

# Reactivity of Mixed Manganese Complexes with Porphyrins and Anionic Ligands. Effect of Modification of the Organic Part of the Molecule

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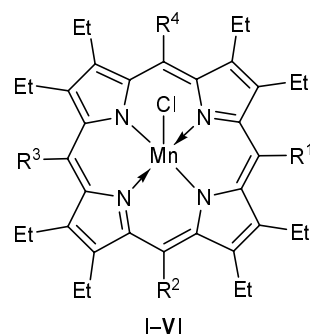
**Abstract**—Manganese(III) complexes with octaethyl-, 5-phenyloctaethyl-, 5,10- and 5,15-diphenyloctaethyl-, 5,10,15-triphenyloctaethyl-, and 5,10,15,20-tetraphenyloctaethylporphyrins were synthesized, and the kinetics and mechanism of their dissociation in mixed AcOH–H<sub>2</sub>SO<sub>4</sub> system were studied. The complete stability series of octaethylporphyrin manganese(III) complexes with increasing number of phenyl substituents at the *meso* positions of the porphyrin ligand was obtained.

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Porphyrins occupy a specific place in coordination chemistry as ligands possessing an extended aromatic system and maximal rigidity of the macrocyclic skeleton. Introduction of substituents into various positions of the porphyrin macroring changes both electronic and geometric structure of coordination compounds derived therefrom. In the recent time, much attention is given to nonplanar (so-called spatially distorted) porphyrin structures, for deformation of porphyrin ring is an effective tool ensuring control over physical, coordination, and catalytic properties of porphyrin metal complexes [1]. The kinetics and mechanisms of dissociation of copper(II) complexes with octaethylporphyrins characterized by increasing distortion of the macroring due to introduction of *meso*-phenyl substituents were studied in [2, 3]. It was found that the stability of these complexes sharply decreases as the number of *meso*-phenyl groups rises. In order to estimate the contribution of a substituent in the macroring to variation of the stability of the complex on stepwise substitution, we believed it necessary to perform analogous studies on complexes with metals having different valence electron shell structures and forming different kinds of dative bonds. It was also interesting to compare four-coordinate copper(II) complexes with mixed five-coordinate complexes containing an anionic ligand in addition to porphyrin. In the present work we studied the effect of increasing *meso*-phenyl substitution on the

kinetics and mechanism of dissociation and the stability of (octaethylporphyrinato)manganese(III). The dissociation of complexes I–VI was examined in mixed AcOH–H<sub>2</sub>SO<sub>4</sub> systems with different compositions at different temperatures.

Complexes I–VI are readily soluble in glacial acetic acid and are stable in solution; the electron absorption spectra of solutions of I–VI in glacial acetic acid do not change on storage and on heating. Complexes I–VI undergo dissociation in acetic acid in the presence of sulfuric acid. Figure 1 shows that the final dissociation product is the corresponding porphyrin dication which displays one strong absorption band in the long-wave region of the electron spectrum. The

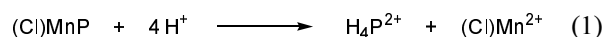


I, R<sup>1</sup> = R<sup>2</sup> = R<sup>3</sup> = R<sup>4</sup> = H; II, R<sup>1</sup> = Ph, R<sup>2</sup> = R<sup>3</sup> = R<sup>4</sup> = H;  
III, R<sup>1</sup> = R<sup>2</sup> = Ph, R<sup>3</sup> = R<sup>4</sup> = H; IV, R<sup>1</sup> = R<sup>3</sup> = Ph, R<sup>2</sup> = R<sup>4</sup> = H;  
V, R<sup>1</sup> = R<sup>2</sup> = R<sup>3</sup> = Ph, R<sup>4</sup> = H; VI, R<sup>1</sup> = R<sup>2</sup> = R<sup>3</sup> = R<sup>4</sup> = Ph.

**Table 1.** Apparent kinetic parameters of the dissociation of manganese(III) complexes I–VI with *meso*-phenyl-substituted octaethylporphyrins in mixed AcOH–H<sub>2</sub>SO<sub>4</sub> solvent

