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Synthesis and Dissociation Kinetics of Zinc, Copper, Cobalt, and Manganese Complexes with 2,3,7,8,12,18-Hexamethyl-5-phenyl-13,17-diethylporphin and Its Nitro-Substituted Analogs in Proton-Donor Media

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Abstract—Nitro-substituted 2,3,7,7,8,12,18-hexamethyl-5-phenyl-13,17-diethylporphins with nitro groups in positions 10 and 20 of the porphyrin core and in the *para*-position of the benzene ring have been synthesized. The structure of the obtained compounds has been confirmed by H^1 NMR, UV, and IR spectroscopy as well as mass spectrometry. The kinetics of dissociation of zinc, copper, cobalt, and manganese complexes of the obtained porphyrins in proton-donor media has been studied. The stability of the porphyrin metal complexes has been related to the electronic effects of the substituents in the tetrapyrrole cycle and spatial distortion of the latter.

Keywords: porphyrins, coordination properties, dissociation kinetics, metal complexes

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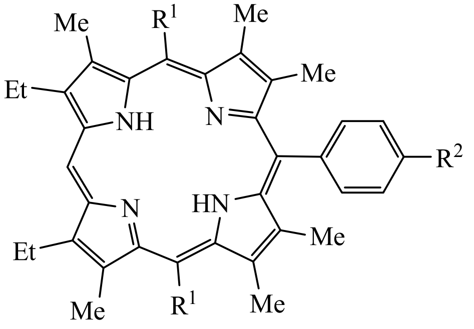
Porphyrins are known for catalyzing of a series of chemical, electrochemical, and photochemical reactions [1, 2]; therefore, the synthesis of novel porphyrins and the study of their physico-chemical properties are among the topical issues in modern science. Incorporation of nitro groups in the porphyrin molecule is one of the approaches to its modification leading to the distortion of the macrocycle and the changes in its physico-chemical properties [3–5]. Extending our earlier studies on the effect of deformation of the tetrapyrrole macrocycle on its coordination properties, we investigated the stability of zinc, copper, cobalt, and manganese complexes with 2,3,7,8,12,18-hexamethyl-5-phenyl-13,17-diethylporphin and its nitro-substituted derivatives in proton-donor media (Scheme 1).

2,3,7,8,12,18-Hexamethyl-5-phenyl-13,17-diethylporphin **1** and 2,3,7,8,12,18-hexamethyl-5-(4-nitrophenyl)-13,17-diethylporphin **3** were prepared via acid condensation of 3,4-dimethylpyrrole-2-carbaldehyde **4** with 3,3'-diethyl-4,4'-dimethyldipyrrolylmethane **5**, followed by cyclization of the intermediate biladiene **6** with benzaldehyde (R^2 = H) or 4-nitrobenzaldehyde ($R^2 = NO_2$) and oxidation (Scheme 2) [6, 7].

2,3,7,8,12,18-Hexamethyl-10,20-dinitro-5-phenyl-13,17-diethylporphyn **2** was prepared via oxidative electrophilic nitration of porphyrin **1** with sodium

