ISSN 1070-3632, Russian Journal of General Chemistry, 2015, Vol. 85, No. 8, pp. 1876–1884. © Pleiades Publishing, Ltd., 2015.
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Synthesis and Physico-Chemical Properties of 2,7,12,17-Tetraphenylporphycene and Its Metal Complexes

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Received February 20, 2015

Abstract—Porphycene, β-phenyl-substituted analog of tetraphenylporphyrin, and its complexes with Cu(II) and Zn(II) have been prepared. Spectral parameters of the porphycene, its acid-base properties and thermal stability in the solid phase as well as its complexes stability towards dissociation in acidic medium have been studied by means of electronic absorption and NMR spectrometry, mass spectroscopy, thermogravimetry, and quantum chemistry simulation.

Keywords: porphyrinoid, porphycene, synthesis, N-basicity, tautomerism, thermal stability, metal complex, dissociation

DOI: 10.1134/S1070363215080150

Unique optical and catalytic properties of isomeric analogs of porphyrins result in a broad range of their potential applications in development of advanced materials, including the second generation photo sensibilizers for photodynamic tumor therapy and photo deactivation of pathogenic bacteria [1, 2].

Porphycenes (H_2Por) are the *meso*-bridged (2.0.2.0)[1] isomers of the porphyrins (H_2P) (1.1.1.1) [1, 3]. Due to the special features of porphycenes macrocycle structure (the coordination center having the environment of lower symmetry as compared to the H_2P molecules), the porphycenes are usually classified as porphyrin analogs or porphyrinoids [1, 3, 4]. The distribution of π-electron density in the porphycenes macrocycle differs from that in the porphyrins; the nature and number of the coordinating ligand atoms are the same (N_4H_2), however the square planar coordination node of the porphyrins turns rectangular in the porphycenes [1]. Approach of the =N and NH groups in the coordination center of the molecule favor formation of the hydrogen bonds between them [5] and reduces reactivity of H_2Por towards coordination, acid-base, and other interactions. The H-bonding drastically changes the mechanism of the =N–NH tautomerism [6, 7]. In detail, in the case of porphyrins the heat-activated tunneling of the NH protons without formation of the stable *cis* isomer is typical, whereas the *cis* isomer has been detected in the case of the porphycenes (in the crystal of the β-substituted porphycenes and both in the crystal and in the solution of the *meso*-substituted ones).

Since the porphycenes are poorly available [3, 8], their physico-chemical properties have been scarcely studied so far [3, 9]. In this work, starting from the dipyrrole precursor **I** to prepare 2,7,12,17-tetraphenylporphycene [$H_2(\beta\text{-Ph})_4Por$, **II**] [Eq. (1)] and its complexes with Cu(II) (**III**) and Zn(II) (**IV**) and studied spectral properties of the porphyrinoids, features of protonation and deprotonation of ligand **II** [Eq. (2)], its thermal stability in the solid phase, and stability of complexes **III** and **IV** against dissociation in acidic medium [Eq. (3)]. The obtained data allowed analysis of the reasons for similarity and difference of the properties of the porphyrin [*meso*-tetraphenylporphyrin

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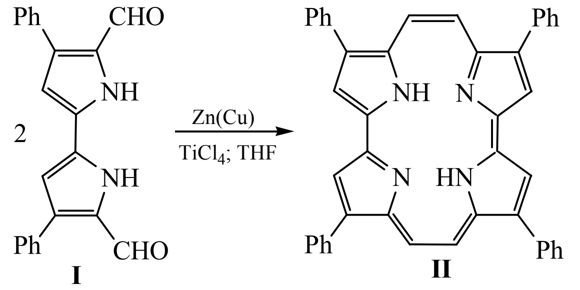
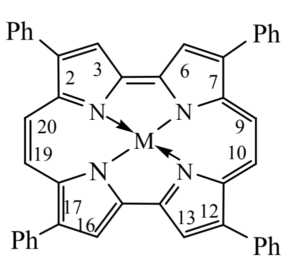
[1] Numbers of carbon atoms at the alternating *meso*-positions 9, 10, 19, 20 of macrocycle **II** and 5, 10, 15, 20 of macrocycle **V** are stated.

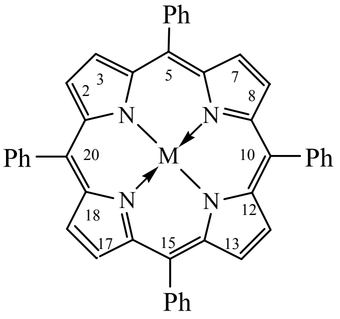
H_2(*ms*-Ph)$_4$P **V**] and its β-substituted *meso*-bridged isomer **II**.



