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COORDINATION COMPOUNDS

Coordination of Pyridine and Piperidine by Cobalt Complexes of Water-Soluble Porphyrin and Phthalocyanines

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Abstract—The extracoordination reactions of nitrogen-containing bases pyridine and piperidine with cobalt complexes of water-soluble porphyrin and phthalocyanines were studied. The stability constants of the axial complexes of cobalt porphyrins and cobalt phthalocyanines with pyridine and piperidine were determined.

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Extracoordination directly defines the manifestation of catalytic or electrocatalytic activity by metal porphyrins and metal phthalocyanines. In this content, considerable recent attention has focused on these extracoordination reactions in both experimental and theoretical studies [1–3].

The purpose of the present work is to study the equilibrium of the extracoordination of the nitrogen-containing bases pyridine (Py) and piperidine (Pip) by cobalt complexes of water-soluble porphyrin and phthalocyanines.

EXPERIMENTAL

The cobalt complex of water-soluble porphyrin $CoC_{48}H_{32}N_8O_8$ (**I**) was synthesized as described in [4] through three stages: (1) the synthesis of 5,10,15,20-tetra-4-pyridylporphyrin, (2) the synthesis of 5,10,15,20-tetra(4N-carboxymethylenepyridyl)porphyrin tetrabromide (H_2**PI**), and (3) the synthesis of the cobalt complex of H_2**PI** (Co**PI**).

Stage 1. A mixture of pyrrole (5 mL, 0.072 mol) and pyridine-4-carboxaldehyde (7.7 g, 0.072 mol) was added dropwise to boiling propionic acid (200 mL). The resulting mixture was refluxed for 45 min, and propionic acid was distilled off in a vacuum of a water-jet pump. The residue was mixed with benzene (600 mL), washed with an ammonia solution and water, and dried over sodium sulfate. The benzene solution was chromatographed on a column packed with alumina (Brockmann activity grade III) and eluted with benzene, and the red band of porphyrin was collected. The eluate was evaporated, and the porphyrin was precipitated with methanol. The precipitate was filtered off, washed with methanol, and dried in air at 75°C. The yield was 0.85 g (7.6%), $R_f = 0.71$ (Silufol, chloroform–methanol (5 : 1)). UV-Vis (chloroform, λ_{max}, nm ($\log\varepsilon$)): 643 (3.43), 589 (3.82), 546 (3.79), 514 (4.30), 417 (5.62).

Step 2. A solution of 5,10,15,20-tetra-4-pyridylporphyrin (0.5 g, 0.808 mmol) and bromoacetic acid (3.0 g, 21.6 mmol) in DMF (30 mL) was refluxed for 1 h. Then, the solution was cooled and diluted with benzene (30 mL). The precipitate was filtered off, washed with acetone, and dried at 75°C in air. The yield was 0.9 g (91%). UV-Vis (water, λ_{max}, nm ($\log\varepsilon$)): 630 (3.49), 585 (3.91), 556 (3.86), 519 (4.23), 423 (5.41 (water). ^{1}H NMR (δ, ppm, D_2O, TMS as internal standard): 8.91 (d, $J = 6.6$ Hz, pyridine α-H) 9.25 (d, $J = 6.6$ Hz, pyridine β-H), 9.07 (s, pyrrole β-H).

Stage 3. Freshly prepared poorly soluble cobalt hydroxide (the solubility of $Co(OH)_2$ in water is ~2×10^{-4} wt %) was added to an aqueous solution of porphyrin H_2**PI** in a ratio of 1 : 100, and the mixture was magnetically stirred for 8 h at 50°C. The formation of the metal porphyrin was monitored by spectrophotometry. The solution was purified by repeated filtration, and the complex was reprecipitated from a benzene solution. The resulting precipitate was washed with acetone and dried at 75°C. The yield was 96%. UV-Vis (water, λ_{max}, nm ($\log\varepsilon$)): 540 (3.78), 429 (5.00).

The cobalt complex of phthalocyanine $CoC_{36}H_{20}N_4O_{12}S_4$ (**II**) was obtained by the condensation of sulfophthalic and phthalic acids with urea and cobalt chloride in the presence of a catalyst as described in [5].[1] Cobalt tetracarboxyphthalocyanine **III** ($CoC_{40}H_{20}N_4O_8$) was synthesized by the Wyler method, namely, by smelting hemimellitic acid (1,2,3-

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[1] Porphyrin **I** and cobalt phtalocyanines **II** and **III** were kindly supplied by, respectively, Prof. A.S. Semeikin and Dr. V.E. Maizlish (Ivanovo State University of Chemical Technology).

tricarboxybenzene) with urea in the presence of ammonium chloride and ammonium molybdate as a catalyst at 200–210°C according to a known procedure [6].

