

PHYSICAL METHODS  
OF INVESTIGATION

Synthesis, Chemical Stability, and Electrocatalytic Properties  
of Zinc(II) and Cobalt(II) Complexes  
of N-Methyltetraphenylporphine

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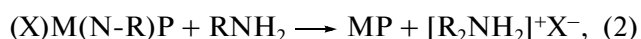
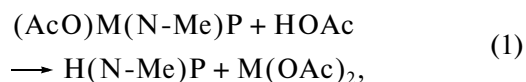
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**Abstract**—Distortion of flat ligand structure in metal complexes of porphyrins caused by N-methyl substitution considerably decreases the kinetic stability of these compounds in DMSO–HOAc proton-releasing medium ((AcO)Zn(N-Me)TPP (**Ib**) < (AcO)Co<sup>II</sup>(N-Me)TPP (**Ia**) < ZnTPP (**Ib**) < Co<sup>II</sup>TPP (**IIa**)) and their resistance to thermal destruction in crystal state {(AcO)Co<sup>II</sup>(N-Me)TPP (**Ia**) < (AcO)Zn(N-Me)TPP (**Ib**) < H(N-Me)TPP (**I**) < H<sub>2</sub>TPP (**II**) < Co<sup>II</sup>TPP (**IIa**) < ZnTPP (**Ib**)}, however, exerts a positive effect on the electrocatalytic activity of the compounds in the electroreduction of molecular oxygen, which changes in the following order: **II** < **I** < **IIa** < **Ib** << **Ia**. It was proved by thermogravimetry and electron spectroscopy that N-substituted metal complexes with Zn(II) and Co(II), in contrast to the corresponding ligands, undergo dealkylation to form metal porphyrins (MP) when heated above 200°C under both an inert and air oxygen atmosphere.

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N-substituted analogs of porphyrins (H(N-Me)TPP (**I**)) are strongly nonplanar molecules where macrocycle distortion is achieved by the introduction of bulky intracyclic substituent (R-) at the N atom, while nonplanarity extent is controlled by the size of R and aromaticity of initial unsubstituted porphyrin (for example, H<sub>2</sub>TPP (**II**)) [1–8]. The distortion leads to electron density redistribution and macrocycle polarization [6], changes the hybrid state of substituted nitrogen atom, and sharply changes complexes reactivity [1, 2, 5, 7, 8]. A change in molecular structure considerably affects the resistance of N-substituted ligands H(N-R)P and their complexes (X)M(N-R)P toward different physical factors and chemical reagents. Thus, the complexes with N-substituted ligands are known to be unstable, the most stable complexes undergo dissociation when exposed to protons of acids (1) even at pH > 3 [1, 9]. In the medium of organic bases such as aliphatic amines, (X)M(N-R)P undergo nucleophilic substitution reactions (2) and eliminate N-substituent [1], whereas their ligands do not undertake dealkylation. The authors [7] supposed similar dealkylation process takes place also in the initial stage of thermo-oxidative destruction (3) of N-substituted metal complexes. However, no products of reaction (3) were identified by spectral methods, it

was also unclear whether the presence of atmospheric oxygen affects the stage of thermal destruction (3).

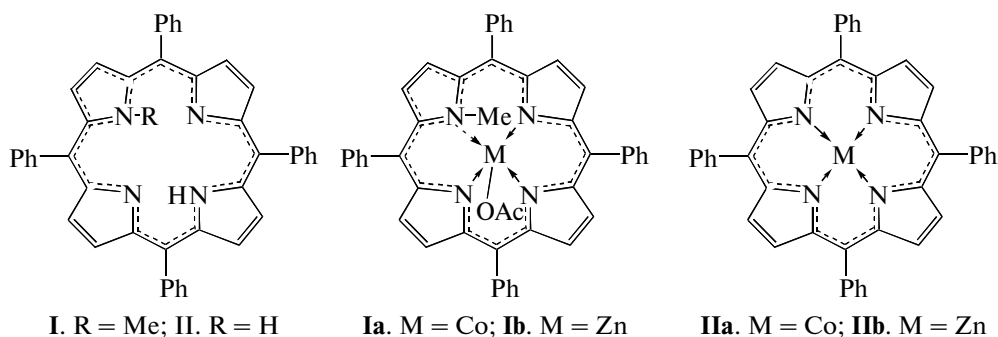


The interest in N-substituted porphyrins is caused by not only their high biological activity [1] but also the ability of N-substituted porphyrins to stabilize metal ions in the lowest oxidation states [8–10], which can be used, for example, in metal-complex catalysis and electrocatalysis of chemical processes [11]. To assess the applicability of N-substituted compounds for practical applications, one needs information on their stability under different conditions, which is not available in the literature [7, 8].

