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Effect of Ligand Nonplanarity and Solvent Nature on the Kinetic Stability of Zinc Porphyrin Complexes

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Abstarct— Planarity disturbance in metal porphyrin macrorings produces destabilization of complexes in dimethyl sulfoxide–acetic acid and benzene–acetic acid systems, except for cases where the coordination center is additionally stabilized by endocyclic substituents and/or extra ligands. The first dissociation stage of complexes with N-substituted analogs of porphyrins involves substitution of the acido ligand in the strongly shielded coordination sphere by an electron-donor solvent molecule. The revealed dependences of dissociation rate constants on acid concentration in DMSO, untypical of most metal porphyrins, are explained by a change in the type of the attacking species with changing solvent composition. The dissociation rate constants of complexes in an electron donor solvent can be lower by several orders of magnitude than in a weakly solvating medium.

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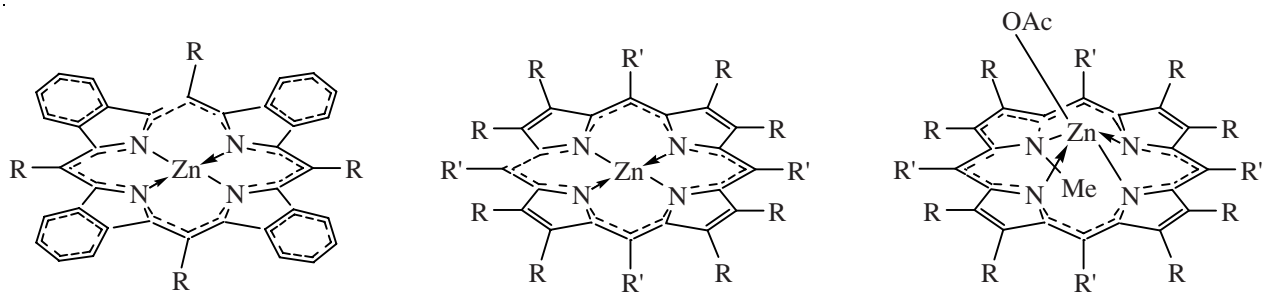
The main research activities in porphyrin (H_2P) chemistry initially focused on preferentially planar molecules, such as bioporphyrins (hemes, chlorophilles, etc.) isolated from natural objects [1, 2]. Over the recent years, in view of the growing interest in biological processes involving conformationally flexible in vivo porphyrins and their metal complexes [3], molecules greatly differing from "classical" [4] in geometry and π-electron characteristics have received much attention.

There are several structural groups of synthetic porphyrins with a defined nonplanar structure [3, 5]. These are largely compounds with bulky substituents at the nitrogen atom in the coordination center, specifically *N*-substituted porphyrins [6], or compounds in which most or all β- and *meso*-hydrogen atoms in the H_2P molecule are substituted by various hydrocarbon residues or functional groups [5, 7]. Strong distortion takes place in complexes of porphyrins with metal cations whose size is smaller or, vice versa, larger than the diameter of the coordination cavity of the ligand (4.02 ± 0.02 Å) [7].

Nonplanar porphyrins and their complexes in crystal and in solutions can adopt, depending on macroring structure, several typical conformations some of which, such as structures **I–VIII**, can be characterized by X-ray diffraction deviations of β (saddle conformation) and *meso* (waved) atoms of the mean plane of the porphyrin nucleus (ΔC_β and ΔC_{meso}, respectively; Table 1) [3]. As shown by ^{1}H NMR spectroscopy, in going from solid phase to solution nonplanar porphyrins scarcely change their structure [3, 5, 7, 9]. Information on the molecular geometry of nonplanar porphyrins can also be obtained from quantum-chemical data [10].

The mechanisms of functioning sterically distorted metal porphyrins in biological systems are impossible to understand not knowing their state and stability in solutions [11]. Therefore, in the present work we set ourselves the goal to explore the kinetic stability of zinc complexes with nonplanar porphyrins of various structure: dodecasubstituted tetraphenyltetrabenzoporphine ZnTPhTBP (**III**), octabromotetraphenylporphine Zn(β-Br)$_8$TPhP (**IV**), dodecaphenylporphine Zn(β-Ph)$_8$·TPhP (**V**), and octaethyltetraphenylporphine Zn(β-Et)$_8$·TPhP (**VI**), as well as with *N*-methyloctaethylpor-phine (AcO)Zn·(NMe)(β-Et)$_8$P (**VII**) and *N*-methyltetraphenylporphine (AcO)Zn(NMe)TPhP (**VIII**) in media on the basis of acetic acid.