The cobalt phthalocyanine complexes were purified by reprecipitation from concentrated sulfuric acid followed by the extraction of admixtures soluble in organic solvents with acetone and ethanol in a Soxhlet extractor [5, 6].

Pyridine (Py) and piperidine (Pip) were purified by standard methods [7–9].

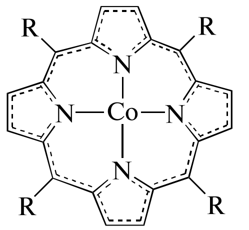
The water content was determined by the Fischer titration, and it did not exceed 0.01%.

Phosphate buffers were prepared as described in [10].

The extracoordination of Pip and Py by the cobalt porphyrin and phthalocyanine complexes were studied by spectrophotometry on a Specord M-400 instrument in 50-mL cells (the absorbing layer thickness was 100 mm) at 293.15 ± 0.10 K. A specified volume of the solution of the extraligand was added to a solution of metal porphyrin, using a microsyringe (the dosage error was ≤0.05%). The increase in the solution volume in the cell after the end of titration did not exceed 0.05%.

RESULTS AND DISCUSSION

The extracoordination processes of the nitrogen-containing ligands were studied for the cobalt complexes of water-soluble porphyrin **I** and the sulfo- and carboxy-substituted derivatives of phthalocyanines **II** and **III**.



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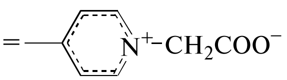

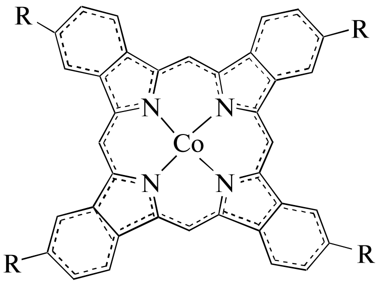

II: R = SO_3H; **III**: R = COOH

Table 1. Absorption spectra of aqueous solutions of cobalt porphyrin **I** and cobalt phthalocyanines **II** and **III**

Metal complex	pH	λ_{max}, nm (logε)
I	7.6	427 (5.02), 540 (4.06), 595 (sh)
II	7.6	338, 475, 664
III	7.6	617, 674
III	9.2	620, 678

Table 2. Stability constants of the axial complexes of Co porphyrins and Co phthalocyanines with piperidine and pyridine

Metal complex	Extraligand	pH	K_{st}, mol^{-1}
I	Pip	7.6	200 ± 50
II	Pip	7.6	45 ± 10
III	Pip	7.6	300 ± 110
II	Py	7.6	14 ± 2
III	Py	9.2	160 ± 30
III	Pip	9.2	130 ± 40

The electronic absorption spectra of for aqueous solutions of the cobalt complexes of compounds **I**–**III** are given in Table 1.

The cobalt phthalocyanine complex containing four carboxyl groups exists in aqueous solutions as an equilibrium mixture of monomeric and associated forms. The degree of dissociation of the carboxyl groups increases with pH, favoring the equilibrium shift to the monomeric form of the complex. Therefore, the absorption bands in the spectrum of compound **III** exhibit the bathochromic shift from 615 to 622 nm with increasing pH.

The stability constants (K_{st}) of the piperidine and pyridine extracomplexes of compounds **I**–**III** in aqueous solutions were determined to model the reactions that occur in biological systems.

In organic solvents, extracoordination processes can proceed via one and two steps, depending on the nature of the complexing atom in the metal porphyrin [1–3]. In our case, in aqueous buffer solutions, the spectral changes of cobalt complexes **I**–**III** (CoP) upon the addition of Py and Pip occur with the retention of distinct isosbestic points (the characteristic spectrum is shown in Fig. 1). This asserts that only two colored forms at equilibrium exist in the solution. The analysis of the data given below suggests the following equilibrium in the solution:

$$\mathrm{CoP} + \mathrm{L} \rightleftharpoons \mathrm{CoP(L)} \quad (1)$$

where L is Py or Pip.

The absorbances of the solutions at the analytical wavelengths listed in Table 1 were used for the calculation of the equilibrium constants (Table 2). Solutions with very low concentrations of the reactants (c_{CoP} <