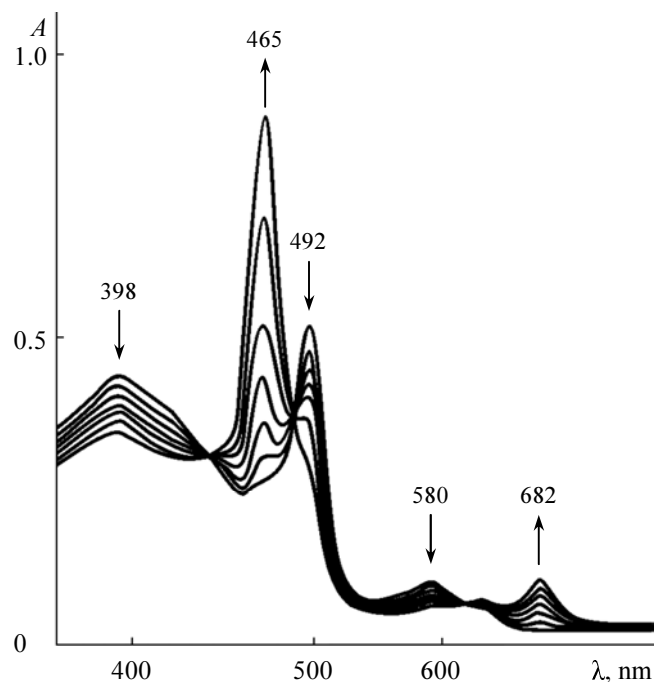
Complex	$c_{\text{H}_2\text{SO}_4}$ , M	$k^{298} \times 10^4$ , s <sup>-1</sup>	$E$ , kJ/mol	$\Delta S^\ddagger$ , J mol <sup>-1</sup> K <sup>-1</sup>
<b>I</b>	5.16	$(0.08 \pm 0.01) \times 10^{-2}$	116 ± 2	2 ± 6
	5.48	$(0.14 \pm 0.01) \times 10^{-2}$	114 ± 1	-1 ± 3
	5.80	$(0.50 \pm 0.05) \times 10^{-2}$	102 ± 2	-30 ± 6
	6.12	$(0.94 \pm 0.08) \times 10^{-2}$	99 ± 1	-35 ± 3
	6.44	$(1.25 \pm 0.10) \times 10^{-2}$	102 ± 1	-23 ± 3
<b>II</b>	4.73	0.41 ± 0.01	76 ± 2	-81 ± 6
	4.99	0.80 ± 0.02	71 ± 2	-93 ± 6
	5.26	2.70 ± 0.01	55 ± 1	-136 ± 3
	5.79	5.5 ± 0.2	47 ± 4	-157 ± 13
	6.05	7.9 ± 0.3	44 ± 1	-164 ± 3
<b>III</b>	0.66	0.92 ± 0.04	79 ± 1	-64 ± 3
	0.98	2.39 ± 0.06	92 ± 1	-13 ± 3
	1.15	4.1 ± 0.1	83 ± 1	-38 ± 3
	1.31	5.20 ± 0.06	72 ± 4	-73 ± 13
	1.64	11.9 ± 0.2	78 ± 2	-46 ± 6
	1.97	23.9 ± 1.7	69 ± 1	-71 ± 3
	2.62	0.84 ± 0.02	82 ± 1	-55 ± 3
<b>IV</b>	2.95	1.63 ± 0.08	70 ± 3	-90 ± 10
	3.28	3.4 ± 0.1	61 ± 5	-114 ± 16
	3.61	6.3 ± 0.3	63 ± 6	-102 ± 20
	3.93	11.0 ± 0.3	56 ± 2	-121 ± 6
	4.26	16.7 ± 0.6	57 ± 4	-114 ± 13
	4.99	22.00 ± 0.04	50 ± 4	-135 ± 13
<b>V</b>	0.019	2.11 ± 0.05	60 ± 3	-121 ± 10
	0.025	3.6 ± 0.03	60 ± 1	-117 ± 3
	0.032	5.41 ± 0.05	60 ± 1	-113 ± 3
	0.044	9.8 ± 0.1	56 ± 1	-122 ± 3
	0.057	16.3 ± 0.02	45 ± 2	-154 ± 6
<b>VI</b>	0.0018	2.6 ± 0.1	52 ± 1	-150 ± 3
	0.0024	4.0 ± 0.1	52 ± 1	-143 ± 3
	0.0027	5.0 ± 0.1	48 ± 1	-154 ± 3
	0.003	6.5 ± 0.2	50 ± 1	-145 ± 3
	0.0036	9.3 ± 0.3	47 ± 1	-152 ± 3
	0.0042	12.5 ± 0.3	43 ± 1	-163 ± 3

observed set of absorption curves gives rise to isobestic points which indicate the presence of two absorbing species, initial complex and the corresponding porphyrin dication.

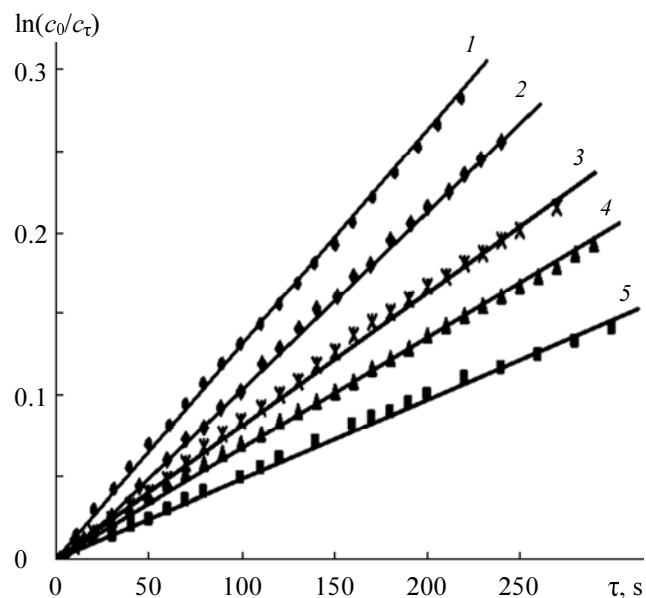


The parameter  $\ln[(A_0 - A_\infty)/(A_\tau - A_\infty)]$  [or  $\ln(c_0/c_\tau)$ ] is linear in  $\tau$ ; here,  $A_0$ ,  $c_0$ ,  $A_\tau$ ,  $c_\tau$ , and  $A_\infty$  are, respec-