The ligands in the studied porphyrin complexes prefer the saddle conformation both in solid phase and in solutions (Table 1, Fig. 1), and, therewith, in



I, III **II, IV–VI** **VII, VIII**

R = H (**I**); R = H, R' = Ph (**II**); R = Ph (**III**); R = Br, R' = Ph (**IV**); R = R' = Ph (**V**); R = Et, R' = Ph (**VI**); R = Et, R' = H (**VII**); R = H, R' = Ph (**VIII**).

Table 1. Mean deviations of β- and *meso*-carbon atoms in H_2P and metal porphyrins on the initial macroring plane by X-ray diffraction data [3]

Compound	Ligand		Zinc complex **II**		Conformation
	ΔC_β, Å	ΔC_{meso}, Å	ΔC_β, Å	ΔC_{meso}, Å	
II	–	–	0.23	0.12	Planar
III	–	–	0.77	–	Saddle
IV	1.26	0.32	0.92	0.25	Saddle–waved
V	1.28	0.07	0.96	0.01	Saddle
VI	1.17	0.03	1.09	–	Saddle
VII	~0.1[a]	–	–	–	Planar
VIII	~0.5[a]	–	–	–	Saddle

[a] Quantum-chemical data [8].

compound **IV** there is an essential fraction of the waved conformation [3]. Substitution at the endocyclic NH group, along with tetrameso- or octa-β-substitution (compounds **VII** and **VIII**) makes the porphyrin ligand markedly nonplanar with the *N*-substituted pyrrole ring slightly displaced from the macroring plane, but the distorted saddle conformation is generally preserved [3, 5, 8]. The nonplanar saddle conformation of the ligand is also stabilized by complex formation with zinc ion [3].

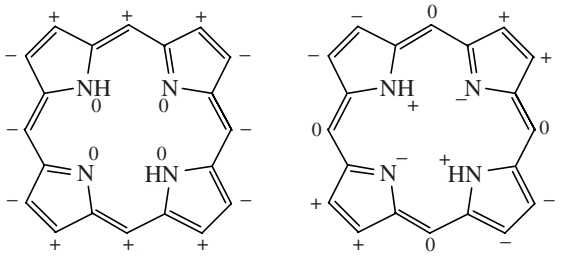


Fig. 1. (Left) Waved and (right) saddle nonplanar conformations of porphyrin ligands (+ and – related to atoms located above, below, and in the macroring plane, respectively).

The effect of nonplanarity of a porphyrin complex on its ability for dissociation is controlled by various factors [11]. Disturbed planarity of the aromatic macroring attenuates the macrocyclic effect [5, 12], thus isolating the pyrrole rings and increasing the positive charge on the endocyclic nitrogen atoms [7] and facilitating their interaction with solvated proton. Electron-donor substituents in the β-, *meso*-, or *N*-positions accelerates dissociation of the complex due to transfer of additional electron density on macroring nitrogens, but the macroring nonplanarity not infrequently creates steric hindrances to interaction of endocyclic porphyrin nitrogens with solvated proton. A combination of these two factors, electronic and steric [11], defines the rate of solvoprotolytic dissociation reactions of sterically distorted porphyrins.

The coordination bonds in zinc porphyrin complexes are largely formed due to the covalent

contribution, but the ionic contribution still takes place [2]. The complexes in study dissociate according to Eqs. (1) and (2).

$$ZnP + 2\,AcOH \rightarrow H_2P + Zn(OAc)_2, \quad (1)$$

$$(OAc)Zn(NMe)P + AcOH \rightarrow H(NMe)P + Zn(OAc)_2. \quad (2)$$

The dissociation kinetics data for compounds **III–VIII** (Table 2) give evidence showing that the complexes of zinc with strongly distorted porphyrin ligands dissocate much faster than their planar analogs [11–15], both in the coordinating (DMSO–AcOH) and in the weakly coordinating (C_6H_6–AcOH) solvents. Disturbed planarity of the macroring in complexed H_2P unfavors mutual adjustment of the metal and ligand reaction centers, produces additional polarization of N–M bonds, and adversely affects stability of the complexes. The kinetic stability of the complexes in proton-donor media decreases as their nonplanarity is enhanced over series of compounds [13–16] with increasing number of peripheral substituents and in nonplanar complexes whose ligands belong to various structural types (compounds **III–VI** and **VII–VIII**) (Table 2).