(1)



III, **IV**



V–VII

M = Cu(II) (**III**, **VI**), Zn(II) (**IV**, **VII**), 2H (**V**).

$$H_4(\beta\text{-Ph})_4Por^{2+} \xrightleftharpoons{pK_{3,4}} H_2(\beta\text{-Ph})_4Por + 2H^+, \qquad (2)$$

$$M(\beta\text{-Ph})_4Por + 2H^+ \rightarrow H_2(\beta\text{-Ph})_4Por + M^{2+}. \qquad (3)$$

Porphycene **II** was prepared via the procedure adopted from [8] including synthesis of the tetrasubstituted pyrrole followed by formation of its α,α-dipyrrole derivative **I**, its cyclization yielding two ethylene bridges, and aromatization of the macrocycle [Eq. (1)].

Porphycene is the most stable *meso*-bridged isomer of porphine, their formation energies differing by 1.5 kcal/mol [1, 3]. According to our simulation using the DFT B3LYP method in the CC-pVDZ basis set, the corresponding value for compound **II** was low as well, of 6.7 kcal/mol (Table 1).

^{1}H NMR spectrum of porphycene contained the signals of the exocyclic β- (δ = 9.72 ppm) and *meso*-protons (δ 9.95 ppm) shifted towards the low field as compared to those in the porphyrin spectrum, whereas the phenyl group protons resonated at the same position (δ = 7.7–8.6 ppm). Accounting for the presence of strong absorption bands in the electronic spectrum (log ε = 4.50–4.95) (Fig. 1 and Table 2) and the NMR data, the macrocycle in the porphycene was aromatic. Aromaticity of the macrocycle in compound **II** resulted in its fairly high thermal stability under inert conditions, atmosphere etc. According to the experimental data, a single stage of the mass loss occurred at 448.5–486.6°C (Table 3), i.e., the decomposition onset temperature (t_s) of compound **II** was only 21.8° lower than that of H_2P (**V**).

The lower symmetry of the macrocycle in compound **II** (as compared to that in the isomeric compound **V**) was not directly reflected in the splitting of the proton signals in the ^{1}H NMR spectrum, due to the β-phenyl substitution of the macrocycle. At the same time, the quantum-chemical simulation data (Table 1) revealed that polarity of β-tetraphenylporphycene (the dipole moment was of 0.011 D, close to zero) was similar to that of the highly symmetrical molecule of compound **V**.

Even though the electronic absorption spectra of compound **II** differed from those of the porphyrins in the presence of three bands in the visible spectrum range and the strong Soret-like band at the UV edge of the spectrum (Fig. 1), the porphycenes spectra can be interpreted in the frame of the four-orbital Gouterman model [3, 4].

Since the coordination cavity of the porphycenes (2.799 and 2.732 Å) was smaller than that of the porphyrins (2.916 Å), porphycenes form the complexes with metal ions of smaller radius (for example, with zinc rather than with cadmium) exhibiting certain orientation of the binding orbitals [1]. β-Tetraphenyl-substituted porphycene **II** does not form complexes with majority of the metal ions (Ni, Mg, Co, Cd, etc) under standard preparation conditions. However, a number of methods to prepare complexes of β-alkyl-substituted porphycenes have been described [3, 11, 12]. Owing to the spatial interactions between pairs of the β-alkyl substituents, coordination center of the macrocycle is known to deform as compared with the starting rectangular shape to approach the square planar geometry [1]. Hence, change of the porphycene structure and its coordination properties due to the substitution at the β- or *meso*-positions can be more pronounced than in the case of H_2P [1]. Stability of zinc complexes of porphycenes in the solution in the presence of acids has been found a function of the type and position of the alkyl substituent, decreasing in the Zn(β-Et)$_4$Por ≥ Zn(β-Pr)$_4$Por >> Zn(*ms*-Pr)$_4$Por series; the *meso*-substituted complex is not practically formed [1].