tively, the optical densities of solutions and concentrations of porphyrin metal complex at the initial moment, at a time  $\tau$ , and at a time equal to  $\infty$ . These data suggest first order of reaction (1) with respect to the porphyrin metal complex (Fig. 2). The apparent rate constants for dissociation of the complexes and the corresponding activation parameters are given in Table 1. As follows from the data in Table 1, manganese(III)



**Fig. 1.** Variation of the electron absorption spectrum of complex VI during its dissociation in acetic acid containing 0.002 mol/l of sulfuric acid at 298 K;  $c_{VI} = 2 \times 10^{-5}$  M.



**Fig. 2.** Plots of  $\ln(c_0/c_\tau)$  versus time  $\tau$  for the dissociation of complexes (1) V, (2) II, (3) VI, (4) IV, and (5) III in mixed AcOH–H<sub>2</sub>SO<sub>4</sub> solvent. Sulfuric acid concentration, M: (3) 0.0042, (1) 0.057, (5) 1.64, (4) 3.61, (2) 4.73. Temperature, K: (5) 298, (1, 3, 4) 308, (2) 343. Approximation reliability  $R^2 > 0.98$ .

complexes with porphyrins having different numbers of *meso*-phenyl substituents dissociate in mixed solvents with different compositions and acidities. For each complex, the rate of dissociation increases as the

concentration of sulfuric acid in the mixed solvent rises. The complexes show different dependences of the reaction rate on the initial concentration of sulfuric acid in acetic acid. Complexes V and VI undergo dissociation at a sulfuric acid concentration of 0.0018 to 0.07 M and are characterized by nonlinear  $k_{ap}-f(c_{H_2SO_4})$  dependences (Fig. 3a, 3b), which are well described by power Eq. (2):

$$k_{ap} = const_1 (c_{H_2SO_4}^0)^{const_2}. \quad (2)$$

Here,  $k_{ap}$  is the apparent dissociation rate constant, and  $c_{H_2SO_4}^0$  is the initial concentration of sulfuric acid in acetic acid.

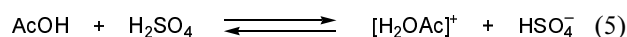
Comparison of Eq. (2) with the expression for the true rate constant [Eq. (3)] shows that  $const_1$  and  $const_2$  are, respectively, the true rate constant and the order of the reaction with respect to sulfuric acid.

$$k_{ap} = k (c_{H_2SO_4})^n. \quad (3)$$

On the basis of the experimental data,  $const_2$  in Eq. (2) was estimated at  $\sim 2$ , and the values of  $const_1$  ( $k$ ) are given in Table 2. Plotting the dependence given by Eq. (2) in log coordinates also gives a reaction order  $n$  close to 2. Thus the rate of dissociation of complexes V and VI can be expressed by Eq. (4).

$$-\partial c_{(Cl)MnP} / \partial \tau = k c_{(Cl)MnP} (c_{H_2SO_4}^0)^2. \quad (4)$$

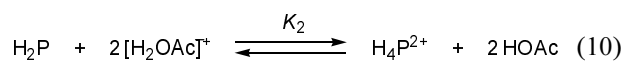
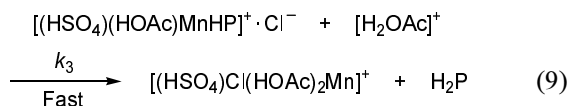
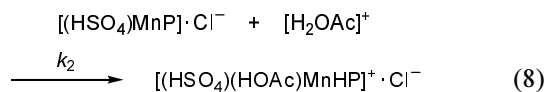
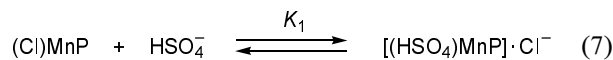
Presumably, at low sulfuric acid concentrations which are sufficient for dissociation of complexes V and VI (Table 1), all sulfuric acid molecules are ionized, so that equilibrium (5) is displaced to the right.