The concentration dependences of the apparent dissociation rate constants of the complexes in the DMSO–AcOH medium (Fig. 2a, Table 2) proved to be untypical of classical porphyrins studied previously [2]. For example, the apparent dissociation rate constants of complexes **V, VI**, and **VIII** vary unproportionally in the concentration of acetic acid with the DMSO–AcOH system (Fig. 2a). As a result, there is no sense to compare the stabilities of the complexes in glacial acetic acid for constructing their stability series in dissociation reactions (1) and (2). Therefore, as an arbitrary criterion for stability of the complexes we chose the concentration of AcOH in DMSO, at which the dissociation rate is 1×10^{-4} s^{-1}. Under this condition, complexes **I–VI** can be arranged in the following series in terms of their decreasing stability: ZnTBP (**I**) > ZnTPhP (**II**) > (AcO)Zn(NMe)·(β-Et)$_8$P (**VII**) > ZnTPhTBP (**III**) > Zn(β-Br)$_8$TPhP (**IV**) > (AcO)Zn(NMe)TPhP (**VIII**) > Zn(β-Et)$_8$TPhP (**VI**) > Zn(β-Ph)$_8$TPhP (**V**).

The dependences of the apparent dissociation rate complexes of the zinc complexes on the concentration of acetic acid have two different curve patterns. The

Table 2. Kinetic parameters of dissociation reactions (1) and (2) of complexes **III–VIII** in the DMSO–AcOH and C_6H_6–AcOH systems, 298 K (c_{MP} 4×10^{-5} M)

Solvent system	c_{AcOH}, M	$k_{app}\times10^3$, s^{-1}	E_a, kJ mol^{-1}	$\Delta S^{\neq}$, J mol^{-1} K^{-1}
		Compound **V**		
DMSO–AcOH	2.60	0.21±0.01	85±6	33±2
	3.50	0.32±0.01	71±4	–2±0.1
	4.40	8.88±0.50	36±2	–92±6
	5.25	51.39±3.53	78±3	64±4
C_6H_6–AcOH	$1.31\cdot10^{-2}$	2.51±0.11	14±3	–255±22
	$2.62\cdot10^{-2}$	7.45±0.63	30±5	–193±18
	$4.36\cdot10^{-2}$	10.08±0.87	37±5	–169±15
	$6.09\cdot10^{-2}$	17.05±0.17	37±7	–163±24
		Compound **VI**		
DMSO–AcOH	5.25	0.31±0.01[a]	34±1	–125±4
	6.50	0.17±0.01[a]	39±1	–107±2
	8.80	1.51±0.07[a]	25±1	–136±7
	10.9	0.40±0.02[a]	38±1	–104±4
	12.8	1.50±0.04[a]	24±1	–142±8
C_6H_6–AcOH	$2.62\cdot10^{-2}$	1.09±0.05	51±10	–139±35
	$4.36\cdot10^{-2}$	2.73±0.02	26±4	–215±15
	$6.09\cdot10^{-2}$	4.35±0.32	21±6	–228±30
	$8.69\cdot10^{-2}$	11.66±0.69	13±3	–248±11

Table 2. (Contd.)