Therefore, with the aim to analyze the effect of N-methylation and metal nature in (X)M(N-R)P on the physicochemical properties of macroheterocycles, we synthesized zinc(II) and cobalt(II) complexes of N-methyltetraphenylporphyrin (compounds **Ia** and **Ib**) and studied their stability toward dissociation in solutions containing proton-releasing component and in solid state under polythermal conditions (thermal

destruction and thermo-oxidation) by chemical kinetics and thermogravimetry, respectively; moreover, we obtained data on the catalytic activity of the com-

pounds in the electroreduction of molecular oxygen using cyclic voltammetry (CVA).



## EXPERIMENTAL

H(N-Me)TPP (**I**) was obtained by direct alkylation of unsubstituted tetraphenylporphyrin (H<sub>2</sub>TPP, **II**) with dimethyl sulfate in refluxing *o*-xylene in the presence of K<sub>2</sub>CO<sub>3</sub> [12]. Its complexes with cobalt(II) and zinc(II) (compounds **Ia** and **Ib**) were prepared by reacting the ligand with tenfold molar excess of the corresponding metal acetate on slight heating (50°C) in DMF solution for 30 min [1, 7]. Next, the reaction mixture was cooled, diluted with water, and the complex was extracted with chloroform. The reaction was monitored by spectrophotometry (electronic absorption spectrum), the purity and individuality of the compounds were monitored by thin layer chromatography (silica, CHCl<sub>3</sub>). The yield of complexes (AcO)Co<sup>II</sup>(N-Me)TPP (**IIa**) and (AcO)Zn(N-Me)TPP (**IIb**) was 83 and 61%, respectively.

Thermogravimetric study was performed on a DSC 204 F1 differential scanning calorimeter equipped with a NETZSCH TG 209 F1 Iris thermobalances (Germany). A weighed ~5-mg crystalline sample was placed into a platinum crucible and heated under a static argon atmosphere at a rate of 10 K/min in the range 298–1223 K. The studied samples were dried for several hours in vacuum (<1 mmHg) at ambient temperature prior to experiment.

The kinetics of dissociation reaction (1) for complex **Ia** was registered spectrophotometrically in HOAc–DMSO medium according to the previously described procedure [13].

The active masses of catalyst based on compounds **I**, **Ia**, and **Ib** as well as electrochemical and electrocatalytic studies were performed by the previously described procedure [14] using cyclic voltammetry (CV) in 0.1 M KOH (reagent grade) aqueous solution upon its saturation with argon or oxygen. The values of redox potentials of working graphite electrode coated with a layer of catalytically active paste ( $E_{\text{red/ox}}$  =

$\frac{E_{\text{car}} + E_{\text{an}}}{2}$ ) were determined from voltammetric curves recorded in the range from –1.5 to 0.5 V as average from the series of 5–6 parallel experiments. Relative error in  $E_{\text{red/ox}}$  determination was not higher 3%.

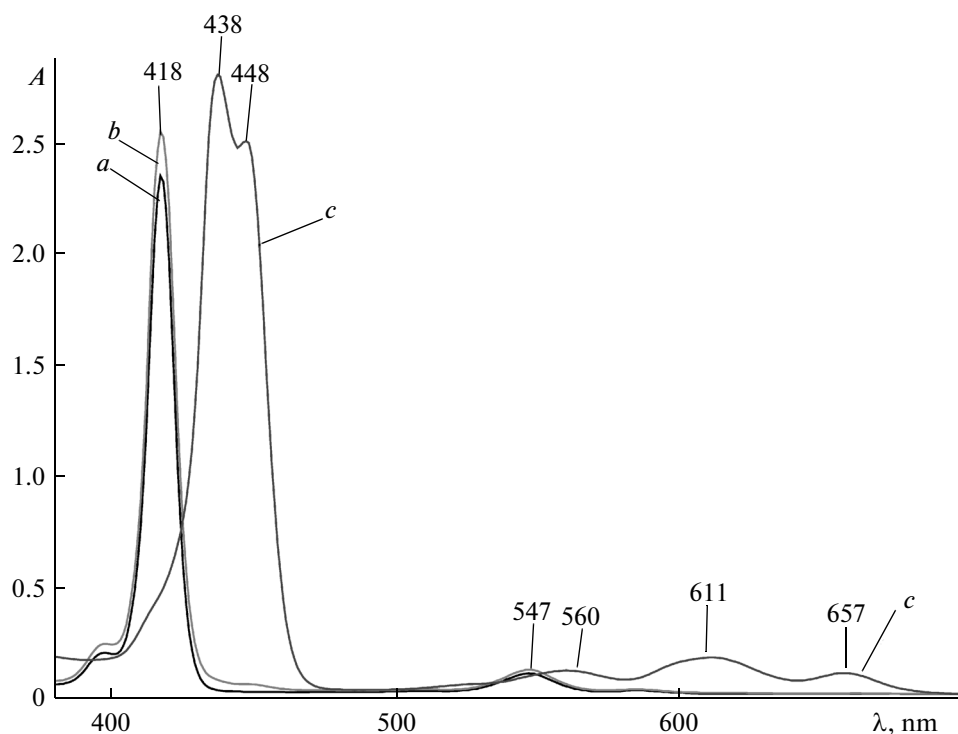
Organic solvents (CHCl<sub>3</sub> (reagent grade), DMF (analytical grade), HOAc (pure grade), DMSO (analytical grade)), and water used in experiment were purified according to recommendations [15].