Taking this assumption into account, kinetic Eq. (4) may be rewritten as

$$-\partial c_{(Cl)MnP} / \partial \tau = k c_{(Cl)MnP} (c_{[H_2OAc]^+})^2. \quad (6)$$

Equation (6) is consistent with the stoichiometric dissociation mechanism including reactions (7)–(10). In the first stage [reaction (7)], equilibrium establishes in the replacement of anionic ligand (Cl<sup>−</sup>) by HSO<sub>4</sub><sup>−</sup> ion which is present in excess, and Cl<sup>−</sup> ion is likely to be held in the field of the metal cation via electrostatic forces. The subsequent stages involve irreversible dissociation of the covalent Mn–N bonds. The rate of the limiting stage is described by Eq. (11).



$$-\partial c_{[(HSO_4)MnP] \cdot Cl^-} / \partial \tau = k_2 c_{[(HSO_4)MnP] \cdot Cl^-} c_{[H_2OAc]^+} \quad (11)$$

By expressing the concentration  $c_{[(HSO_4)MnP] \cdot Cl^-}$  through the constant of equilibrium (7) we obtain Eq. (12) for the rate of the limiting stage.

$$\begin{aligned} -\partial c_{[(HSO_4)MnP] \cdot Cl^-} / \partial \tau &= -\partial c_{(X)MnP} / \partial \tau \\ &= k_2 c_{[H_2OAc]^+} K_1 c_{(Cl)MnP} c_{(HSO_4)^-} \end{aligned} \quad (12)$$

Taking into account a large excess of  $H_2SO_4$  with respect to  $(Cl)MnP$  and the state of equilibrium (5) (see above),

$$c_{(HSO_4)^-} \approx c_{[H_2OAc]^+} \quad (13)$$

Then

$$-\partial c_{(Cl)MnP} / \partial \tau = k_2 K_1 c_{(Cl)MnP} (c_{[H_2OAc]^+})^2 \quad (14)$$

Equations (6) and (14) are similar; this means that our conclusions and the proposed mechanism of dissociation of complexes **V** and **VI** are valid.

Dissociation of complexes **I–IV** requires a higher concentration of  $H_2SO_4$  (Table 1), and the dependence  $k_{ap} - f(c_{H_2SO_4}^0)$  is nonlinear as well. We observed a linear correlation between  $\log k_{ap}$  and the solvent acidity function  $H_0$  at 298 K [4], the slope being close to 2 (Fig. 4).

Insofar as the range of sulfuric acid concentration in acetic acid, corresponding to dissociation of complexes **I–IV**, is relatively narrow, the product of activity coefficients  $P\gamma_i$  in the equation  $H_0 = -\log h_0 P\gamma_i$  may be assumed to be constant. Then the kinetic equation for dissociation of complexes **I–IV** will include the overall acidity  $h_0$ :

$$-\partial c_{(Cl)MnP} / \partial \tau = k' c_{(Cl)MnP} h_0^2 \quad (15)$$

Here,  $h_0$  is the acidity of the medium, and  $k' = kP\gamma_i$ .

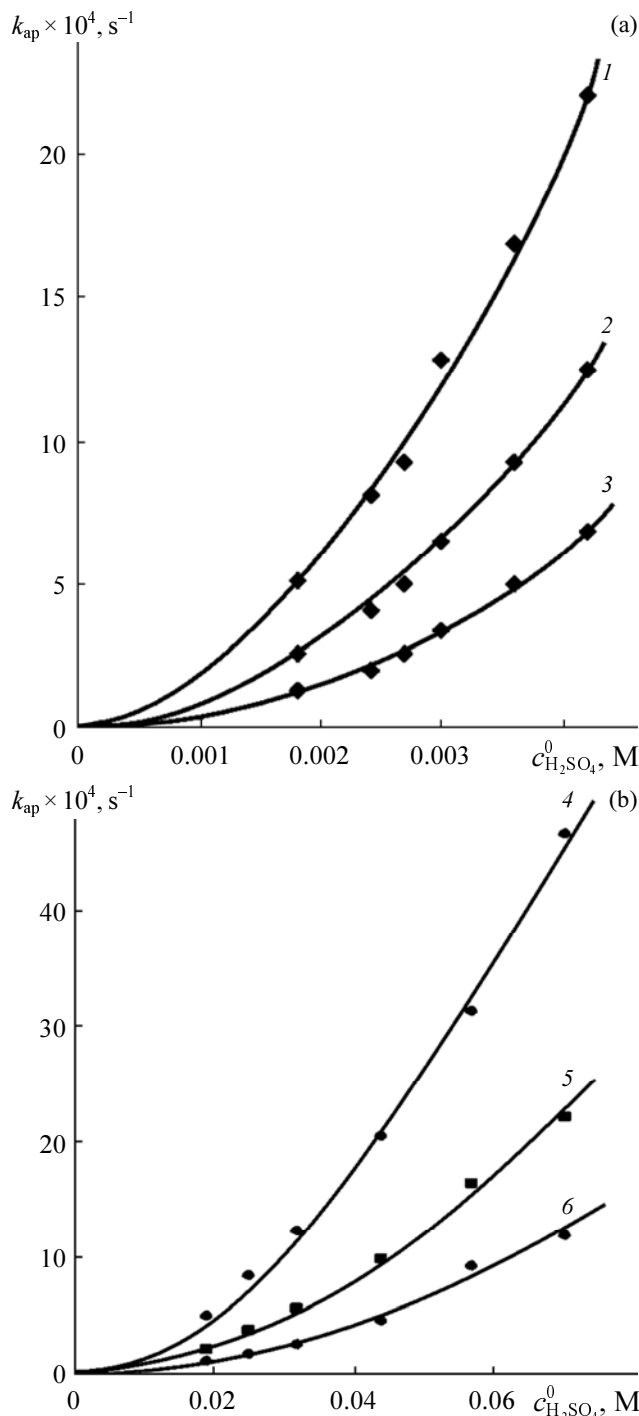
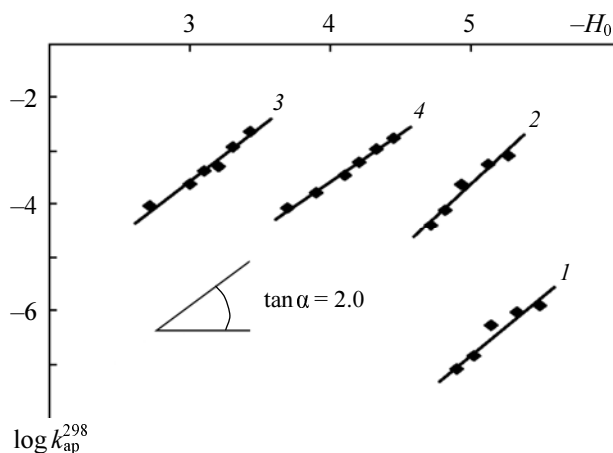