Solvent system	c_{AcOH}, M	$k_{app} \times 10^3$, s^{-1}	E_a, kJ mol^{-1}	$\Delta S^{\neq}$, J mol^{-1} K^{-1}
		Compound **IV**		
DMSO–AcOH	10.9	0.11±0.01	53±4	–66±10
	12.8	1.55±0.12	27±1	–128±9
	14.1	3.73±0.22	27±2	–122±12
C_6H_6–AcOH	1.59	1.58±0.05	19±4	–243±14
	2.28	3.16±0.09	16±1	–248±1
	2.91	6.54±0.24	15±4	–244±16
	3.49	6.79±0.03	20±6	–228±20
	4.36	6.80±0.05	21±7	–224±25
		Compound **III**		
DMSO–AcOH [15]	13.35	0.24±0.06	–	–
	15.04	1.99±0.06	49±3	–145±9
C_6H_6–AcOH	5.57	0.44±0.07	42±13	–178±44
	9.06	1.07±0.25	56±4	–123±15
	11.88	1.30±0.02	50±2	–140±7
	15.02	2.80±0.03	40±7	–168±22
$AcOH_{ice}$	17.5	5.12±0.62	45±3	–148±15
		Compound **VII** [16]		
DMSO–AcOH	17.5			63±4
	16.2	0.97±0.06	112.3±9.6	144±10
	12.8	0.11±0.01	159.1±11.3	284±20
		Compound **VII** [16]		
DMSO–AcOH	17.5	26.65±0.39	44.5±2.3	–58±4
	16.2	34.18±0.07	47.3±3.2	–48±3
	14.1	47.36±0.48	66.3±5.1	16±1
	10.9	30.88±0.64	74.1±4.3	39±2
	9.43	9.19±0.97	38.4±7.0	–163±24

[a] Calculated by the Arrhenius equation.

dissociation rates of complexes ZnTPhTBP (**III**), Zn(β-Br)$_8$TPhP (**IV**), Zn(β-Ph)$_8$TPhP (**V**), and (AcO)·Zn(NMe)(β-Et)$_8$P (**VII**) either linearly increase with the concentration of acetic acid or this dependence is fitted by a curve that looks like a branch of a parabola. The dependences of the apparent dissociation rate constants of complexes **VIII** [16] and VI look like curves with their maxima at 11–14 M AcOH (Fig. 2a). Such $k_{app} = f(c_{AcOH})$ dependences are uncharacteristic of porphyrins and probably explained by existence, at the given concentration of acetic acid in DMSO, of several species active in the dissociation reaction, specifically DMSO·H^+, $AcOH^{2+}$, AcOH, etc., whose equilibrium concentrations are unknown. According to [17], the exponent of autoprotolysis constant $pK_{app} = -\log K_{app}$ smoother varies with the composition of the DMSO–AcOH system at small fractions of each of the reagents, and the dependence has a diffuse maximum at the AcOH concentration of 9–15 M. The intricate concentration dependences in reactions (1) and (2) can be associated with a change in the attacking species with varied composition of the solvent; a mixed dissociation mechanism is also possible. Reactions (1) and (2) may take different pathways, including those induced by undissociated acetic acid [18].

The stability series of the porphyrin complexes in reactions (1) in the benzene–acetic acid medium is as follows (Table 2, Fig. 2b): ZnTBP (**I**) > ZnTPhP (**II**) > ZnTPhTBP (**III**) > Zn(β-Br)$_8$TPhP (**IV**) > Zn(β-Et)$_8$·TPhP (**VI**) > Zn(β-Ph)$_8$TPhP (**V**).

This series is consistent with the concept that the stability of zinc porphyrin complexes decreases (Table 1) with enhancing degree of their planarity disturbance. A