Obtained experimental results and calculation data are represented in Tables 1–3 and Figs. 1–4.

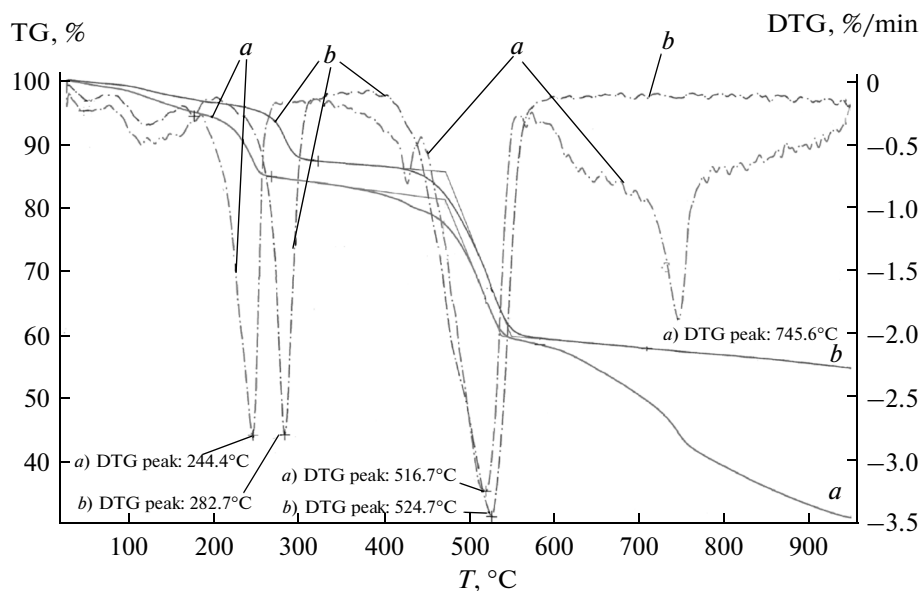
## RESULTS AND DISCUSSION

N-Substituted porphyrin analogs produce several types of complexes, simple and bridging including. Simple chelate N-substituted metal derivatives {(X)M(N-R)P}, like metal porphyrins (MP), form only from <sup>21</sup>N-monosubstituted ligands, for example, compound **I** [1]. The feature of H(N-R)P ligands is their ability to produce complexes with metals in oxidation states that are unstable for MP itself (Co(II), Mn(II), Fe(II)) [1, 8]. The N-substituted ligand in fact is a tridentate and forms formally one covalent and two strong coordination bonds with metal in the complexes. The second metal covalence is compensated due to acido ligand X. The bond of metal with the substituted nitrogen atom, which seems to be in *p*<sup>3</sup> valence state [1, 2, 5, 8], is the weakest coordination bond of aminne type ( $l(\text{M}-\text{N}) = 2.26\text{--}2.80 \text{ \AA}$  [1]).

In the context of monoanionic structure of the N-substituted ligand, one should expect that its complexes will be reactive in the processes of substitution of charged extra ligand X<sup>–</sup> (OAc<sup>–</sup> in our case). However, as we showed previously [5, 8, 18], solvent nature has no considerable effect on the position and intensity of bands in electronic absorption spectra and fluorescence emission for complexes, in particular, in coordinating and non-coordinating solvents. The



**Fig. 1.** Electronic absorption spectra of zinc complexes with porphyrins **I** and **II** in  $\text{CHCl}_3$  solution: ZnTPP (*a*) obtained by heating of  $(\text{AcO})\text{Zn}(\text{N-Me})\text{TPP}$  (*c*) up to  $300^\circ\text{C}$  and direct chemical synthesis (*b*).

