*Russian Journal of General Chemistry, Vol. 72, No. 6, 2002, pp. 963–967. Translated from Zhurnal Obshchei Khimii, Vol. 72, No. 6, 2002, pp. 1030–1034.*

# Reactions of Nitro and Halonitro Derivatives of Aluminum(III) and Copper(II) Phthalocyanines with Concentrated Sulfuric Acid

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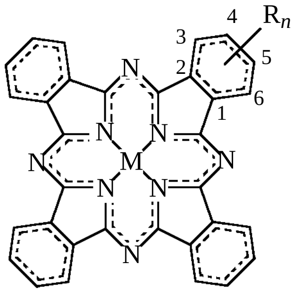
Received August 22, 2000

**Abstract**—Transformations of the complexes CuPc(4-$NO_2$)$_4$, CuPc(4-Br)$_4$(5-$NO_2$)$_4$, (OH)AlRs(4-$NO_2$)$_4$, and (OH)AlPc(4-Cl)$_4$(5-$NO_2$)$_4$ in concentrated sulfuric acid were studied by spectrophotometry. One protonated form of CuPc(4-Br)$_4$(5-$NO_2$)$_4$ and (OH)AlPc(4-$NO_2$)$_4$ and two protonated forms of CuPc(4-$NO_2$)$_4$ and (OH)AlPc(4-Cl)$_4$(5-$NO_2$)$_4$ were detected experimentally and also by ZINDO1 calculations. Step protonation constants of CuPc(4-$NO_2$)$_4$ and (OH)AlPc(4-Cl)$_4$(5-$NO_2$)$_4$ were determined by quantum–chemical calculations and acid–base titration; these complexes can be regarded as weak bases with respect to $H_2SO_4$. The kinetics of dissociation of the complexes at the M–N bonds were studied. The rate of dissociation of the Cu(II) complexes and (OH)AlPc(4-$NO_2$)$_4$ is proportional to [MPc(R)$_n$] and $[H_3O^+]^2$. The rate of dissociation of (OH)AlPc(4-Cl)$_4$(5-$NO_2$)$_4$ showed a weak extremal dependence on the composition of the medium, which was explained by change of its structure in 17.0 M $H_2SO_4$. The electronic effect of substituents on the reaction center was considered with account taken of a complex mechanism of activation and fine details of the molecular structure of macrocyclic complexes.

We previously studied the state and reactions of copper(II) phthalocyanines CuPc(R)$_n$ containing chlorine atoms and carboxy groups in various positions of the benzene fragments in concentrated sulfuric acid at different temperatures [1, 2]. It was found that their electron absorption spectra (298 K) depend on the solvent composition, and stepwise protonation of the complexes was proposed. The number of protonated forms was presumed to be specific for different functional derivatives of copper(II) phthalocyanine complexes. Quantitative parameters of dissociation at the M–N bonds were obtained in the range of $H_2SO_4$ concentrations where the complexes exist in the same protonated form. On the other hand, it is well known [3] that the abilities to dissociation of protonated and nonprotonated forms of metal complexes with porphyrins are strongly different. Protonation equilibria of substituted phthalocyanine complexes were quantitatively studied in [4, 5], where the titration was performed in water [for water-soluble complexes like CuPc(4-$SO_3$Na)$_4$] or nitrobenzene [for copper(II) tetra- and octanitrophthalocyanines]. In acid medium, metal phthalocyanines undergo not only acid–base transformations but also irreversible dissociation of the coordination entity at various rates. Therefore, it seems important to perform a joint study of their protonation and dissociation with the goal of establishing relations between these processes.

The present article reports the results of our quantitative study of protonation equilibria and kinetics of dissociation of substituted phthalocyanine complexes MPc(R)$_n$ **I**–**IV** (R = 4-$NO_2$, 4-Br-5-$NO_2$, 4-Cl-5-$NO_2$) with Cu(II) and Al(III) which form dative $\sigma\pi$ and $\sigma$ bonds, respectively.



**I**, M = Cu, R = 4-$NO_2$; **II**, M = Cu, R = 4-Br-5-NO; **III**, M = (OH)Al, R = 4-$NO_2$; **IV**, M = (OH)Al, R = 4-Cl-5-NO.