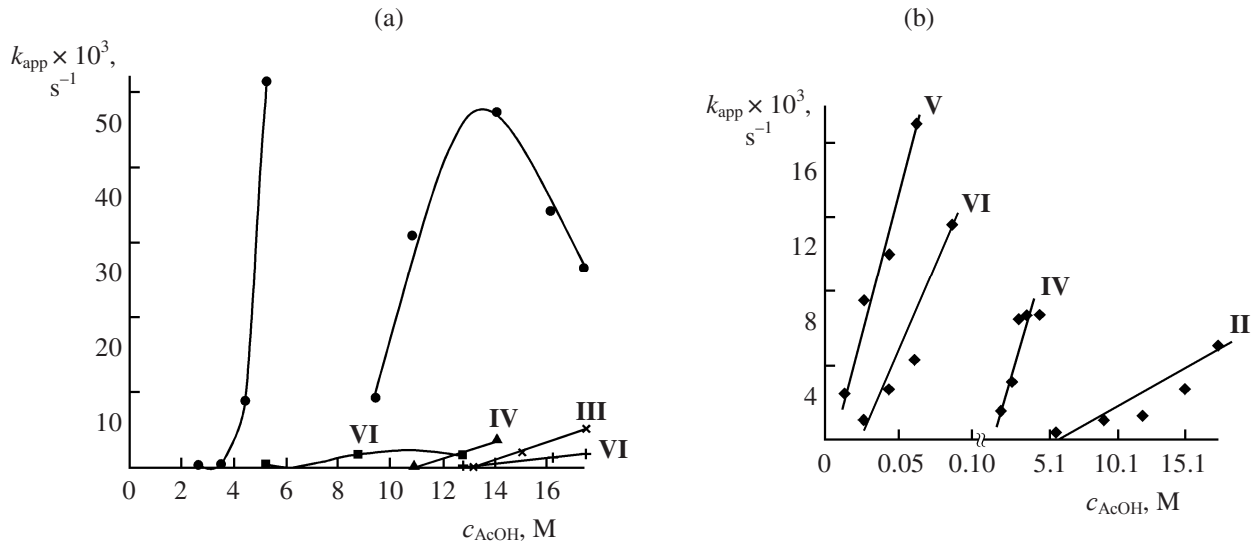


Fig. 2. Plots of the rate constants of reactions (1) and (2) vs. concentration of acetic acid in (a) DMSO–AcOH and (b) C_6H_6-AcOH for compounds **III–VIII**. c_{MP} 4×10^{-5} M, 298 K.

planar zinc tetrabenzoporphine (I) undergoes no dissociation even in glacial acetic acid [2]. A fairly planar zinc tetraphenylporphine (II) (ill-defined saddle conformation) dissociates in glacial acetic acid, k_{app}^{298} = $(0.26 \pm 0.02) \times 10^{-3}$ s^{-1} [2], whereas a markedly distorted zinc tetraphenyltetrabenzoporphine (**III**) (ΔC_β = 0.77 Å) under the same conditions is 20 times more active in reaction (1) [k_{app}^{298} = = $(5.12 \pm 0.62) \times 10^{-3}$ s^{-1}, Table 2, Fig. 2]. A still more facile dissociation is characteristic of zinc octabromotetraphenylprophine (**IV**) whose reaction (1) in the benzene–acetic acid medium can be studied by classical kinetic methods only in the range c_{AcOH} 0.5–5.0 M. The fact that complex **IV** is more stable than complexes **V** and **VI** (Table 2, Fig. 2) can be explained by a considerable contribution of polarization factor (*–I* effect of bromine) which operates here along with the macroring distortion factor whose contribution is slightly smaller (ΔC_β = 0.92 Å, the. A less planar zinc octaethyltetraphenylporphine (**VI**) is even less stable and dissociates at c_{AcOH} 0.02–0.10 M. Probably, the eight alkyl groups increase, due to their *+I* effect, the effective charge of porphyrin nitrogens, thus additionally driving reaction (1). Zinc dodecaphenylporphine (**V**) was found be the most unstable in the C_6H_6–AcOH medium among the complexes studied: Its dissociative ability is enhanced by a still stronger destabilizing effect of the β-phenyl substitution (Fig. 2). Stability decrease is observed in spite of the fact that compound **V** has a slightly flattened saddle conformation (ΔC_β = 0.96 Å) compared with complex **VI** (Table 1).

The order of reaction (1) in complexes **III–VIII** is always 1, as evidenced by the straight-line nature of the $\log(c_0/c) = f(\tau)$ plots (Fig. 3, plot *3*).

$$-dC_{MP}/d\tau = k_{app} \cdot C_{MP},\ k_{app} = k_{v_{solv}} \cdot C_{H+}^{n}. \qquad (3)$$

The reactions orders in proton–donor species, determined by Eq. (3) as the slopes of the $\log k_{app} = f(\log c_{AcOH})$ straight-line plots, are 1.99 ± 0.03 for **III**, 1.54 ± 0.20 for **IV**, and 1.42 ± 0.03 for **V**. With zinc