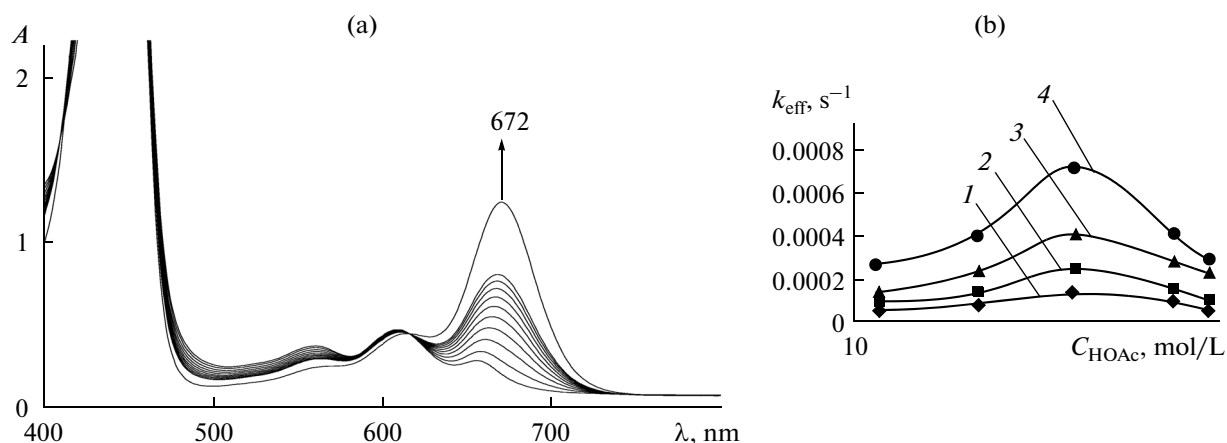


**Fig. 2.** Derivatogram of complexes: *a*,  $(\text{AcO})\text{Co}(\text{N-Me})\text{TPP}$  (**Ia**); *b*,  $(\text{AcO})\text{Zn}(\text{N-Me})\text{TPP}$  (**IIa**) under argon atmosphere (TG, solid line; DTG, dashed line).

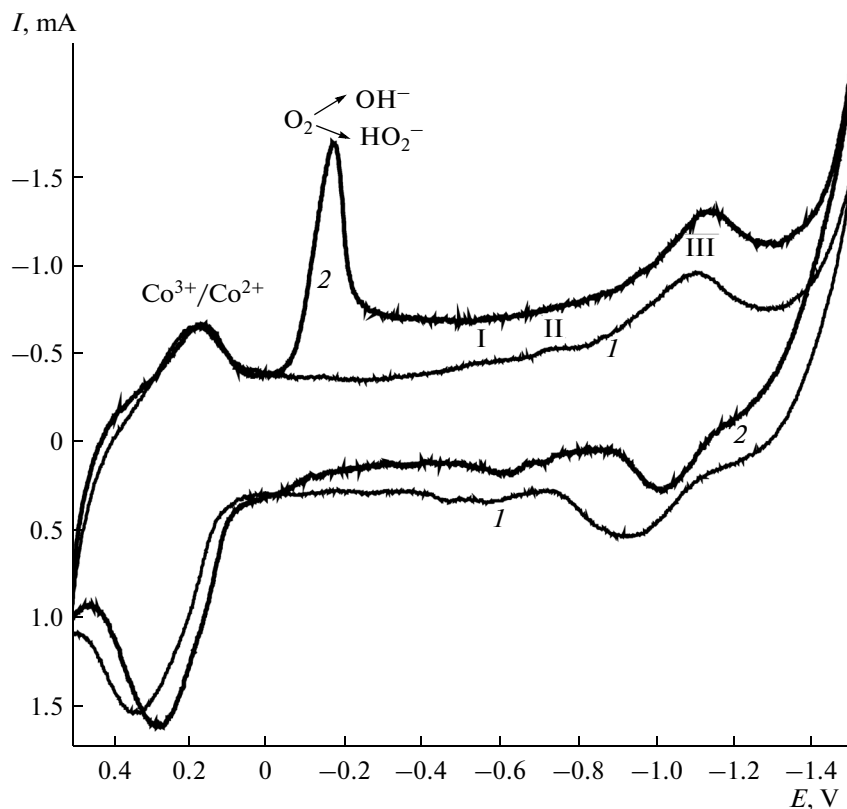
electronic absorption spectra of complexes **Ia** and **Ib** retain three-band structure in the region 550–700 nm, in contrast to unsubstituted MPs, which show two bands (500–600 nm) and characteristic split Soret band at 430–450 nm (Fig. 1).