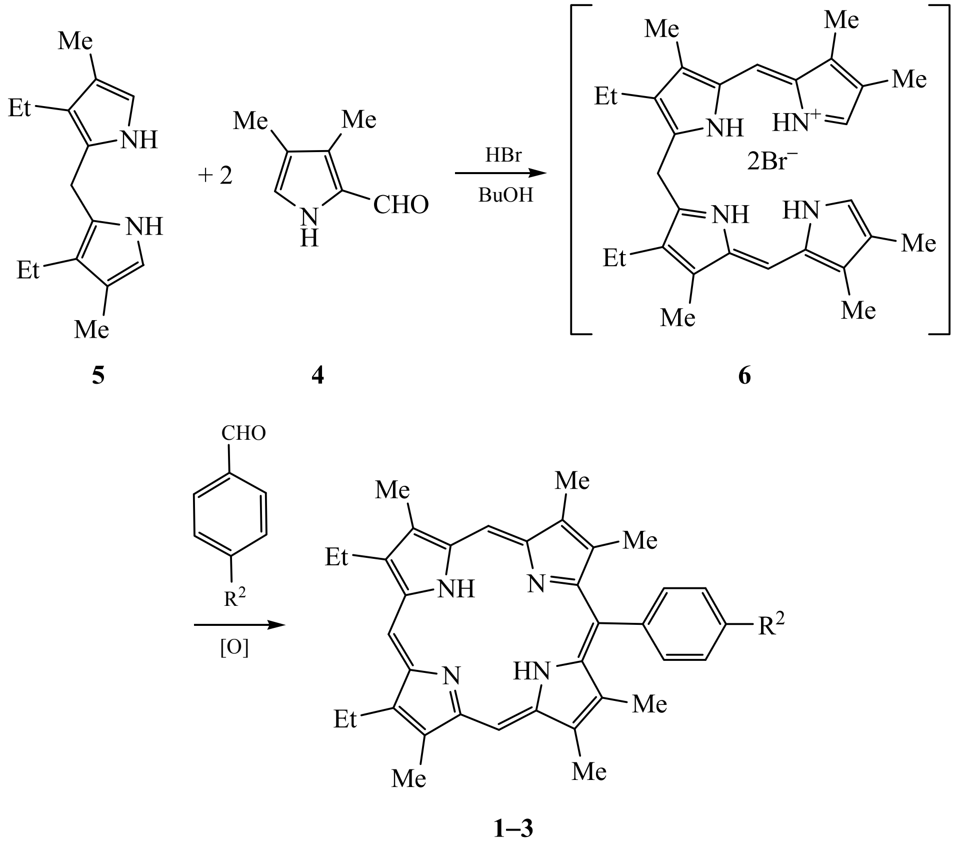
Scheme 1.



1–3

$R^1 = R^2$ = H (**1**); $R^1 = NO_2$, R^2 = H (**2**); R^1 = H, $R^2 = NO_2$ (**3**).

Scheme 2.



nitrite in trifluoroacetic acid [7] (Scheme 3) followed by separation of the side product, 10,15-isomer **7**, via preparative thin-layer chromatography on Silufol in benzene.

Composition and structure of the formed compounds were confirmed by means of MALDI-TOF mass spectrometry as well as UV, H^1 NMR, and IR spectroscopy.

Kinetics of dissociation of zinc (ZnP), copper (CuP), cobalt (CoP), and manganese [(AcO)MnP] complexes of porphyrins **1**–**3** was studied in the solutions in acetic acid containing 1.5 wt % of a H_2SO_4–CF_3COOH mixture (1 : 1). The considered metal complexes (MP) dissociated (1) with the formation of the doubly protonated porphyrins form (H_4P^{2+}). The spectra of the reacting mixtures contained distinct isosbestic points (see the figure).

$$MP + 4H^+ = M^{2+} + H_4P^{2+}. \tag{1}$$

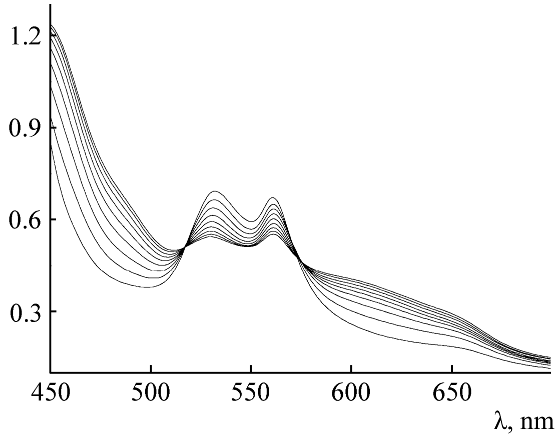
The kinetic experiments were performed with ~100-fold excess of the H_2SO_4–CF_3COOH mixture with respect to MP, which allowed calculation of the effective rate constants (k_{eff}) using Eq. (2).

$$k_{\text{eff}} = (1/t)\ln [(A_0 - A_\infty)/(A - A_\infty)]. \tag{2}$$

Here A_0, A, and A_∞ are absorbances of the solution at the start of the experiment, at time t, and after the reaction was complete, respectively.