Fig. 3. Plots of the apparent rate constants for dissociation of complexes (a) **V** and (b) **VI** versus initial concentration of sulfuric acid in acetic acid at (1, 4) 308, (2, 5) 298, and (3, 6) 288 K. Approximation reliability  $R^2 > 0.99$ .

A satisfactory linear correlation between  $\log k_{ap}^{298}$  and  $H_0$  and the second order of reaction with respect to  $h_0$  were found previously for the complexes  $(Cl)MnTPP$ ,  $(Cl)RhTPP$ ,  $(AcO)MnTPP$ , and  $(AcO)MnTPP(X)_4$  ( $X = p\text{-Br}, p\text{-F}, p\text{-OMe}$ ) [5]. The overall acidity of mixtures



**Fig. 4.** Semilog plots of the apparent rate constants for dissociation at 298 K of complexes (1) **I**, (2) **II**, (3) **III**, and (4) **IV** versus acidity function of mixed AcOH–H<sub>2</sub>SO<sub>4</sub> solvent. Approximation reliability  $R^2$ : (1, 2) 0.92, (3) 0.97, (4) 0.99.

of acetic and sulfuric acids with a sufficiently high concentration of the latter is determined by the presence of  $[\text{H}_2\text{OAc}]^+$ ,  $\text{H}_3\text{SO}_4^+$ ,  $\text{H}_2\text{SO}_4$ , and  $\text{HOAc}$  species and ion pairs [4], for in this case equilibrium (5) is not displaced toward ionization products and autoprotolysis of  $\text{H}_2\text{SO}_4$  becomes appreciable due to its high concentration. Unlike labile complexes **V** and **VI** which dissociate in the presence of  $\text{H}_2\text{SO}_4$  at a fairly small concentration, dissociation of stable complexes **I–IV** is likely to involve all species possessing acidic properties, which are present in solution at different concentrations. Presumably, the mechanism of dissociation of such complexes is analogous to that considered above [reactions (7)–(10)]. This is confirmed by the experimental kinetic equation (15).

The data in Tables 1 and 2 show that the kinetic stability of the complexes under study decreases as the number of *meso*-phenyl substituents increases:



The rate of dissociation of complex **I** at a sulfuric acid concentration in acetic acid of 5.8 M (298 K) is lower by 3 orders of magnitude than the rate of dissociation of its monophenyl-substituted analog **II**. Complexes **II–VI** dissociate at 298 K at comparable rates when the concentration of sulfuric acid is 5.8, 1.3, 3.6, 0.032, and 0.0027 M, respectively. The values of  $k'$  calculated by Eq. (15) are  $1.6 \times 10^{-17}$ ,  $2.5 \times 10^{-14}$ ,  $2.5 \times 10^{-12}$ , and  $2.7 \times 10^{-10} \text{ l}^2 \text{ mol}^{-2} \text{ s}^{-1}$  for complexes **I**, **II**, **IV**, and **III**, respectively.

The stability series (16) is characterized by increase in the red shift of absorption bands in the electronic spectra of the complexes in  $\text{CHCl}_3$ . Probably, decrease in their kinetic stability is related to electron-acceptor effect of the *meso*-phenyl substituents on the macro-ring, which weakens coordination bonding, i.e.,  $\sigma$ - and dative  $\text{N} \rightarrow \text{Mn} \pi$ -bonds, which are guided in the same direction (in manganese complexes). On the whole, this statement is consistent with variations in the activation energy. Electron-acceptor properties of phenyl groups in porphyrins were confirmed by quantum-chemical calculations [6]. Introduction of one *meso*-phenyl substituent into an octaethylporphyrin complex with conservation of the planar macro-ring structure (as in metal-free porphyrin and its copper complex [1, 2]) sharply reduces the energy of activation (Tables 1 and 2). Further substitution at the *meso*-carbon atoms leads to increasing deformation of the macro-ring [1], which should hamper effective conjugation and transmission of electronic effect of the phenyl groups to the dative  $\text{N} \rightarrow \text{Mn} \pi$ -bonds; as a result, the energy of activation slightly increases. In addition, complexes **V** and **VI** characterized by maximal distortion of the macro-ring give rise to a less rigid transition state than that derived from their analog having no substituents in the *meso*-positions; such transition state should be solvated to a stronger extent, and the value of  $\Delta S^\ddagger$  should become appreciably more negative. Complex **III** with unsymmetrically substituted diphenylporphyrin is con-