As would be expected, the methylation of the central nitrogen atom in the macrocycle **II** leads to a con-

siderable (by  $50^\circ\text{C}$  under inert (argon) atmosphere and by  $150^\circ\text{C}$  under air oxygen atmosphere [7]) decrease of onset degradation temperature ( $T_0$ ) for porphyrin (Table 1). Under thermal degradation conditions in the absence of  $\text{O}_2$ , this is mainly caused by the localization of  $\pi$  bonds in the macrocycle due to decrease in its aromaticity (which is small as evidenced



**Fig. 3.** (a) Alteration of electronic absorption spectrum of  $(\text{AcO})\text{Co}^{\text{II}}(\text{N-Me})\text{TPP}$  complex in the course of dissociation in DMSO–HOAc solution ( $\Delta\tau = 4$  min,  $T = 308$  K,  $C_{\text{HOAc}} = 17.5$  mol/L); (b) dependences of efficient rate constant for complex **Ia** in reaction (1) on acetic acid concentration.  $T$ , K: 1, 298; 2, 308; 3, 318; 4, 328.



**Fig. 4.** Voltammetric curves for working electrode coated with  $(\text{AcO})\text{Co}^{\text{II}}(\text{N-Me})\text{TPP}$  (**Ia**), electrolyte is 0.1 M KOH ( $I$ , in argon medium; 2,  $\text{O}_2$ ). Scan rate is  $0.02$  V  $\text{s}^{-1}$ . I–III are electroreduction stages.

by electronic absorption spectrum and  $^1\text{H}$  NMR data [8]) due to the out-of-plane location of the N-methyl group and therefore the nonplanarity of the molecule as a whole. In its turn, the molecule nonplanarity and unstable hybrid state of the substituted nitrogen atom lead to the growth of electron donation of macrocycle **I**, which considerably decreases  $T_0$  of thermo-oxidation. The thermal stability of the studied compounds in the

absence of oxygen is always higher: for ligands by  $65^\circ\text{C}$  for  $\text{H}_2\text{TPP}$  (**II**) and  $160^\circ\text{C}$  for its N-methylated analog (**I**), for complexes by  $160^\circ\text{C}$  for ZnTPP (**IIb**),  $135^\circ\text{C}$  for CoTPP (**IIa**), and  $37^\circ\text{C}$  for  $(\text{AcO})\text{Zn}(\text{N-Me})\text{TPP}$  (**Ib**). Thermal degradation conditions (Ar,  $\text{O}_2$ ) seem to have low effect on the thermal conditions of N-demethylation stage for complex **Ib** (Table 1) because it proceeds via not oxidative mechanism.

**Table 1.** The results of thermogravimetric measurements for the processes of destruction of N-methyltetraphenylporphine (**I**), its unsubstituted analog (**II**) and their Zn and Co complexes under argon and air oxygen atmosphere

Compound	Atmo- sphere	$m_0$ , mg	$T_o$ , °C	$T_m$ , °C	$T_f$ , °C	$\Delta m_a^{\text{theor}}$ , %	$\Delta m_a^{\text{exp}}$ , %	$T_o$ , °C	$T_m$ , °C	$T_f$ , °C	$\Delta m_a^{\text{exp}}$ , %	Literature
H <sub>2</sub> TPP ( <b>II</b> )	O <sub>2</sub>	—	407	478	530							[16]
	Ar	5.631	470.2	486.1	498.5		51.54					
H(N-Me)TPP ( <b>I</b> )	O <sub>2</sub>	—	260	625	682							[7]
	Ar	5.621	420.6	441.8	448.6		11.82	478.6	493.9	515.5	7.97	
ZnTPP ( <b>IIb</b> )	O <sub>2</sub>	—	340	520	540							[16]
	Ar	5.747	497.6	537.4	577.4		41.72					
CoTPP ( <b>IIa</b> )	O <sub>2</sub>	—	340	—	—							[16]
	Ar	2.702	475.0	514.2	534.0		34.29	715.0	749.5	773.6	16.92	
(AcO)Zn(N-Me)TPP ( <b>Ib</b> )	O <sub>2</sub>	—	230	476	598	10.82						[7]
	Ar	5.933	*266.9 467.8	282.7 524.7	294.8 548.6	9.52	9.85 31.78					
(AcO)Co(N-Me)TPP ( <b>Ia</b> )	Ar	4.318	*223.1 481.0	244.4 516.7	254.2 536.4	10.50	9.93 21.13	688.8	745.6	787.8	26.83	

Studied processes: (AcO)M(N-Me)TPP  $\longrightarrow$  MeOAc + ZnTPP;  $T_o$ , process onset temperature;  $T_m$ , maximal exo effect temperature;  $T_f$ , final process temperature;  $\Delta m_a^{\text{theor}}$  and  $\Delta m_a^{\text{exp}}$ , theoretical and experimental weight value for MeOAc.

