ISSN 0036-0236, Russian Journal of Inorganic Chemistry, 2010, Vol. 55, No. 9, pp. 1494–1498. © Pleiades Publishing, Ltd., 2010.
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PHYSICAL CHEMISTRY OF SOLUTIONS

Kinetics of the Formation of Copper β-Octaphenylporphyrin Complexes in Pyridine and Acetic Acid

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Received February 25, 2009

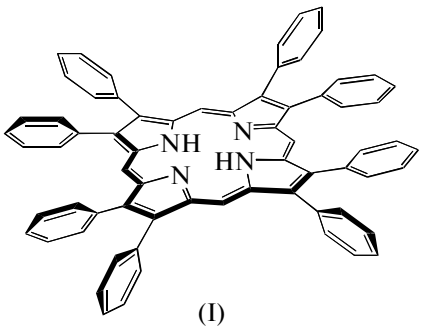
Abstract—The formation kinetics of copper β-octaphenylporphyrin complexes in pyridine and acetic acid is reported and is compared with that of copper β-octamethylporphyrin and dodecaphenylporphyrin complexes. The introduction of electron-donating or electron-withdrawing substituents in the β-positions of the porphyrin macrocycle change the rate of the complexation reaction by at most one order of magnitude. On passing from the planar porphyrin macrocycle to the heavily distorted one, the rate of the reaction in pyridine (electron donor solvent) and acetic acid (electron acceptor solvent) increases and decreases, respectively, by several orders of magnitude.

DOI: 10.1134/S0036023610090275

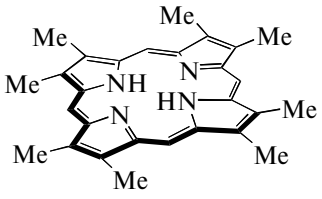
The most important coordination property of the porphyrins is their capacity to form a complex with any metal of the periodic table. The most favorable substances for porphyrin coordination are salts of doubly charged transition metal ions [1].

Studies of complexation between porphyrins and 3*d*-metal salts in organic solvents demonstrated that the rate of this reaction depends markedly on the composition and structure of the metal solvato complex and on the electronic structure and geometry of the porphyrin macrocycle [1–7].

Continuing the systematic investigation of the effect of the system of substituents in the porphyrin macrocycle on its coordination properties, we studied the kinetics of complexation between β-octaphenylporphyrin (**I**) and copper(II) acetate in pyridine and acetic acid and compared the results with earlier data for β-octamethylporphyrin (**II**) and dodecaphenylporphyrin (**III**) [3, 4].



(I)



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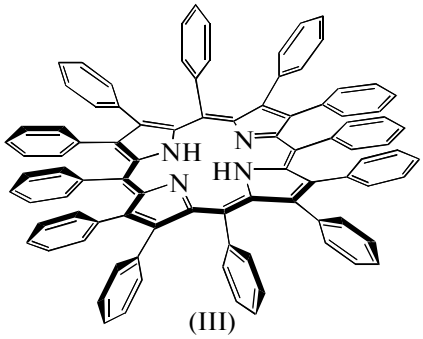

(III)

EXPERIMENTAL

2,3,7,8,12,13,17,18-Octaphenylporphyrin (I) Ethylmagnesium bromide (2.13 g, 16 mmol) dissolved in diethyl ether (10 ml) was added to 2-dimethylaminomethyl-3,4-diphenylpyrrole (4.15 g, 15.4 mmol) dissolved in xylene (200 ml), and the mixture was stirred for 20 h in a nitrogen atmosphere. The resulting precipitate was filtered and was then purified by extraction with a benzoquinone solution in benzene in a Soxhlet apparatus and by recrystallization from dimethylformamide [8]. A solution of the magnesium complex of **I** (0.80 mg, 0.083 mmol) in glacial acetic acid was stirred in a nitrogen atmosphere for 24 h. Thereafter, the solution was cooled and was neutralized with sodium carbonate. The resulting crystals of **I** were collected on a filter. The yield of the product was 0.41 mg (0.043 mmol), or 51.8%. Porphyrin **I** was purified chromatographically on alumina, activity II and III. The eluent was chloroform. The purity of the product was checked by thin layer chromatography on aluminum plates coated with a 0.5-mm-thick F_{254} silica gel layer (Merck). The mobile phase was $CHCl_3$–C_6H_6 (1 : 1). Electronic absorption spectrum, λ_{max}