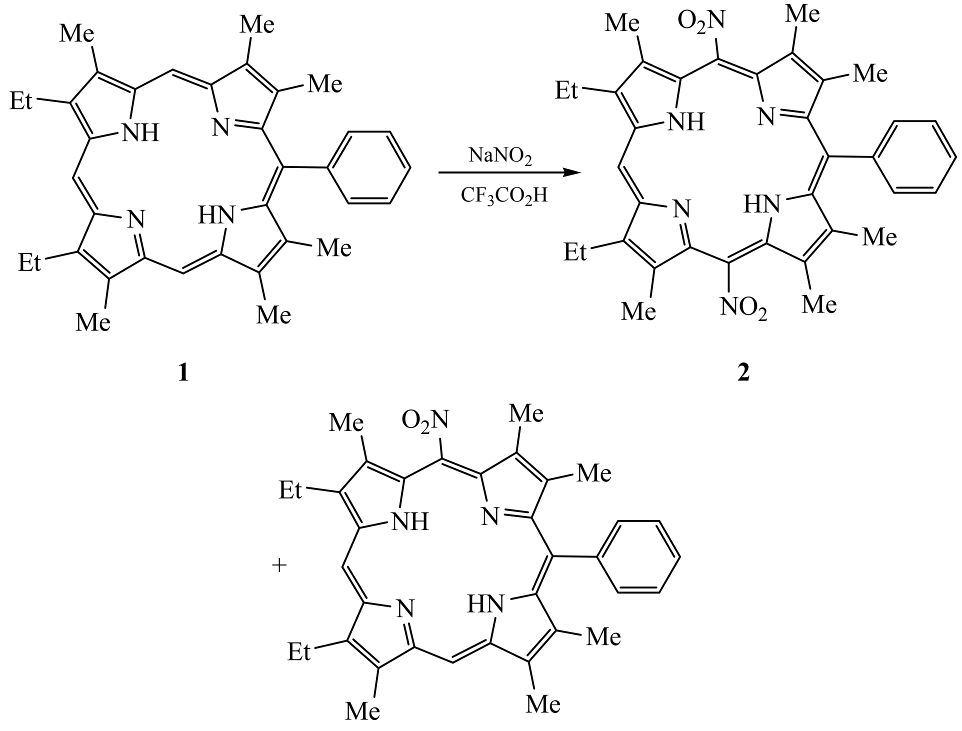
The activation energy (E) was calculated using Eq. (3).

$$E = 8.3T_1T_2/(T_2 - T_1)\ln(k_2/k_1). \tag{3}$$



Evolution of electronic absorption spectra in the course of dissociation of CoP(**1**) in acetic acid with 1.5 wt % of a 1 : 1 H_2SO_4–CF_3COOH mixture.

Scheme 3.



1 **2** **7**

Kinetic parameters of dissociation of the ZnP, CuP, CoP, and (AcO)MnP complexes are collected in the table.

Comparative analysis of the data in the table showed that the increase in the number of the nitro groups in the porphyrin molecule led to the decrease in the rate constant of dissociation of the Mn^{3+}, Co^{2+}, and Cu^{2+} complexes and the increase in the activation energy.

The simulation of geometry parameters of the structures by means of the PM3 method (force field MM+) showed that the aromatic tetrapyrrole core of porphyrin **1** was planar. The introduction of nitro groups at the *meso*-positions 10 and 20 led to significant distortion of the macrocycle due to the steric interaction of the nitro groups with neighboring methyl substituents. The distortion of the molecule core taking a grooved shape was typical of nonplanar porphyrins [8–10].

Distortion of the tetrapyrrole macrocycle in the porphyrin molecule reduced its aromaticity and enhanced the electron density at the central nitrogen atoms [8, 11]. Therefore, the basic properties of the porphyrins were strengthened [12, 13]. The increase in the degree of the planarity distortion made the M–N bonds more available for the attack by the solvated proton, which reduced the said bond strength.