Table 1. Geometry and energy parameters of macrocycles **II** and **V** and their H-associates with DMF[a]

Parameters	Orbitals and electron pairs involved in the H-bonding	**V**	**V**·DMF	**II**	2·DMF
$-E$, kJ/mol		1913.87	2162.40	1913.86	2162.39
ΔE, kJ/mol		0.00	–23.60[b]	28.12	–27.71[c]
μ, D		0.029	3.218	0.011	3.572
ΔE_{int}, kJ/mol		–	–26.06	–	–29.77
BSSE		–	2.46	–	2.06
$\Delta E^{\text{NBO}}_{\text{stab}}$,	LP N → BD* N–H	14.94	–	205.94	–
kJ/mol	LP N → BD* N–H	14.94	–	205.94	–
	LP1 O → BD* C–H	–	5.15	–	7.53
	LP2 O → BD* C–H	–	6.94	–	4.27
	Σ	–	12.09[c]	–	11.78[c]
	LP N → BD* C–H	–	1.46	–	7.15
$q^{\text{NBO}}_{\text{stab}}$, ch. units	LP N → BD* N–H	0.007	–	0.100	–
	LP N → BD* N–H	0.007	–	0.100	–
	LP1 O → BD* C–H	–	0.002	–	0.004
	LP2 O → BD* C–H	–	0.004	–	0.002
	Σ	–	0.006	–	0.006
	LP N → BD* C–H	–	0.001	–	0.002
$\varphi_{\text{X}\leftrightarrow\text{Y–H}}$, deg	N → N–H	43.9		15.6	
	N → N–H	43.9		15.6	
	O → C–H	–	11.5	–	15.7
	O → C–H	–		–	15.1
	N → C–H	–	12.9	–	5.1
$r_{\text{X}\leftrightarrow\text{H}}$, Å	N → N–H	2.32		1.59	
	N → N–H	2.32		1.59	
	O → C–H		2.37		2.50
	O → C–H				2.47
	N → C–H		2.66		2.80
$r_{\text{X}\leftrightarrow\text{Y-H}}$, Å	N → N–H	2.94		2.59	
	N → N–H	2.94		2.59	
	O → C–H		3.43	–	3.54
	O → C–H			–	3.51
	N → C–H		3.73	–	3.90

[a] E, total electronic energy; ΔE_{int} energy of the molecules interaction; BSSE superposition error; E_{stab}, stabilization energy of the hydrogen bond; q_{stab}, the charge transferred upon the hydrogen bond formation; $\varphi_{\text{X-Y–H}}$, $r_{\text{X-H}}$, and $r_{\text{X-Y–H}}$, angle and distances between the centers of the H-bond; LP, lone-electron pairs of N or O atoms involved in formation of the H-bonds with the unoccupied orbitals (BD*) of hydrogen atoms of the N–H or C–H bond. [b] For the interacting phenyl fragment. [c] Calculated relative to the corresponding free macrocyclic ligand.

We prepared the complexes of compound **II** with copper(II) (**III**) and zinc(II) (**IV**). Complex **III** was formed in a 100-fold molar excess of the metal acetate both in the electron-donating DMF and the proton-donating AcOH media within 2.5 h [Eq. (4)], whereas complex **IV** was only formed in DMF, other conditions being the same. The ligand conversion into the manganese complex Mn(β-Ph)$_4$Por was not complete under the similar conditions, and the electronic absorption spectrum of the reaction mixture contained the free ligand bands (Table 2) along with those of the complex (389 and 634 nm; Fig. 2a). Refluxing of the reaction mixture in DMF during 1 h as well as addition of a weak base (Et$_2$NH) did not shift the equilibrium (4) towards formation of the product. We attempted to prepare the manganese complex in a strongly basic medium (DMF + 5 × 10^{-3} mol/L Me_4NOH). Porphycene **II** formed the dianionic form $(\beta\text{-Ph})_4Por^{2-}$ under those conditions as confirmed by the absorption spectroscopy (λ = 360 and 574 nm); however, contrary to the expectations, that form did not react via scheme (4), being instead decomposed to form the colorless products within minutes (Fig. 2b).

$$\begin{gathered}H_2(\beta\text{-Ph})_4Por + M(OAc)_2(Solv)_{n-2}\\ \rightleftarrows M(\beta\text{-Ph})_4Por + 2AcOH + (n-2)Solv,\end{gathered} \tag{4}$$

Solv = DMF, AcOH; M = Cu, Zn, Mn.