**Table 2.** True kinetic parameters of the dissociation of manganese(III) complexes **V** and **VI** with *meso*-phenyl-substituted octaethylporphyrins in mixed AcOH–H<sub>2</sub>SO<sub>4</sub> solvent

Complex	$c_{\text{H}_2\text{SO}_4}$ , M	Temperature, K	$k$ , $\text{l}^2 \text{ mol}^{-2} \text{ s}^{-1}$	$E$ , kJ/mol	$\Delta S^\ddagger$ , $\text{J mol}^{-1} \text{ K}^{-1}$
<b>V</b>	0.019–0.070	288	$0.25 \pm 0.02$	61 ± 3	–53 ± 10
		298	$0.55 \pm 0.03$		
		308	$1.3 \pm 0.1$		
<b>VI</b>	0.0018–0.0042	288	$36.0 \pm 2.3$	48 ± 1	–56 ± 3
		298	$69.0 \pm 0.6$		
		308	$134.1 \pm 9.2$		

siderably less stable than its symmetric isomer **IV**; presumably, the reason is stronger distortion of the macroring in **III**. The apparent energy and entropy of activation for dissociation of complex **III** are higher.

An analogous kinetic stability series was revealed by us previously for copper complexes with octaethylporphyrins having different numbers of *meso*-phenyl substituents [2]; however, the stabilities of copper(II) and manganese(III) complexes with the same porphyrin ligand are different. The rates of dissociation of copper(II) and manganese(III) complexes with octaethylporphyrin at 343 K are similar at  $c_{\text{H}_2\text{SO}_4}^0 = 0.10$  and 6.12 M, respectively; the complexes with triphenyloctaethylporphyrin dissociate at 298 K at equal rates at a sulfuric acid concentration of  $2.5 \times 10^{-4}$  and  $3.2 \times 10^{-2}$  M, respectively (Table 1) [2]. Unlike manganese(III) complex with 5,10,15,20-tetraphenyloctaethylporphyrin, the corresponding copper(II) complex undergoes dissociation even in glacial acetic acid. Presumably, the manganese(III) complexes are more stable due to the presence of extra anionic ligand (Cl<sup>-</sup>) which interacts with the Mn–N bonds, so that the energy required for dissociation increases for stereochemical reasons.

We can conclude that multiple substitution changes the stability of porphyrin metal complexes and makes the mechanism of their dissociation specific due to both electronic effects of the substituents and distortion of the macroring structure, the latter factor considerably increasing in going to porphyrin complexes with high-charged metal ions.

## EXPERIMENTAL

The electronic absorption spectra were recorded on Hitachi U-2000 and SF-26 spectrophotometers. *meso*-Phenyl-substituted octaethylporphyrins were synthesized by the procedures described in [3] and were kindly provided by Prof. A.S. Semeikin. Complexes **I–VI** were prepared by reaction of MnCl<sub>2</sub>·4H<sub>2</sub>O of analytical grade with the corresponding porphyrin in boiling DMF (reaction time 20–30 min). The reaction mixture was diluted with an equal volume of water and extracted with chloroform, the extract was repeatedly washed with water to remove excess manganese salt and DMF, and the complex was purified from the unreacted ligand and its partial decomposition products by column chromatography on Al<sub>2</sub>O<sub>3</sub> (Brockmann activity grade II) using chloroform as eluent. After repeated chromatography, the electron absorption spectrum of the isolated complex did not change on subsequent chromatographic treatment.

Solutions of sulfuric acid in acetic acid with required concentrations were prepared from 100% sulfuric acid and acetic acid of chemically pure grade. Acetic acid was dehydrated by repeated defrosting; 100% sulfuric acid was prepared from 60% oleum and commercial sulfuric acid of chemically pure grade by conductometry.

The rate of dissociation of the complexes was measured by spectrophotometry. Solutions of complexes in a special spectrophotometric cell were maintained at a constant temperature within  $\pm 0.1$  K using a water thermostat. The apparent rate constants  $k_{\text{ap}}$  were optimized by treatment of linear dependences in appropriate coordinates by the least-squares procedure using Microsoft Excel program. The values of  $k_{\text{ap}}$  for complexes **I** and **II** at 298 K were determined from the  $\log k_{\text{ap}} - 1/T$  dependences.

