted complex (A)Zn(N-X)P only slightly affects the position of the first band in its electronic absorption spectrum. Depending on the nature of the counterion (Ac^-, $Acac^-$, NO_3^-), this band shifts only by 1.5–4 nm, although A enters the inner coordination sphere of the *N*-substituted metal complex.

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