The reaction (4) was not catalyzed by bases due to the low NH-acidity of the porphycenes. In detail, the signals of the protons of the NH group in the coordination cavity of compound **II** exhibited the downfield shift by more than 6.5(!) ppm, the effect being to a large extent caused by formation of strong intramolecular H-bonds between the =N and NH centers [1, 5]. Breaking down of those bonds upon formation of the doubly deprotonated form of compound **II** in the acidic medium [Eq. (2)] caused the upfield shift of that signal by 5–8 ppm [12]. The presence of the intramolecular H-bond was one of the reasons why the porphycenes have not revealed pronounced reactivity of the N–H bond in contrast to porphyrinoids of other classes [4, 13, 14]. In particular, the electronic absorption spectrum of the porphycene was not changed when the nonpolar solvent (C_6H_6 or $CHCl_3$) was changed with the electron-donating one (DMF or Py) (Fig. 1) [14]. According to the results of the $H_2(\beta\text{-Ph})_4Por{\cdot}DMF$ structure optimization, the interaction between the NH centers of the macrocycle and the donating center O of the solvent was practically absent (Table 1).

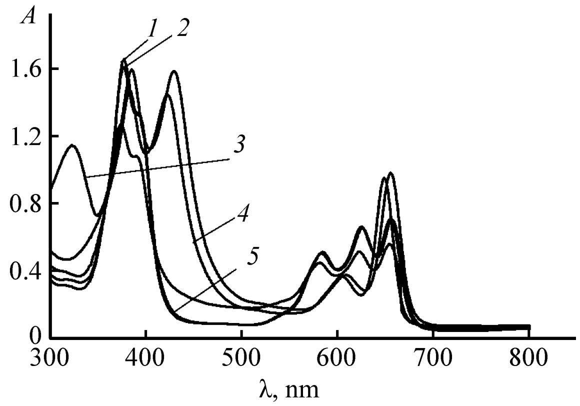


Fig. 1. Absorption spectra of β-tetraphenylporphycene **I** in different solvents at 298 K: (*1*) $CHCl_3$, (*2*) DMF, (*3*) H_2SO_4, (*4*) CF_3COOH, and (*5*) AcOH.

The formation enthalpy of the dianion Por^{2-} ($\delta\Delta H_{0-2}$) as determined via the AM1 simulation was negative

Table 2. Parameters of electronic absorption spectra of compounds **II** and **V** in organic media

Solvent	Electronic absorption bands, λ (log ε)				
	Soret	I	II	III	IV
			Compound **II**		
C_6H_6	377 (4.95)	658 (4.59)	627 (4.54)	586 (4.44)	–
$CHCl_3$	377 (4.94)	657 (4.57)	626 (4.54)	584 (4.44)	–
Py	379 (4.94)	658 (4.58)	628 (4.56)	586 (4.43)	–
DMF	377 (4.93)	655 (4.58)	625 (4.55)	583 (4.43)	–
DMSO	378 (4.87)	656 (4.52)	626 (4.49)	585 (4.36)	–
AcOH	377	654	622	582	–
CF_3COOH	383 (4.89)	648 (4.70)		–	–
	422 (4.89)		604 (4.29)		
H_2SO_4	385 (4.93)	655 (4.72)		–	–
	429 (4.93)		609 (4.30)		
			Compound **V**		
$CHCl_3$	418 (5.67)	646 (3.55)	590 (3.71)	549 (3.87)	514 (4.29)
DMF	416 (5.62)	646 (3.68)	590 (3.73)	548 (3.91)	513 (4.28)
$CHCl_3$ + 0.36 M CF_3COOH	436 (5.69)	652 (4.73)	602 (3.98)	–	–

Table 3. Parameters of thermal decomposition of macrocycles **II** and **V**[a]

Compound no.	Atmosphere	m_o, mg	t_s, °C	t_m, °C	t_f, °C	m_a^{exp}, %
II	Ar	2.444	448.5	466.6	486.6	45.18
V	O_2	–	407.0	478.0	530.0	–
	Ar	5.631	470.2	486.1	498.5	51.54

[a] t_s, t_m, t_f are temperatures of the onset, of the fastest mass loss, and of the finish of the thermal decomposition; m_a, mass loss at the given decomposition stage.

for both compound **II** (–21.3 kcal/mol) and the porphyrin **V** (–14.0 kcal/mol), evidencing about depolarization of the N–H bonds in the molecule of the latter [14]. That was further confirmed by formation of the anionic forms of compound **II** exclusively upon the action of strong bases (for instance, Me_4NOH) and no or weak H-association of the porphycene with weak electron donors (DMF, DMSO, or Et_2NH) (Fig. 1, Tables 1 and 2).