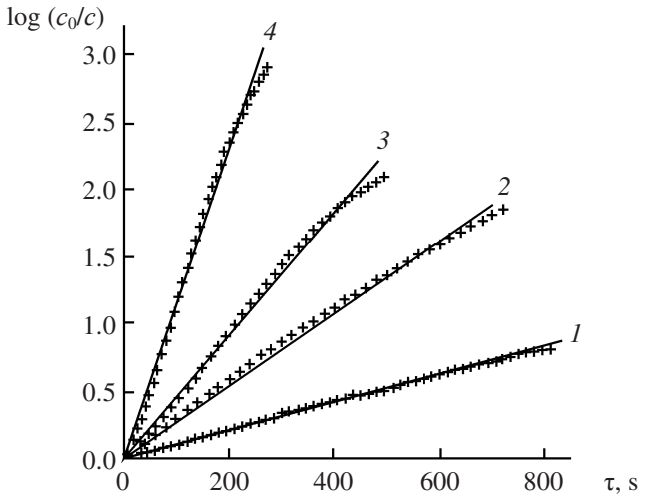


Fig. 3. Plots of log (c_0/c) vs. time of reaction (1) in C_6H_6–AcOH for zinc octaethyltetraphenylporphine (**VI**). 298 K, c_{AcOH}, M: (*1*) 2.62×10^{-2}; (*2*) 4.36×10^{-2}; (*3*) 6.09×10^{-2}; and (*4*) 8.69×10^{-2}.

octaethyltetraphenylporphine **VI**, the reaction order in proton–donor species decreased from 1.93 at 298 K to 1.12 at 318 K. The noninteger dissociation reaction orders in active reagent, as well as their tendency to change with increasing temperature point to a mixed mechanism of dissociation in the C_6H_6–AcOH medium.

N-Methyl substitution not only disturbs planarity of the porphyrin macroring, but also produces a strong shielding of the reaction center [6]; as a result, the reaction center in complexes **VII** and **VIII** can only be attacked along the *z* axis, which makes them kinetically more stable.

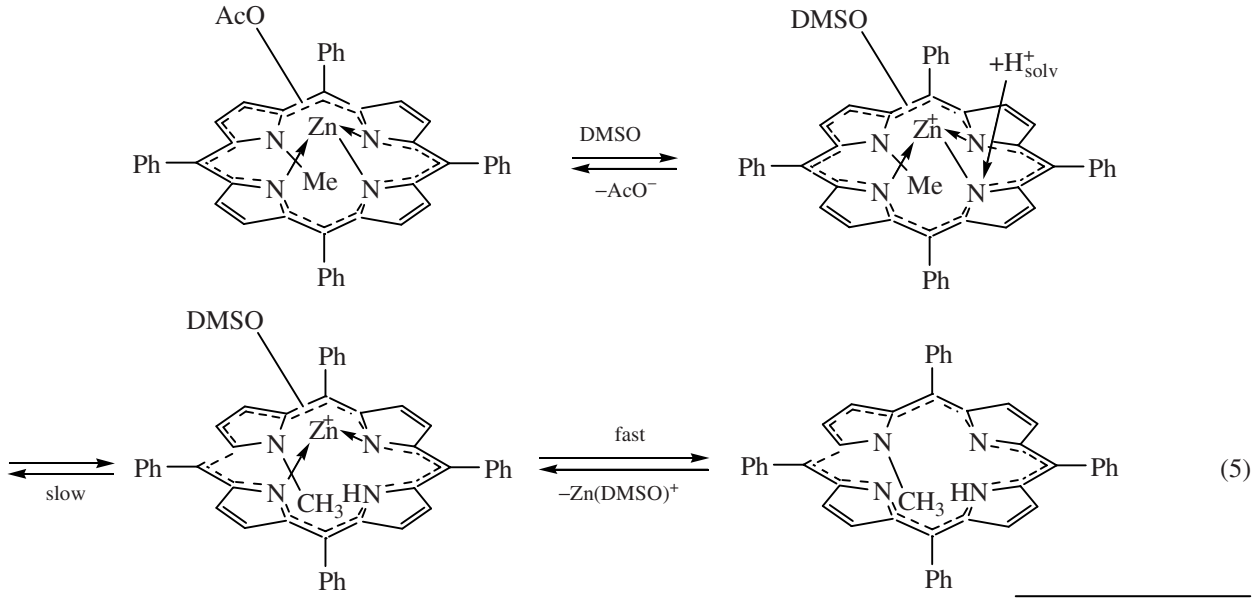
The dissociation of compound **VIII** in the C_6H_6–AcOH medium was found to be reversible, i.e. Eq. (2) for this complex transforms into Eq. (4).