The apparent and true energies of activation ( $E'$  and  $E$ ) were determined by optimization of the linear dependences  $\log k_{\text{ap}} - 1/T$  and  $\log k - 1/T$ , respectively, by the least-squares procedure. The entropy of activation  $\Delta S^\ddagger$  was calculated from the principal equation of the transition state theory, reduced to the following form:

$$\Delta S^\ddagger = 19.1 \log k^T + E/T - 19.1 \log T - 205. \quad (17)$$

Here,  $k^T$  is the dissociation rate constant at a temperature  $T$ . Likewise, the apparent values ( $\Delta S^\ddagger$ ) were determined from  $k_{\text{ap}}^T$ .

**Chloro(2,3,7,8,12,13,17,18-octaethylporphyrinato)manganese(III) (I).** Electronic absorption spectrum,  $\lambda_{\text{max}}$ , nm ( $\log \epsilon$ ): in CHCl<sub>3</sub>: 357 (4.87), 428 (4.17), 473 (4.68), 559 (4.01), 590 (3.76); in AcOH: 368 (4.86), 425 (4.16), 466 (4.45), 549 (3.95). IR spectrum (KBr), cm<sup>-1</sup>: 728, 749  $\gamma(\text{C}_\beta\text{-C})$ ; 841  $\gamma(\text{C-H}_{\text{meso}})$ ; 962, 989, 1019  $\delta(\text{C-H}_{\text{py}})$ ; 1055  $\delta(\text{C}_\beta\text{-C})$ ; 1062, 1112, 1148, 1272 (skeletal vibrations of macroring); 1315  $\nu(\text{C-N})$ ; 1373, 1386, 1451, 1464, 1480  $\delta(\text{CH}_3)$  and  $\delta(\text{CH}_2)$ ; 1604, 1632 (skeletal vibrations of pyrrole rings); 2931  $\nu(\text{CH}_2)$ ; 2872, 2966  $\nu(\text{CH}_3)$ .

**Chloro(2,3,7,8,12,13,17,18-octaethyl-5-phenylporphyrinato)manganese(III) (II).** Electronic absorption spectrum,  $\lambda_{\text{max}}$ , nm ( $\log \epsilon$ ): in CHCl<sub>3</sub>: 362 (4.51), 428 (3.75), 476 (4.37), 565 (3.70), 594 sh; in AcOH: 372 (4.54), 424 sh, 465 (4.23), 549 (3.65), 580 sh. IR spectrum (KBr), cm<sup>-1</sup>: 668, 706, 717  $\gamma(\text{C-H}_{\text{ph}})$ ; 735, 745  $\gamma(\text{C}_\beta\text{-C})$ ; 759  $\gamma(\text{C-H}_{\text{py}})$ ; 838  $\gamma(\text{C-H}_{\text{meso}})$ ; 982, 1004  $\delta(\text{C-H}_{\text{py}})$ ; 1034, 1057  $\delta(\text{C}_\beta\text{-C})$ ; 874, 1106, 1119, 1142, 1156, 1269 (skeletal vibrations of macroring); 1324  $\nu(\text{C-N})$ ; 1384, 1399, 1451, 1465, 1497  $\delta(\text{CH}_3)$  and

$\delta(\text{CH}_2)$ ; 1561  $\nu(\text{C}=\text{C}_{\text{Ph}})$ ; 1601, 1631 (skeletal vibrations of pyrrole rings); 2852, 2923  $\nu(\text{CH}_2)$ ; 2870, 2963  $\nu(\text{CH}_3)$ ; 3021, 3057  $\nu(\text{C}-\text{H}_{\text{Ph}})$ .

**Chloro(2,3,7,8,12,13,17,18-octaethyl-5,10-diphenylporphyrinato)manganese(III) (III).** Electronic absorption spectrum,  $\lambda_{\text{max}}$ , nm ( $\log \epsilon$ ): in  $\text{CHCl}_3$ : 370 (4.41), 481 (4.36), 571 (3.55), 606 sh; in AcOH: 381 (4.55), 475 (4.31), 559 (3.57), 596 sh. IR spectrum (KBr),  $\text{cm}^{-1}$ : 703  $\gamma(\text{C}-\text{H}_{\text{Ph}})$ ; 744  $\gamma(\text{C}_{\beta}-\text{C})$ ; 760  $\gamma(\text{C}-\text{H}_{\text{Py}})$ ; 961, 989, 1003, 1021  $\delta(\text{C}-\text{H}_{\text{Py}})$ ; 1055  $\delta(\text{C}_{\beta}-\text{C})$ ; 1071, 1112, 1140, 1161, 1259, 1281 (skeletal vibrations of macroring); 1314  $\nu(\text{C}-\text{N})$ ; 1376, 1384, 1401, 1444, 1465, 1494  $\delta(\text{CH}_3)$  and  $\delta(\text{CH}_2)$ ; 1556  $\nu(\text{C}=\text{C}_{\text{Ph}})$ ; 1603, 1632 (skeletal vibrations of pyrrole rings); 2850, 2920  $\nu(\text{CH}_2)$ ; 2869, 2964  $\nu(\text{CH}_3)$ ; 3060  $\nu(\text{C}-\text{H}_{\text{Ph}})$ .