The increase in the distortion of the porphyrin molecule **3** in comparison with porphyrin **1** decelerated the dissociation of the studied metal complexes and increased the activation energy of the process. Likely, that was due to the partial compensation for the distortion of the porphyrin in the metal complexes, making the macrocycle more planar. The steric distortions of the planar structure of the porphyrins gave relatively minor effect on the kinetic parameters of the solvoprotolytic dissociation of the metal complexes. The effect of distortion and the –*I*-effect of the nitro groups affected oppositely the dissociation rate [5]. Evidently, the major contribution to the energy of the transition state was due to the stretching of the M–N bonds owing to the presence of electron-accepting nitro groups in the *meso*-positions 10, 20 of the porphyrin and the *para*-position of the benzene ring.

The obtained data revealed that the stability of the metal complexes was affected by the nature of the salt cation, being decreased in the [(AcO)MnP](**1**–**3**) > CoP(**1**–**3**) > CuP(**1**–**3**) > ZnP(**1**–**3**) series. Expectedly, the complexes of triply charged Mn^{3+} cation were the

Kinetic parameters of dissociation of zinc, copper, cobalt, and manganese complexes of porphyrins **1**–**3** in acetic acid containing 1.5 wt % of the H_2SO_4–CF_3COOH mixture (1 : 1)

Porphyrin	E, kJ/mol	λ, nm	$k_{\text{eff}}\times10^3$, s^{-1}			
			298 K	308 K	318 K	328 K
ZnP						
Reaction occurred during the solutions mixing						
CuP						
1	56±1	564	13±0.6	27.00±1.350	55.00±2.70	–
2	58±2	563	3.2±17	6.90±0.290	14.00±0.72	0.54±0.000
3	65±2	650	–	0.11±0.008	0.24±0.01	24
CoP						
1	59±1	532	2.30±0.1100	5.000±0.2500	10.5±0.5	–
2	63±2	553	0.60±0.0300	1.400±0.0600	3±0.14	–
3	72±2	643	0.03±0.0013	0.079±0.0039	0.187±0.009	–
MnP						
1	78±1	600	–	0.1100±0.0050	0.3±0.012	0.700±0.030
2	82±2	578	–	0.0720±0.0030	0.2±0.01	0.520±0.025
3	129±2	568	–	0.0048±0.0001	0.023±0.0011	0.103±0.006

most stable in the proton-donor medium, due to high strength of the Mn–N covalent bonds. The higher stability of the CoP(**1**–**3**) complexes in comparison with the CuP(**1**–**3**) ones was due to the capacity of the $3d^9$ cation of Cu^{2+} to form the square-pyramidal complexes with the M–Solv bonds weakened owing to the Jahn–Teller effect. The zinc complexes of porphyrins **1**–**3** dissociated immediately during the solutions mixing. The acceleration of dissociation of the zinc complexes in comparison with the cobalt ones was also related to the structure of the complexes [14].

EXPERIMENTAL

Acetic acid ("chemical pure" grade) was dried via refluxing with the calculated amount of acetic anhydride during 20 h and distillation with reflux condenser. The content of water in the solvent (0.02 wt %) was determined via the Fischer's titration. Monohydrate of H_2SO_4 was prepared via saturation of 95% sulfuric acid with oleum (potentiometric monitoring of the water content). Trifluoroacetic acid ("pure" grade) was mixed with concentrated sulfuric acid in the 10 : 1 ratio. The dried acid was distilled off at atmospheric pressure with reflux condenser, collecting the fraction with bp 72–73°C, which was then distilled again.

Electronic absorption spectra were recorded using a SPEL SSP-715 scanning spectrometer in chloroform. IR spectra were recorded using an Avatar 360 FT-IR spectrometer in KBr pellets. ^{1}H NMR spectra were recorded using a Bruker 500 spectrometer in deuterated chloroform (residual solvent signals as internal reference). Mass spectra were recorded using a Shimadzu Axima Confidence MALDI-TOF spectrometer.