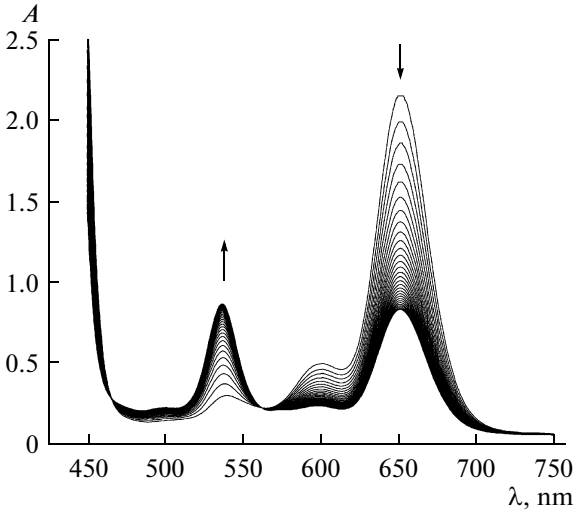

Fig. 1. Evolution of the electronic absorption spectrum in porphyrin **I** coordination to copper acetate in acetic acid at 298 K.

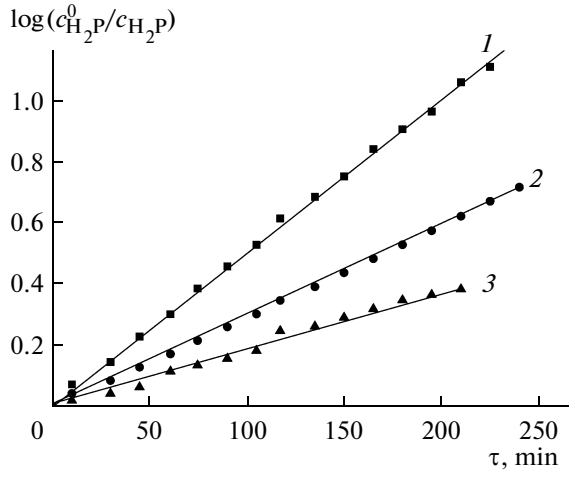

Fig. 2. $\log(c^0_{H_2P}/c_{H_2P})$ versus τ for the formation of copper–porphyrin **I** complexes in pyridine at (*1*) 348, (*2*) 338, and (*3*) 328 K.

($\log\varepsilon$): 635 (3.47), 583 (3.95), 550 (4.04), 518 (4.23), 423 (5.13) (chloroform). These data are in excellent agreement with the literature [8, 9].

Copper acetate (analytical grade) was purified by recrystallization from aqueous acetic acid and by dehydration at 380–390 K [10].

Acetic acid was dehydrated by fractional freezing followed by fractional distillation. The residual water content of acetic acid was 0.02% or below, as determined by Fischer titration. Pyridine (reagent grade) was purified using a standard technique. The residual water content of pyridine was not higher than 0.03% [11, 12].

The rate of complexation of **I** was measured on Specord M-400 and Hitachi U-2000 spectrophotometers between 288 and 348 K using temperature-controlled cells with ground-glass joints. The temperature variations did not exceed 0.1 K. Well-defined isosbestic points were observed in the spectra of all reacting systems (Fig. 1).

RESULTS AND DISCUSSION

The complex between porphyrin **I** and copper acetate forms via the reaction

$$H_2P + Cu(OAc)_2 \rightarrow CuP + 2AcOH \qquad (1)$$

and obeys the rate law

$$d[H_2P]/dt = -k[H_2P][Cu(OAc)_2]^n, \qquad (2)$$

where H_2P is the porphyrin, CuP is its complex, and k is the rate constant of reaction (1). The complexation reaction of β-octaphenylporphyrin is first-order with respect to the ligand. This is indicated by the linearity of $\log(c^0_{H_2P}/c_{H_2P})$ as a function of τ ($c^0_{H_2P}$ are the initial and current porphyrin concentrations; Fig. 2). Kinetic experiments were carried out under conditions of a hundredfold excess of the salt over the porphyrin. This allowed the apparent rate constant (k_{app}) of reaction (1) to be calculated via the equation

$$k_{app} = (1/\tau)\ln[(A_0 - A_\infty)/(A - A_\infty)], \qquad (3)$$

where A_0, A, and A_∞ are, respectively, the initial absorbance of the solution and those at the point in time t and after the reaction (Table 1).