**Chloro(2,3,7,8,12,13,17,18-octaethyl-5,15-diphenylporphyrinato)manganese(III) (IV).** Electronic absorption spectrum,  $\lambda_{\text{max}}$ , nm ( $\log \epsilon$ ): in  $\text{CHCl}_3$ : 365 (4.80), 428 (4.10), 478 (4.72), 569 (4.02), 614 sh; in AcOH: 375 (4.88), 428 sh, 472 (4.63), 559 (3.94). IR spectrum (KBr),  $\text{cm}^{-1}$ : 450  $\nu(\text{Mn}-\text{N})$ ; 670, 702, 707, 714  $\gamma(\text{C}-\text{H}_{\text{Ph}})$ ; 744  $\gamma(\text{C}_{\beta}-\text{C})$ ; 763  $\gamma(\text{C}-\text{H}_{\text{Py}})$ ; 838, 846  $\gamma(\text{C}-\text{H}_{\text{meso}})$ ; 981, 1001  $\delta(\text{C}-\text{H}_{\text{Py}})$ ; 1053  $\delta(\text{C}_{\beta}-\text{C})$ ; 879, 1080, 1103, 1122, 1140, 1158, 1255, 1281 (skeletal vibrations of macroring); 1308  $\nu(\text{C}-\text{N})$ ; 1383, 1392, 1446, 1472, 1483  $\delta(\text{CH}_3)$  and  $\delta(\text{CH}_2)$ ; 1500, 1542  $\nu(\text{C}=\text{C}_{\text{Ph}})$ ; 1599 (skeletal vibrations of pyrrole rings); 2928  $\nu(\text{CH}_2)$ ; 2870, 2966  $\nu(\text{CH}_3)$ ; 3015, 3053  $\nu(\text{C}-\text{H}_{\text{Ph}})$ .

**Chloro(2,3,7,8,12,13,17,18-octaethyl-5,10,15-triphenylporphyrinato)manganese(III) (V).** Electronic absorption spectrum,  $\lambda_{\text{max}}$ , nm ( $\log \epsilon$ ): in  $\text{CHCl}_3$ : 374 (4.36), 488 (4.42), 583 (3.55), 616 sh; in AcOH: 389 (4.40), 485 (4.31), 567 (3.57), 612 sh. IR spectrum (KBr),  $\text{cm}^{-1}$ : 452  $\nu(\text{Mn}-\text{N})$ ; 702, 708  $\gamma(\text{C}-\text{H}_{\text{Ph}})$ ; 743  $\gamma(\text{C}_{\beta}-\text{C})$ ; 750, 767  $\gamma(\text{C}-\text{H}_{\text{Py}})$ ; 960, 985, 1008, 1020  $\delta(\text{C}-\text{H}_{\text{Py}})$ ; 1053  $\delta(\text{C}_{\beta}-\text{C})$ ; 880, 891, 1114, 1152, 1180, 1252, 1298 (skeletal vibrations of macroring); 1311  $\nu(\text{C}-\text{N})$ ; 1376, 1444, 1464, 1481  $\delta(\text{CH}_3)$  and  $\delta(\text{CH}_2)$ ; 1518, 1540  $\nu(\text{C}=\text{C}_{\text{Ph}})$ ; 1598 (skeletal vibrations of pyrrole rings); 2923  $\nu(\text{CH}_2)$ ; 2851, 2951  $\nu(\text{CH}_3)$ ; 3010, 3047  $\nu(\text{C}-\text{H}_{\text{Ph}})$ .

**Chloro(2,3,7,8,12,13,17,18-octaethyl-5,10,15,20-tetraphenylporphyrinato)manganese(III) (VI).** Electronic absorption spectrum,  $\lambda_{\text{max}}$ , nm ( $\log \epsilon$ ): in

$\text{CHCl}_3$ : 378 (4.54), 495 (4.67), 593 (3.75), 625 sh; in AcOH: 397 (4.57), 492 (4.63), 577 (3.81), 614 sh. IR spectrum (KBr),  $\text{cm}^{-1}$ : 452  $\nu(\text{Mn}-\text{N})$ ; 702  $\gamma(\text{C}-\text{H}_{\text{Ph}})$ ; 744  $\gamma(\text{C}_{\beta}-\text{C})$ ; 764, 796  $\gamma(\text{C}-\text{H}_{\text{Py}})$ ; 958, 978, 1008  $\delta(\text{C}-\text{H}_{\text{Py}})$ ; 1052  $\delta(\text{C}_{\beta}-\text{C})$ ; 876, 1073, 1161, 1180, 1244 (skeletal vibrations of macroring); 1317  $\nu(\text{C}-\text{N})$ ; 1364, 1456, 1465, 1479  $\delta(\text{CH}_3)$  and  $\delta(\text{CH}_2)$ ; 1501, 1538, 1558  $\nu(\text{C}=\text{C}_{\text{Ph}})$ ; 1597 (skeletal vibrations of pyrrole rings); 2844, 2923  $\nu(\text{CH}_2)$ ; 2860, 2968  $\nu(\text{CH}_3)$ ; 3008, 3052  $\nu(\text{C}-\text{H}_{\text{Ph}})$ .

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