Basicity of the porphycene **II** was lower than that of the isomeric porphyrin **V**, the latter forming the dication with the characteristic absorption spectrum even in glacial acetic acid [15]. On the contrary, the general view of electronic absorption spectrum of 2,7,12,17-tetraphenylporphycene in AcOH was not changed (Fig. 1 and Table 2), and the stable dication was formed only in the strong acids [(H_2SO_4 or CF_3COOH (TFA)] (Fig. 1) as well as in the $CHCl_3$–CF_3COOH (0.1–0.5 mol/L of the acid) or MeCN–CF_3COOH systems (0.2–0.6 mol/L of the acid) (Fig. 3). The dissociation constants $pK_{3,4}$ of the dications [Eq. (2)] of the macrocycles **II** and **V** in the MeCN–CF_3COOH medium were of 0.55±0.03 and 5.30±0.04, respectively, i.e. the porphycene basicity was about 10 orders of magnitude lower. The data of spectrophotometric titration of $H_2(\beta\text{-Ph})_4$Por in the studied media revealed that the slope of the log Ind = $f(c_{TFA})$ was close to 2 evidencing about the dication formation according to Eq. (2) only in the binary media of the strong acid and the polar solvent (MeCN–CF_3COOH), similarly to the case of $H_2(ms\text{-Ph})_4P$. The tan α value was up to 20 in the course of the titration of compound **II** with TFA in the low-polar solvent ($CHCl_3$) similarly to H_2P and other tetrapyrrole macrocycles in the low-polar media [16].

Protonation of the porphycene results in appearance of two maxima in the visible range of the absorption spectrum (604 and 648 nm; Fig. 1 and Table 2) instead of the three ones, the long-wavelength band Q_x experiencing the slight blue shift by 10 nm and getting stronger (Fig. 3 and Table 2). The Soret band was strongly split upon formation of $H_4(ms\text{-Ph})_4Por^{2+}$ (for example, into the components at 383 and 422 nm in CF_3COOH; Δλ about 40 nm). The Soret band in the spectrum of compound **II** was observed as a bathochromic shoulder with Δλ = 15 nm (Table 2). Splitting

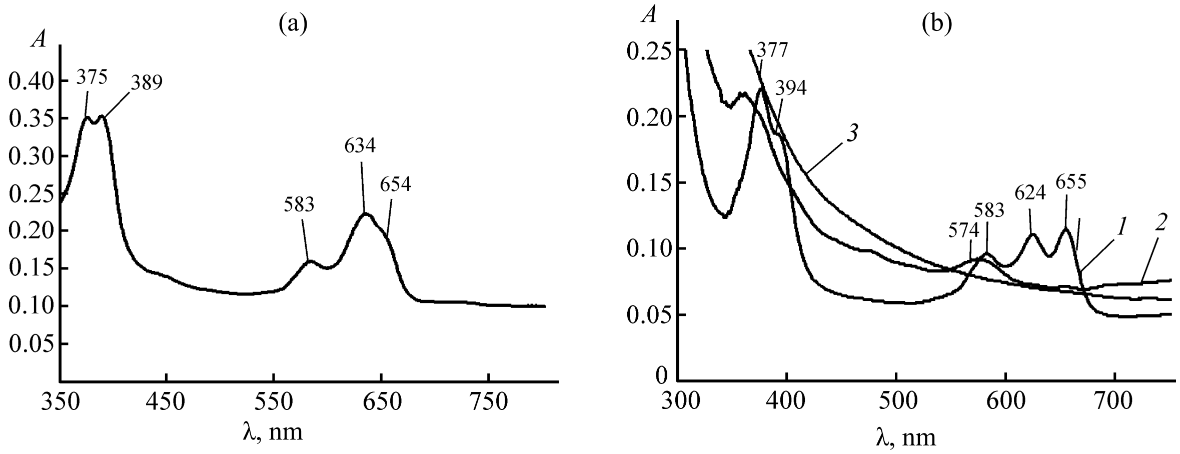


Fig. 2. Absorption spectra of the reaction mixture upon formation of Mn complex with compound **II** in HOAc (a) and that of $H_2(\beta\text{-Ph})_4$Por in DMF. (*1*) $H_2(\beta\text{-Ph})_4$Por, (*2*) $H_2(\beta\text{-Ph})_4$Por + $(CH_3)_4NOH$, (*3*) $H_2(\beta\text{-Ph})_4$Por + $(CH_3)_4NOH$ after 20 min (b).