**Table 2.** Kinetic parameters for reaction (1) of N-substituted compounds **Ia** and **Ib** dissociation in HOAc–DMSO solution,  $T = 298\text{ K}$ 

Compound	HOAc concentration, mol/L	Efficient rate constant $k_{\text{eff}} \times 10^3, \text{ s}^{-1}$	Activation energy, $E, \text{ kJ/mol}$	Activation entropy change $\Delta S^\ddagger, \text{ J mol}^{-1} \text{ K}^{-1}$
(AcO)Co <sup>II</sup> (N-Me)TPP ( <b>Ia</b> )	10.48	0.05*	45 ± 10	-186 ± 35
	12.58	0.06*	50 ± 1	-167 ± 1
	14.68	0.12*	48 ± 3	-176 ± 10
	16.77	0.06*	49 ± 8	-171 ± 29
	17.50	0.04 ± 0.0004	53 ± 14	-160 ± 46
(AcO)Zn <sup>II</sup> (N-Me)TPP ( <b>Ib</b> ) [17]	9.43	9.19 ± 0.97	38.4 ± 7.0	-163 ± 24
	10.90	30.88 ± 3.11	72.8 ± 14.3	-38 ± 9
	14.10	47.36 ± 3.72	66.0 ± 15.1	-57 ± 10
	16.20	34.18 ± 0.32	47.8 ± 11.2	-120 ± 35
	17.50	26.65 ± 2.03	27.9 ± 6.3	-189 ± 30

\*Calculated by Arrhenius equation.

**Table 3.** Potentials of redox transformations (in V) for electrodes coated with N-substituted analog of macrocycle [H(N-Me)TPP], its metal complexes [(X)M(N-Me)P], and their unsubstituted derivatives (scan rate  $V = 0.02\text{ V s}^{-1}$ )

Compound	$\text{M}^{3+} \rightarrow \text{M}^{2+}$			Process I			Process II			Process III			$E_{1/2}(\text{O}_2)$
	$E_{\text{cat}}$	$E_{\text{an}}$	$E_{\text{red/ox}}$	$E_{\text{cat}}^{\text{I}}$	$E_{\text{an}}^{\text{I}}$	$E_{\text{red/ox}}^{\text{I}}$	$E_{\text{cat}}^{\text{II}}$	$E_{\text{an}}^{\text{II}}$	$E_{\text{red/ox}}^{\text{II}}$	$E_{\text{cat}}^{\text{III}}$	$E_{\text{an}}^{\text{III}}$	$E_{\text{red/ox}}^{\text{III}}$	
H <sub>2</sub> TPP ( <b>II</b> ) [11, 14]							-0.664	-0.575	-0.620	-1.081	-0.968	-1.025	-0.275
CoTPP ( <b>IIa</b> ) [11, 14]	0.130	0.260	0.200							-1.210	-1.000	-1.110	-0.230
	-0.580* -0.480* -0.530*												
H(N-Me)TPP( <b>I</b> )				-0.573	-0.454	-0.514	-0.772	-0.619	-0.695	-1.072	-	-	-0.242
(AcO)Zn(N-Me)TPP ( <b>Ib</b> )				-0.552	-0.440	-0.496	-0.754	-0.638	-0.696	-1.089	-	-	-0.189
(AcO)Co <sup>II</sup> (N-Me)TPP ( <b>Ia</b> )	0.172	0.309	0.241	-0.551	-0.476	-0.514	-0.742	-0.613	-0.678	-1.103	-0.917	-1.010	-0.110

\*Transition  $\text{M}^{2+} \rightarrow \text{M}^{1+}$  or  $\text{L} \rightarrow \text{L}^-$ .

The number of peaks on DTG curve, i.e., the number of destruction stages, is dependent on the nature of ligand and metal. Thus, two stages of thermal destruction under an argon atmosphere are observed for H(N-Me)TPP ( $T_0 = 421$  and  $479^\circ\text{C}$ ) and for cobalt complexes irrespective of ligand nature. Onset destruction temperatures are  $475$  and  $715^\circ\text{C}$  for CoTPP (**IIa**) and  $481$  and  $689^\circ\text{C}$  for (AcO)Co(N-Me)TPP (**Ia**) (Table 1, Fig. 2).