The order of the reaction with respect to the salt (n) is 0.5 in acetic acid [7] and 0.4 in pyridine [13]. The fractional order of the reaction in the former case is due to the fact that copper acetate in acetic acid exists as an equilibrium system of dinuclear and mononuclear solvato complexes, with the equilibrium shifted toward the dinuclear complexes ($K_{dim} > 10^6$ L/mol)

Table 1. Apparent rate constants for porphyrin **I** coordination to copper acetate in acetic acid and pyridine

$c_{Cu(OAc)_2} \times 10^3$, mol/L	λ_a*, nm	$k_{app} \times 10^3$, s^{-1} in acetic acid		
		288 K	298 K	308 K
0.0625	651	3.4 ± 0.5	7.8 ± 0.5	21 ± 2
		$k_{app} \times 10^5$, s^{-1} in pyridine		
		328 K	338 K	348 K
1.48	513	6.6 ± 0.4	12.3 ± 0.6	26.4 ± 0.2

* Analytical wavelength.

Table 2. Kinetic parameters of β-octaphenylporphyrin (**I**), β-octamethylporphyrin (**II**), and dodecaphenylporphyrin (**III**) coordination to copper acetate in acetic acid and pyridine

Porphyrin	$k_{1.4}^{298} \times 10^5$, $L^{0.4}\ mol^{-0.4}\ s^{-1}$	ΔE, kJ/mol	$\Delta S^{\neq}$, J/(mol K)	$k_{1.5}^{298}$, $L^{0.5}\ mol^{-0.5}\ s^{-1}$	ΔE, kJ/mol	$\Delta S^{\neq}$, J/(mol K)	Reference
	Pyridine			Acetic acid			
I	6.3 ± 0.6	69 ± 3	−101 ± 10	0.987 ± 0.005	67 ± 5	−28 ± 15	This work
II	0.10 ± 0.01	153 ± 1	148 ± 2	0.368 ± 0.001	28.3 ± 1.1	−166 ± 3	[3, 4]
III	919 ± 20	21 ± 1	−202 ± 3	No complexation			[3, 4]

[14]. Dinuclear copper(II) carboxylates are kinetically inert in complexation with porphyrins [15–17], so the complex formation reaction involves only the mononuclear solvated species, whose concentration is proportional to the square root of the total salt concentration. In pyridine, the dimerization equilibrium takes place in parallel with the electrolytic salt dissociation equilibrium. The copper monoacetate solvato complexes are at least two orders of magnitude more active in complexation with porphyrins than the diacetate complexes [18]. This is why the kinetic order of the reaction with respect to the salt in pyridine takes a still smaller value of 0.4. The porphyrin concentrations in kinetic experiments are so low that they cannot exert any effect on the equilibrium speciation of the salt. Accordingly, the kinetic order of the reaction with respect to the salt is independent of the nature of the porphyrin.

In acetic acid, transition-metal salts form comparatively labile solvato complexes, which decompose readily when interacting with a porphyrin to yield a metalloporphyrin. Pyridine, a strong electron donor, forms a stable coordination sphere around the metal cation. The partial decomposition of this coordination sphere in complexation with a porphyrin takes a considerable amount of energy, thus slowing down the process. In acetic acid, the copper β-octaphenylporphyrin complex forms several orders of magnitude more rapidly than it does in pyridine.

The $(n + 1)$th-order rate constants calculated via Eq. (4) are listed in Table 2, where they are compared with earlier data for β-octamethylporphyrin and dodecaphenylporphyrin.

$$k_{n+1} = k_{app}/c_{Cu(OAc)_2}^{n}. \quad (4)$$

The coordination properties of porphyrins with respect to metal salts depend directly on the nature of the substituents bonded to the porphyrin core. As was demonstrated in earlier works [3–7], the introduction of a large number of bulky substituents not only changes the effective charge of the reaction center of the molecule through an electron-donating or electron-withdrawing effect, but also causes a marked distortion of the planar structure of the aromatic polyamine. However, the PM3 calculation of the geometry of β-octaphenylporphyrin (with an energy gradient of 0.02 kJ/(mol Å) as the count stopping criterion) demonstrated that the macrocycle of the porphyrin has a near-planar structure in spite of the presence of eight bulky substituents (Fig. 3).

The phenyl fragments in **I** make an angle of ≈75° with the macrocycle plane. Therefore, they can produce an effect on the reaction center N_4 only through the system of σ bonds. The eight phenyl substituents, which exert a $-I$ effect, reduce the negative charge on the central nitrogen atoms. The methyl groups in the β-pyrrole positions of the porphyrin macrocycle (in octamethylporphyrin **II**) show electron-donating properties ($+I$ effect), reducing the electron density on the atoms of the reaction center. However, it is obvious that these factors have no considerable effect on the complexation rate (Table 2). The rate of reaction (1) varies within one order of magnitude. The introduction of four phenyl substituents in the *meso* positions of the porphyrin macrocycle causes substantial geometric changes: the molecule of dodecaphenylporphyrin **III** has a so-called saddle-distorted configuration, as is shown in Fig. 3. The distortion of the macrocycle has a marked effect on the basic properties of the porphyrin as a ligand [19] and increases and decreases the complexation rate by several orders of magnitude in basic and acidic solvents, respectively.