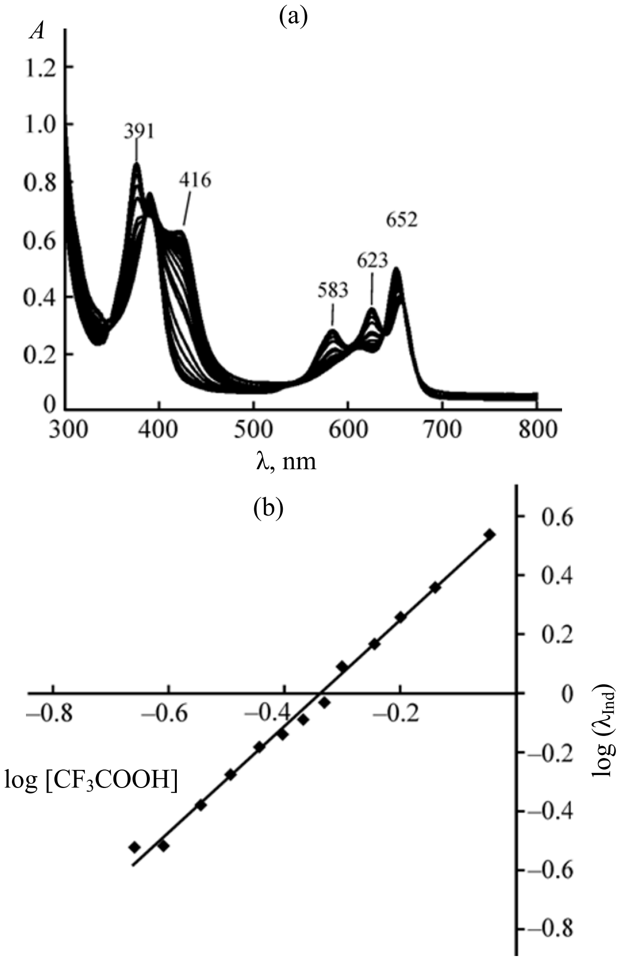


Fig. 3. Evolution of the electronic absorption spectrum of compound **II** in the course of the titration in the $CHCl_3$–CF_3COOH system ($[CF_3COOH]$ = 0–0.27 mol/L) (a). The indicator ratio log (λ_{Ind}) = *f*(log $[CF_3COOH]$) in MeCN at 298 K (b).

of the Soret band generally evidences about the asymmetric distribution of the electronic density in the macrocycle [17, 18].

The porphycene protonated forms were not detected in considerable concentrations in the DMF–CF_3COOH systems with the acid concentrations up to 10 mol/L. Likely, the noticeable decrease of both acidity and basicity of H_2Por as compared with those of H_2P was due to the appearance of the rectangular-shaped coordination center in macrocycle **II** owing to the complementarity of the N and NH centers forming the intramolecular hydrogen bonds [3]. According to the NBO analysis (Table 1), the energy of interaction between those centers was of ≈49 kcal/mol, the interaction being accompanied by the significant charge transfer (0.1 charge units); the hydrogen bonding did not occur in the case of compound **V**.