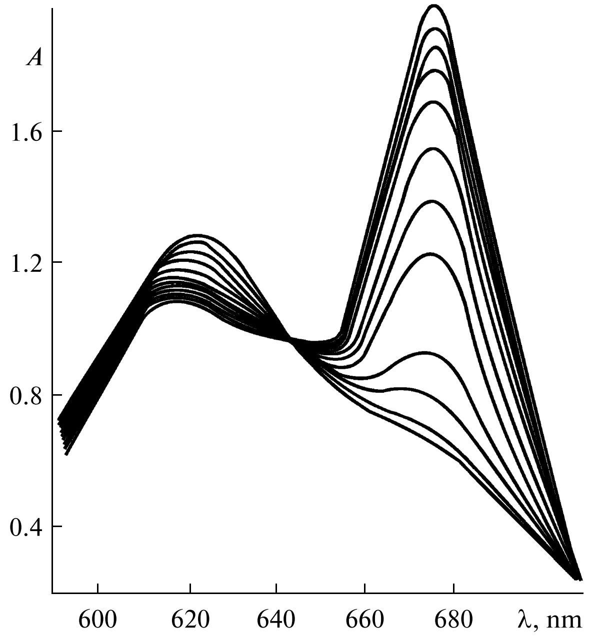

Fig. 1. Changes in the electronic absorption spectra due to the extracoordination of complex **III** with piperidine.

10^{-6}, $c_L < 10^{-4}$ mol/L) were used. Hence, the solutions were considered ideal, and K_{st} were calculated by the equation

$$K_{st} = c_{CoP(L)}/[c_{CoP}\,c_L]. \quad (2)$$

The equilibrium concentrations of the extracomplexes were calculated using the equation

$$c_{CoP(L)} = c^0_{CoP}(A_0 - A_i)/(A_i - A_f), \quad (3)$$

where $c_{CoP(L)}$ is the equilibrium concentration of CoP(L); c^0_{CoP} is the starting concentration of CoP; A_0, A_i, and A_f are the initial, equilibrium, and final absorbance values in the solution, respectively. All studies were carried out under the conditions of a considerable (more than 50-fold) excess of the extraligand over the metal porphyrin, which made it possible to neglect the decrease in the extraligand concentration due to its coordination by the cobalt complexes. This allowed us to calculate the equilibrium constants by the equation

$$K_{st} = (A_0 - A_i)/[(A_i - A_f)c_L]. \quad (4)$$

The number of ligands added to the metal porphyrin can be monitored by the slope of the plots $\log[(A_0 - A_i)/(A_i - A_f)]$ versus $\log c_L$. In all cases, the plots were rectilinear with the slope equal to unity within the determination error (a typical example is shown in Fig. 2).

The K_{st} constant of the axial coordination of Pip by complex **III** is halved with an increase in the pH from 7.6 to 9.2. This is evidently related to an increase in the degree of dissociation of the carboxyl groups, a decrease in their electron-acceptor properties, and the corresponding decrease in the effective positive charge on the cobalt cation.

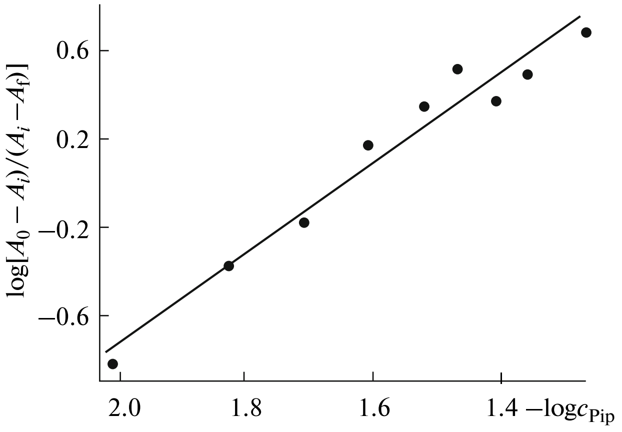

Fig. 2. Plot of $\log[(A_0 - A_i)/(A_i - A_f)]$ vs. $\log c_L$ for the extracoordination of piperidine by phthalocyanine complex **II**.

Piperidine is a substantially stronger donor of a σ electron pair than Py, due to which K_{st} increases threefold on going from the pyridinate to piperidinate extracomplex of tetrasulfonic acid of cobalt phthalocyanine. However, it should be kept in mind that, unlike Pip, Py can participate in π-bonding with the cobalt cation. This likely explains the fact that the pyridinate and piperidinate extracomplexes of compound **III** have equal K_{st} values at pH 9.2.

As compared to the porphyrinates, the phthalocyaninates are characterized by a decreased electron density on the central nitrogen atoms and, accordingly, the effective positive charge on the central metal cation in the phthalocyanine complexes is higher than that in similar metal porphyrins. That is why the extracomplexes of metal phthalocyaninates are more stable than the corresponding metal porphyrin derivatives. In this context, it is important that K_{st} of the piperidinate of porphyrin complex **I** is 4.5-fold higher than that of phthalocyanine derivative **II**, although the former is inferior in stability to the extracomplex formed by compound **III**. It is most likely that four *meso*-pyridyl substituents of compound **I** substantially increase the effective positive charge on the cobalt cation.

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