2,3,7,8,12,18-Hexamethyl-5-phenyl-13,17-diethylporphin (1). IR spectrum, ν, cm^{-1}: 2961, 2923, 2863, 1446, 1264, 1226, 1117, 1062, 1030, 951, 834, 751, 701. Electronic absorption spectrum, $\lambda_{\max}$, nm (log ε): 623 (3.51), 571 (3.83), 536 (3.86), 502 (4.15), 403 (5.22). ^{1}H NMR spectrum, δ, ppm: –3.18 br. s and –3.27 br. s (2H, NH), 10.19 s (2H, $H^{10,20}$), 9.98 s (1H, H^{15}), 8.07 d (2H, $H^{2,6}$-Ph, J = 7.4 Hz), 7.82 t (1H, H^4-Ph, J = 7.4 Hz), 7.75 t (2H, $H^{3,5}$-Ph, J = 7.4 Hz), 4.09 q (4H, CH_2,13, 17-Et, J = 7.7 Hz), 3.67 s (6H, 12,18-CH_3), 3.55 s (6H, 2,8-CH_3), 2.47 s (6H, 3,7-CH_3), 1.90 t (6H, CH_3, 13,17-Et, J = 7.7 Hz). Mass spectrum (MALDI-TOF), *m/z*: 526.184 $[M]^+$. M_{calc} 526.728.

2,3,7,8,12,18-Hexamethyl-10,20-dinitro-5-phenyl-13,17-diethylporphin (2). IR spectrum, ν, cm^{-1}: 2971, 2930, 2876, 1533, 1447, 1361, 1158, 1137, 1058, 947, 855, 798, 705, 664. Electronic absorption spectrum,

λ_{max}, nm (log ε): 648 (3.57), 591 (3.87), 518 (4.15), 413 (5.08). ^{1}H NMR spectrum, δ, ppm: –3.22 br. s (2H, NH), 9.86 s (1H, H^{15}), 8.04 d (2H, $H^{2,6}$-Ph, $J = 7.0$ Hz), 7.85 t (2H, H^4-Ph, $J = 7.0$ Hz), 7.80 t (4H, $H^{3,5}$-Ph, $J = 7.0$ Hz), 3.61 q (4H, CH_2, Et, $J = 7.6$ Hz), 3.20 s (6H, 12,18-CH_3), 3.02 s (6H, 2,8-CH_3), 2.12 s (6H, 3,7-CH_3), 1.56 t (6H, CH_3, Et, $J = 7.6$ Hz). Mass spectrum (MALDI-TOF), *m/z*: 617.169 $[M + H]^+$. M_{calc} 617.793.

2,3,7,8,12,18-Hexamethyl-5-(4-nitrophenyl)-13,17-diethylporphin (3). Electronic absorption spectrum, λ_{max}, nm (log ε): 624 (3.50), 573 (3.82), 537 (3.87), 505 (4.15), 403 (5.18). ^{1}H NMR spectrum, δ, ppm: –3.25 br. s (2H, NH), 10.16 s (2H, $H^{10,20}$), 9.97 s (1H, H^{15}), 8.56 d (2H, $H^{2,6}$-Ph, $J = 7.2$ Hz), 8.20 s (2H, $H^{3,5}$-Ph, $J = 7.2$ Hz), 4.05 q (4H, CH_2, Et, $J = 7.4$ Hz), 3.62 s (6H, 12,18-CH_3), 3.62 s (6H, 2,8-CH_3), 2.38 s (6H, 3,7-CH_3). Mass spectrum (MALDI-TOF), *m/z*: 571,363 $[M]^+$. M_{calc} 571.725.

ZnP, CuP, CoP, and (AcO)MnP complexes were prepared via refluxing of porphyrins **1–3** with excess of the corresponding metal acetate in the 1 : 1 mixture of acetic acid and chloroform and purified twice via chromatography of alumina (activity grade Brockman III) using chloroform as eluent. The complexes purity was confirmed by the electronic absorption spectra.

Kinetics of dissociation of the metal complexes in acetic acid containing 1.5 wt % of the H_2SO_4–CF_3COOH mixture (1 : 1) was studied by means of spectrophotometry using a Shimadzu UV-1800 instrument equipped with a constant-temperature cell (298–338 K within ±0.1 K).

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CONFLICT OF INTERESTS

No conflict of interest was declared by authors.

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