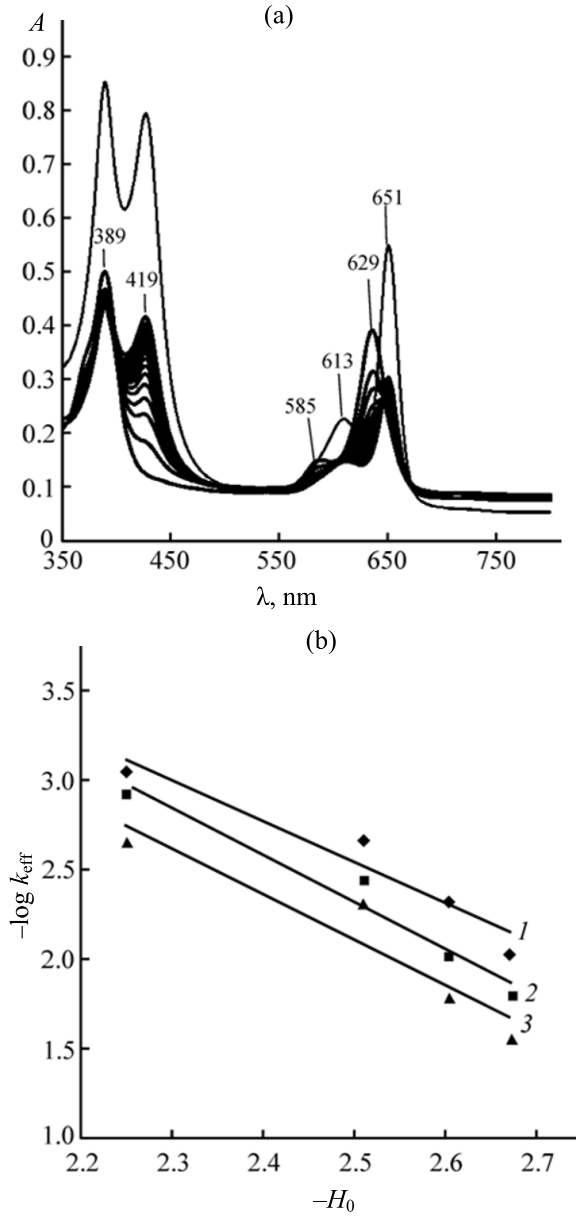


Fig. 4. Evolution of electronic absorption spectrum in the course of complex **III** dissociation in 0.71 mol/L solution of H_2SO_4 in AcOH at 298K (a). The effective rate constant k_{eff} of reaction (3) of complex **III** as function of acidity in the AcOH–H_2SO_4 system (b). $y = -2.6086x + 8.8417$ (*1*), $y = -2.5431x + 8.4637$ (*2*), $y = -2.3054x + 8.3018$ (*3*).

Metal porphycenes (MPor, for example, compounds **III** and **IV**) exhibited the kinetic stability in the acidic media significantly reduced as compared to that of the corresponding metal porphyrins (compounds **VI** and **VII**) [4, 20]. The Cu(β-Ph)$_4$Por complex **III** dissociated within an hour in the AcOH–

Table 4. Kinetic parameters of reaction (3) of dissociation of copper complexes **III** and **VI** with ligands **II** and **V** in the AcOH–H_2SO_4 medium

Complex	$[H_2SO_4]$, mol/L	$-H_0$	T, K	$k_{eff} \times 10^3$, s^{-1}	E, kJ/mol	ΔS, J mol^{-1} K^{-1}
III	0.601	2.25	298	0.88±0.08	36.0±8.6	–191±29
			308	1.20±0.11		
			318	2.18±0.16		
	0.856	2.51	298	2.16±0.25	31.4±5.1	–199±17
			308	3.59±0.22		
			318	4.82±0.32		
	1.197	2.60	298	4.76±0.31	48.3±3.9	–135±13
			308	9.67±0.48		
			318	16.3±0.96		
	1.426	2.67	298	9.32±0.82	41.9±2.1	–152±7
			308	15.5±1.19		
			318	27.00±2.63		
VI	1.0[a]		298	0.11±0.01	76.1	–75
	1.5[a]		298	0.99±0.01	79.0	–46

[a] In $C_2H_5COOH–H_2SO_4$ [20].

H_2SO_4 system at $c(H_2SO_4) > 0.6$ mol/L and T 298 K; the process occurred via Eq. (3) to yield the doubly protonated form of the ligand (Fig. 4 and Table 4). A similar porphyrin **V** complex**,** Cu(*ms*-Ph)$_4$P, dissociated 10–30 times slower at $c(H_2SO_4) = 1.0–1.5$ mol/L in the presence of propionic acid [19]. The characteristic feature of the electronic absorption spectrum evolution in the course of reaction (3) was the vanishing of the bands at 629 and 585 nm (Fig. 4) and appearance of the absorption band at 613 and 651 nm, typical of the dication. The Soret band of the complex (389 nm) was simultaneously split in the two components at 389 and 419 nm. The slope of the log k_{eff} [s^{-1}] value {k_{eff} standing for the effective rate constant of complex **III** dissociation [Eq. (2)]} as function of the acidity parameter H_0 of the AcOH–H_2SO_4 medium [19] was of 2.3–2.6 (Fig. 4). Hence, the mechanism of the solvo-protolytic dissociation earlier suggested for the porphyrinates in acidic media [19] could be applied in the case of the metal porphycenes as well. However, the elementary stages of the process did not occur simultaneously, due to the formation of the intramolecular hydrogen bends in the porphycene molecules. The stability of the zinc complex was lower than that of the copper one. The zinc porphycene decomposed in the presence of 0.17–0.67 mol/L of AcOH in benzene, being less stable than the Zn(*ms*-Ph)$_4$P complex; the latter one dissociated in glacial acetic acid [4].