$$(OAc)Zn(NMe)P + AcOH \leftrightarrow H(NMe)P + Zn(OAc)_2. \quad (4)$$

In acetic acid, complex **VIII** immediately forms the ligand H(NMe)TPhP with doubly protonated endocyclic nitrogen atoms. To obtain evidence for this conclusion, we performed a spectrophotometric titration of H(NMe)TPhP in the C_6H_6–AcOH binary solvent. As seen from the titration curves for complex **VIII** and its corresponding ligand (Fig. 4), protonation of the ligand initiates already at c_{AcOH} about 5 M, but the equilibrium of dissociation reaction (4) shifts to ligand formation only at $c_{AcOH} > 8$ M.

The resulting data suggest that complex **VIII** dissociates along Eq. (2) [scheme (5)]. According to this mechanism, dissociation in the DMSO–C_6H_6 medium begins with exchange of an extra ligand (in our case, acetate ion) for DMSO in the inner coordination sphere of the complex.

The Zn–N bonds in the metal-protonated complex are therewith strongly polarized and weakened, which accelerates reaction (2). As seen from scheme (5), the dissociation reaction involves only one proton-donor molecule. Dissociation by two concurrent pathways, under the action of solvated proton and undissociated AcOH [18], results in a peaked $k_{app} = f(c_{AcOH})$ plot for compound **VIII** in the DMSO–AcOH system. If the solvent unfavors (like C_6H_6–AcOH) extra ligand substitution [scheme (5)], compound **VIII** dissociates equilibrially along pathway (4).



(5)

Comparing the state of complexes **III–VIII** in the two binary systems (Table 2, Fig. 5) we can conclude that the stability series are generally analogous, and dissociation in C_6H_6–AcOH is much faster than in DMSO–AcOH. These findings suggest that in the weakly solvating solvent an acidoprotolytic dissociation mechanism [18] is operative along with solvoprotolytic [2]. The more nonplanar is the complex, the more different acid concentrations are required for it to dissociate at equal rates in the two systems studied (Table 1, Fig. 5).

EXPERIMENTAL

Compounds **III–VIII** were prepared, purified, and identified as described in [6, 19–21].