As distinct from N-substituted ligand, the destruction of the corresponding complexes under both oxy-

gen and argon atmosphere proceeds through low-temperature ( $220$ – $295^\circ\text{C}$  under inert atmosphere) stage of elimination of the N-substituent (R) and covalently bound extra ligand (X) (3), in our case  $\text{CH}_3$ - and  $\text{CH}_3\text{COO}^-$ , with evaporation of methyl acetate molecule (Fig. 2, Table 1). Thus, for example, this is evidenced by weight loss value under inert atmosphere, which for complexes (AcO)Zn(N-Me)TPP (**Ib**) and (AcO)Co(N-Me)TPP (**Ia**) agrees well with calculated value ( $\Delta m^{\text{I}}$  and  $\Delta m^{\text{e}}$  equal to  $9.85$ ,  $9.93\%$  and  $9.52$ ,  $10.50\%$ , respectively, Table 1). On account of dealky-

lation stage, the thermal stability of the N-substituted complexes in contrast to unsubstituted compounds considerably decreases (by 110°C in argon and 230–250°C in air).

The further intramolecular rearrangement of compounds **Ia** and **Ib** including conversion of unstable  $p^3$  valence state of  $^{21}\text{N}$  atom in thermally demethylated compounds leads to formation of virtually flat unsubstituted complexes CoTPP and ZnTPP, which is confirmed by the proximity (6°C for cobalt complexes) of  $T_0$  values for the second stage of (X)M(N-Me)TPP degradation to the onset degradation temperatures of the corresponding MTPP complexes (Fig. 2, Table 1), the similar type of thermograms in the considered temperature range, and complete coincidence of electronic absorption spectrum for the product of RX elimination obtained by the heating of the initial N-substituted compound up to 300°C under inert atmosphere with the spectrum of the corresponding unsubstituted metal porphyrin ( $\lambda_{\text{CHCl}_3}^{\text{max}} = 418, 547 \text{ nm}$ ) (Fig. 1).

Under thermo-oxidation conditions, the degradation of the macrocycle to form gaseous nitrogen and carbon oxides and water [19] follows immediately after dealkylation stage and is characterized by exothermal peaks on DTG curve, whose number depends on metal nature [7], whereas these processes are separated under inert atmosphere ( $T_0 = 267$  and  $468$  for (AcO)Zn(N-Me)TPP and  $T_0 = 223$  and  $468^\circ\text{C}$  for (AcO)Co(N-Me)TPP) (Fig. 2, Table 1). It is seen that the scheme of degradation of N-substituted metal porphyrins **Ia** and **Ib** under argon atmosphere shows a certain feature, process mechanism is unknown.

Thus, the removal of the N-substituent from the molecules of N-substituted porphyrins occurs not only in solutions on exposure to organic bases or strong heating [1, 8] but also in solid state on heating irrespective of experiment medium (Ar,  $\text{O}_2$ ).

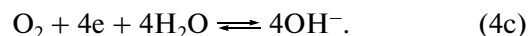
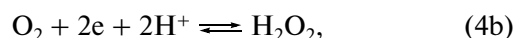
Another important aspect that determines the stability of coordination compounds in solutions is their ability to remain in undissociated form. To analyze the effect of nonplanar structure of metal porphyrin upon introduction of N-methyl substituent on the chemical stability of its complexes toward proton-releasing reagent, we studied the kinetics of dissociation reaction (1) for zinc(II) and cobalt(II) compounds with N-substituted porphyrin **I** in DMSO–HOAc medium. The obtained results show (Table 2) that, under comparable conditions at acetic acid concentration in DMSO of 9.43–17.5 mol/L, the cobalt complex with H(N-Me)TPP (**Ia**) undergoes dissociation to porphyrin dication  $\text{H}_3(\text{N-Me})\text{TPP}^{2+}$  (Fig. 3a) by a factor of 400–700 slower as compared with zinc complex (**Ib**) [17]. The decrease of stability for complex **Ib** in comparison with **Ia** agrees well with the growth of the values of nonplanar shift of the corresponding metal atoms from 0.56 to 0.65 Å and their average radii from 0.077 to 0.080 Å [1, 20], which leads to the further distortion of the flat structure of the compounds. The

drop of stability for the complexes with N-substituted ligand (**I**) toward dissociation in ionizing medium as compared with similar planar complexes (**IIa**, **IIb**) [3] corresponds to the notion on the negative effect of nonplanar structure of macrocycle and factors accompanying distortion on the stability of its complexes [17, 18, 21].