In summary, the change of the coordination node shape (the nature of the coordinating atoms being the same) and formation of the intramolecular hydrogen bonds were responsible for the weaker ability of the porphycenes to form the metal complexes as compared to the similar porphyrins. The complexes formed by the porphycenes were less stable in the acidic medium as well, due to the same reasons.

EXPERIMENTAL

Organic solvents (C_6H_6, $CHCl_3$, MeCN, DMF, DMSO, Py, Et_2NH, AcOH, and CF_3COOH) were purified as described in [20]. Tetramethylammonium hydroxide (Aldrich) was used in the form of the 40 wt % solution in methanol.

Electronic absorption spectra were recorded using a Shimadzu UV-1800 spectrophotometer. ^1H NMR spectra ($CDCl_3$) were registered at 298 K using a Bruker Avance 500 spectrometer operating at 500 MHz. Mass spectra (MALDI FAB) were detected using a Shimadzu AXIMA Confidence spectrometer.

The spectral and kinetic studies were performed as described elsewhere [21, 22]. Thermogravimetry tests were carried out using a NETZSCH TG 209 F1 instrument (specimen mass ≈5 mg, platinum crucible, heating rate 8.75 deg/min at 298–1223 K).

Geometry parameters of macrocycles **II** and **V** and their H-associated forms were optimized using the GAUSSIAN 09 software package [23] taking advantage of the density functional method, the B3LYP hybrid functional [24], and the CC-pVDZ basis set [25]. In order to accomplish the NBO analysis, we computed the energy of stabilization of the formed hydrogen bond (E_{stab}) and the transferred charge (q_{stab}) [26, 27]. See details of the computations in [13].

Porphycene II was prepared via a procedure adopted from [8]. Zinc powder was sequentially washed with 5% HCl, water, methanol, diethyl ether, and dried. 2.6 mL (23.7 mmol) of titanium(IV) chloride was added upon stirring at room temperature to a suspension of 3.1 g (48 mmol) of the zinc powder and 0.48 g (2.4 mmol) of copper(II) chloride in 150 mL THF. The mixture was refluxed during 3 h. A solution of 0.5 g (1.47 mmol) of 5,5-diformyl-4,4-diphenyl-2,2-bispyrrole **I** in 50 mL of THF was then added, the mixture was heated to boiling and stirred upon boiling during 3 min. The mixture was cooled and neutralized with 10 wt% solution of K_2CO_3. The product was purified via chromatography with methylene chloride as eluent. Yield 12%, R_f (Silufol) 0.83 (benzene). IR spectrum (KBr), ν, cm^{-1}: 3640.89, 2957.29, 1625.77, 1435.54, 1154.37, 769.01, 706.11. ^1H NMR spectrum ($CDCl_3$), δ, ppm: 9.95 s (4H, *ms*-H), 9.72 s (4H, β-H), 8.36 d (8H, H^o, *J* 7.5 Hz), 7.85 t (8H, H^m, *J* 7.5 Hz), 7.71 t (4H, H^p, *J* 7.5 Hz), 3.77 br. s (2H, NH). Electronic spectrum ($CHCl_3$), λ_{max}, nm ($\varepsilon \times 10^{-3}$): 657 (45.6), 626 (42.4), 584 (32.7), 376 (119.6). Mass spectrum: *m*/*z* 614.03 $[M]^+$ (calculated: 614.75).

Complex III. 0.1 g (0.455 mmol) of copper(II) acetate dihydrate was added to a solution of 5 mg (0.008 mmol) of compound **II** in 5 mL of DMF. The mixture was refluxed during 2.5 h and then poured into 10 mL of water; sodium acetate was added, and the precipitate was filtered off. The product was purified via chromatography (CH_2Cl_2 as eluent). Yield 99%. Electronic spectrum ($CHCl_3$), λ_{max}, nm (log ε): 636 (4.80); 395 (5.01). Mass spectrum: *m*/*z* 675.94 $[M]^+$ (calculated: 676.28).

Complex IV was prepared similarly. ^1H NMR spectrum ($CDCl_3$), δ, ppm: 9.92 s (4H, *ms*-H), 9.45 s (4H, β-H), 8.30 m (8H, H^o), 7.82 m (8H, H^m), 7.69 m (4H, H^p). Electronic spectrum ($CHCl_3$), λ_{max}, nm (log ε): 658 (4.89), 397 (4.95).

ACKNOWLEDGMENTS

This work was financially supported by Russian Scientific Foundation (agreement no. 14-23-00204).

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