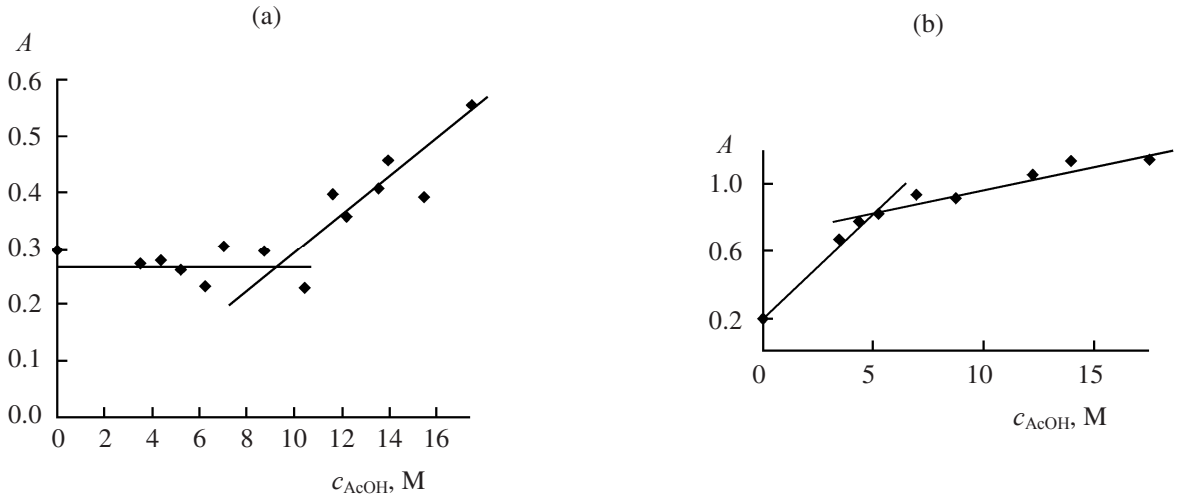


Fig. 4. Plots of the optical density of solutions of (a) com-plex **VIII**, λ 665 nm, and (b) ligand H(NMe)TPhP, λ 669 nm, in C_6H_6–AcOH vs. concentration of AcOH (298 K).

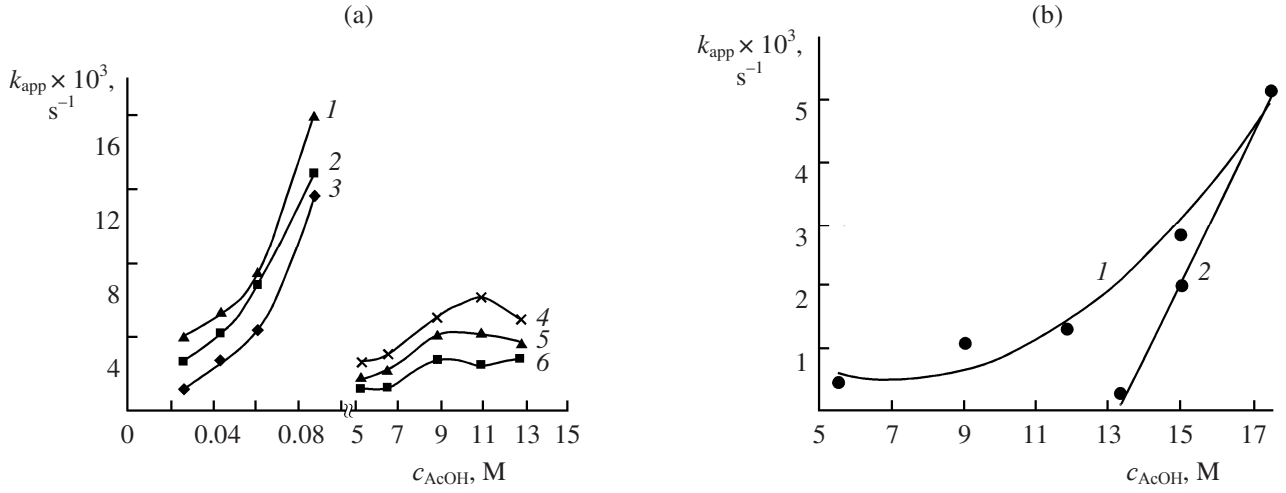


Fig. 5. Plots of the apparent rate constants vs. concentration of acetic acid for dissociation reactions (1) of (a) zinc octaethyltetraphenylporphine (**VI**) in C_6H_6–AcOH at (*1*) 318, (*2*) 308 K, and (*3*) 298 K and in DMSO–AcOH at (*4*) 328, (*5*) 318, and (*6*) 308 K and of (b) zinc tetraphenylbenzoporphine (**III**) (298 K) in (*1*) C_6H_6–AcOH and (*2*) DMSO–AcOH.

Acetic acid of pure grade was twice frozen out, refluxed over acetic anhydride, and distilled at 117.5–118°C. Dimethyl sulfoxide of pure grade was dried over calcined CaO and distilled in a vacuum. Benzene of analytical grade of refluxed over P_2O_5 and distilled [22].

Spectrophotometric study of dissociation of complexes III-VIII. Series of DMSO–AcOH and C_6H_6–AcOH solutions with a preset concentration of acetic acid were preliminarily prepared by the gravimetric procedure. A 4×10^{-5} M benzene solution of a complex (1 ml) was placed into a tube, and the solvent was evaporated. The acid solutions were thermostated, added to the dry residue, let it to dissolve completely, after which the optical density of the solution was monitored in time using Hitachi U-2000, Hitachi U-3000, or SF-46 spectrophotometers. The trend in the concentration of the complex during dissociation was followed by the optical density of the long-wave absorption band.

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