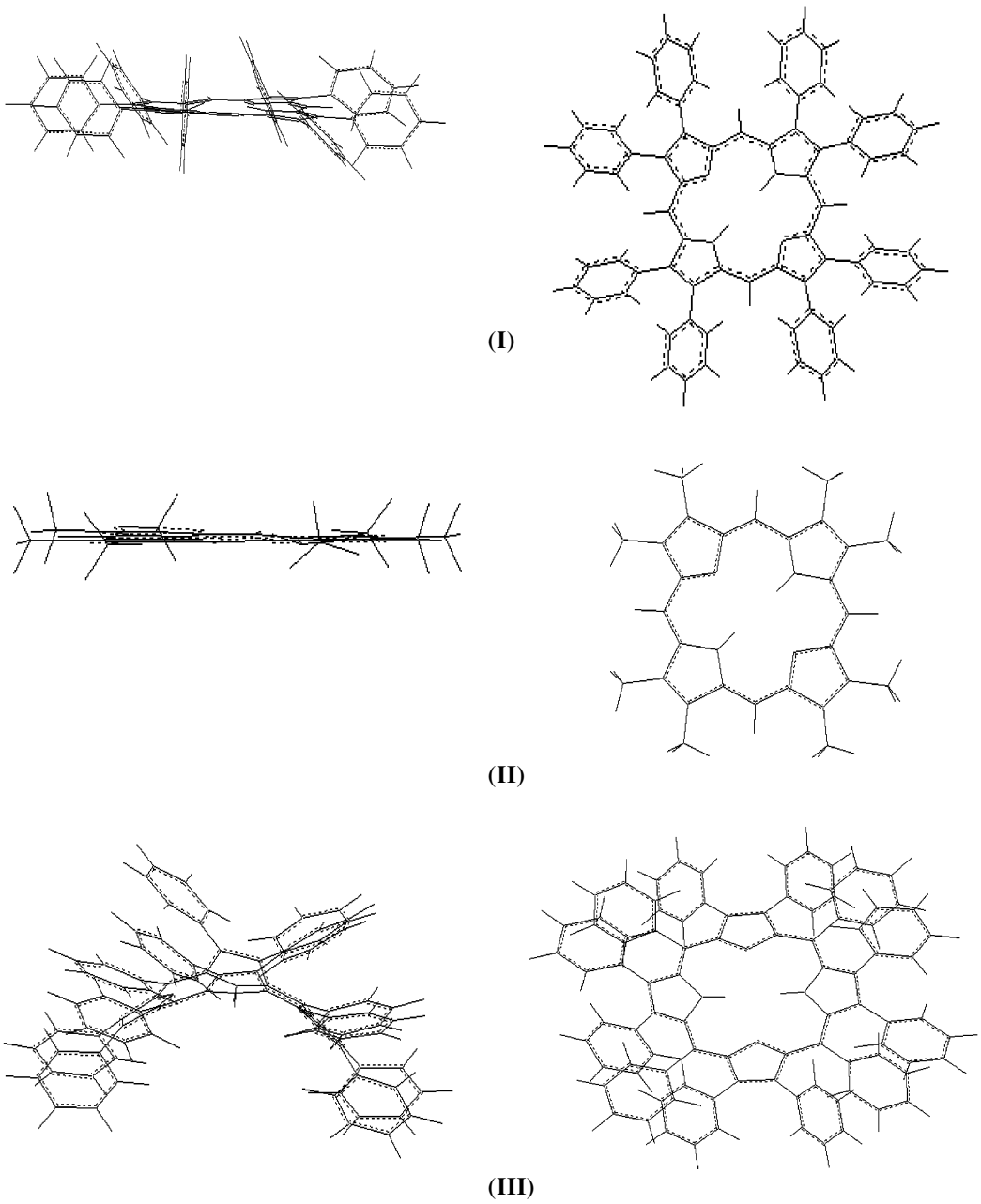

Fig. 3. Structure pf porphyrins **I**–**III** calculated by the PM3 method: different projections.

This is unambiguous evidence that the distortion of the planar porphyrin molecule is of great significance in the complexation kinetics.

ACKNOWLEDGMENTS

This study was supported by the Russian Foundation for Basic Research, grant no. 07-03-00635-a.

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