The dissociation of (AcO)Co(N-Me)TPP (**Ia**) in DMSO–HOAc medium is described by unusual for solvoprotolytic dissociation reaction nonlinear dependence of efficient rate constant for reaction (1) ( $k_{\text{eff}}, \text{s}^{-1}$ ) on acetic acid concentration ( $C_{\text{HOAc}}$ ) (Table 2) with maximum at about 14.5 mol/L acetic acid (Fig. 3b). Similar dependence indicating the similarity of dissociation reaction mechanisms for these MPs was observed previously in similar solvent system for (AcO)Zn(N-Me)TPP (**Ib**) [17] (Table 2). The complication of concentration dependence in reaction (1) may be caused by the change of attacking species upon alteration of solvent composition by either participation of several species simultaneously, possibly including  $\text{DMSO} \cdot \text{H}^+$ ,  $\text{HOAc} \cdot \text{H}^+$ , HOAc, etc.

The comparison of stability characteristics for N-substituted complexes in solution and in solid state indicates the lack of linear correlation between them. Thus, complex (AcO)Co(N-Me)TPP (**Ia**) is more kinetically stable in dissociation reaction as compared with its zinc analog, however, its destruction under polythermal conditions begins at lower temperature than for **Ib** due to N-demethylation stage.

On the basis of analysis of kinetic stability of obtained complexes toward chemicals and thermal impact, we draw conclusions on the fundamental possibility to use H(N-Me)TPP ligand (**I**) and its Co(II) and Zn(II) complexes in the electrocatalysis of cathodic electroreduction of molecular oxygen ((4a)–(4c)), which leads to processes that proceed in the components of low-temperature chemical sources of electric energy [11, 22].



Under argon atmosphere, the cyclic  $I, E$  curves of N-methyl-substituted ligand H(N-Me)TPP (**I**), its cobalt(II) and zinc(II) complexes show three general stages of electroreduction process (**I**, **II**, and **III**, Table 3) related to the addition of electrons to the  $\pi$  electron system of the macrocycle. The first stage of the electroreduction of H(N-Me)TPP and its derivatives under observed conditions proceeds by 0.1 V more “easily” than in the case of unsubstituted macrocycle **II**.

For (AcO)Co<sup>II</sup>(N-Me)TPP complex, we detected  $\text{Co}^{2+} \rightleftharpoons \text{Co}^{3+}$  transition with  $E_{\text{red/ox}} = 0.241 \text{ V}$ , which is shifted toward higher potentials by ~40 mV as compared with the closest analogs, for example CoTPP [14, 22], which agrees well with the stabilization of

metals in lower oxidation states by this ligand. We failed to ascribe value  $E_{\text{red/ox}} = -0.530$  V to  $\text{Co}^+ \leftrightarrow \text{Co}^{2+}$  or  $\text{L} \rightarrow \text{L}^{-1}$  transition.

To analyze the electrocatalytic activity of  $(\text{AcO})\text{M}(\text{N-Me})\text{TPP}$  in the process of electroreduction of molecular oxygen, we took  $I, E$  curves (Fig. 4, curve 2) corresponding to the ultimate saturation of electrolyte with  $\text{O}_2$ . The growth of electrocatalytic activity leads to a considerable depolarization effect that appears as a shift of molecular oxygen electroreduction wave  $E_{1/2}(\text{O}_2)$  to the positive values region.

The high electrolytic effect of  $\text{H}(\text{N-Me})\text{TPP}$  ( $E_{1/2}(\text{O}_2) = -0.242$  V) and  $(\text{AcO})\text{Co}^{\text{II}}(\text{N-Me})\text{TPP}$  ( $-0.111$  V) as compared with the closest analogs  $\text{H}_2\text{TPP}$  ( $-0.275$  V) and  $\text{Co}^{\text{II}}\text{TPP}$  ( $-0.230$  V) [14] is caused by the high electron-releasing ability of the N-substituted macrocycle.

The efficient number of electrons calculated by the Randles–Sevcik equation is close to four, typical value for oxygen electroreduction in the presence of cobalt complex **1a**, this indicates that the reaction proceeds via four-electron mechanism (4c) [11, 14, 22].

Thus, the electrocatalytic activity of the studied tetrapyrrole compounds in the reaction of electroreduction of molecular oxygen increases in the following order:  $\text{H}_2\text{TPP} < \text{H}(\text{N-Me})\text{TPP} < \text{CoTPP} < (\text{AcO})\text{Zn}(\text{N-Me})\text{TPP} < (\text{AcO})\text{Co}^{\text{II}}(\text{N-Me})\text{TPP}$  (Table 3); N-substituted cobalt(II) complex (compound **1a**) shows the best ratio of electrocatalytic activity and thermodynamic stability in solution and solid state. One can suppose that the ability of complex  $(\text{AcO})\text{Co}^{\text{II}}(\text{N-Me})\text{TPP}$  to undergo electrochemically reversible reductive migration of the N-substituent to metal to form unstable in this case  $\text{Co}^{3+}$  state increases the electrocatalytic activity [1].

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