The results of spectrophotometric study of sulfuric acid solutions of metal phthalocyanines are given in

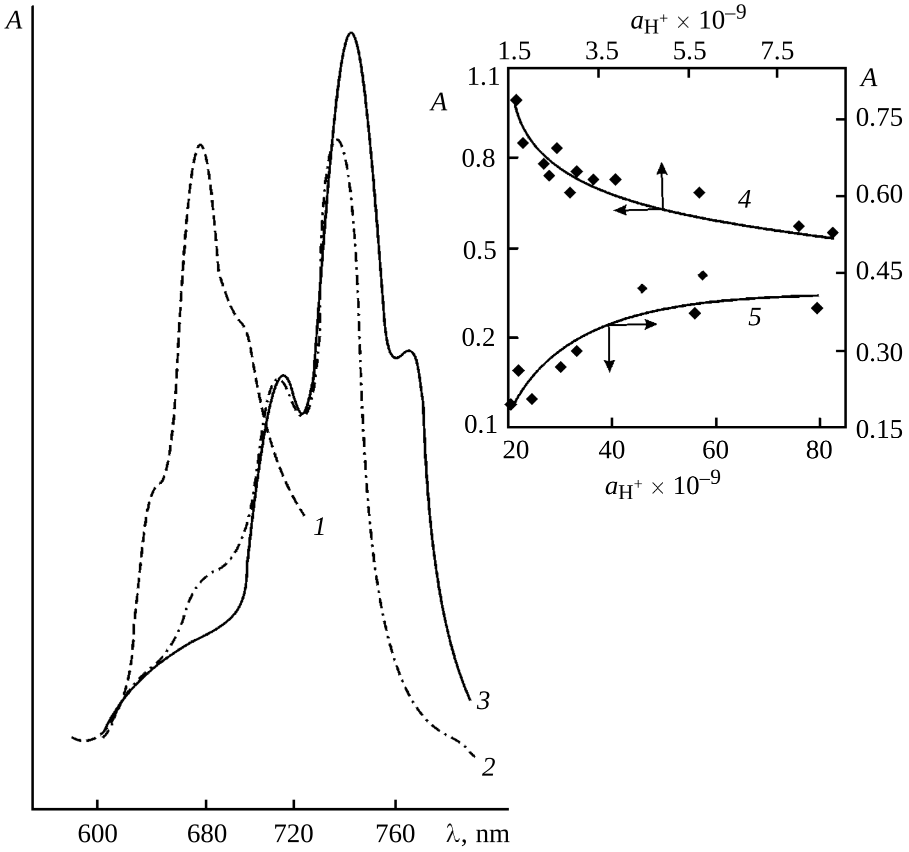


**Fig. 1.** Electronic absorption spectra of (*1*) $(OH)AlPc(4\text{-}Cl)_4\text{-}(5\text{-}NO_2)_4$ in pyridine and its (*2*) mono- and (*3*) diprotonated forms in concentrated sulfuric acid and the corresponding titration curves at (*4*) λ 735 and (*5*) 770 nm.

Table 1 and Fig. 1. The protonation equilibrium of $(OH)AlPc(4\text{-}Cl)_4(5\text{-}NO_2)_4$ was studied quantitatively. The first stage of equilibrium (1) was examined in the range of sulfuric acid concentrations from 15.2 to 17.0 M, and the second stage (2), in the range from 17.1 to 18.0 M.

**Table 1.** Positions of the long-wave absorption maxima and their shifts in the electronic spectra of substituted metal phthalocyanines and their protonated forms

| Comp. no. | Number of protonated forms[a] | $\lambda_{max}$, nm | | | $\Delta\lambda_{max}$, nm | |
|---|---|---|---|---|---|---|
| | | neutral (pyridine) | mono-cation | di-cation | mono-cation | di-cation |
| **I** | 2 | 669[b] | 727 | 760 | 58 | 33 |
| **II** | 1 | 686 | 743.7 | – | 57.7 | – |
| **III** | 1 | 685 | 745.7 | – | 60.7 | – |
| **IV** | 2 | 678 | 738.2 | 742.6 | 60.2 | 4.4 |

[a] The number of protonated forms of complexes **I–III** and the corresponding $\lambda_{max}$ were determined from the dependence of spectral parameters of the true solution upon $H_2SO_4$ concentration. [b] In DMF.

$$(OH)AlPc(4\text{-}Cl)_4(5\text{-}NO_2)_4 + H^+ \rightleftarrows (OH)AlPc(4\text{-}Cl)_4(5\text{-}NO_2)_4H^+, \qquad (1)$$

$$(OH)AlPc(4\text{-}Cl)_4(5\text{-}NO_2)_4H^+ + H^+ \rightleftarrows (OH)AlPc(4\text{-}Cl)_4(5\text{-}NO_2)_4H_2^{2+}. \qquad (2)$$

During titration the spectrum of the neutral complex, $\lambda_{max}$ 678 nm, is converted into the spectrum of monoprotonated form, which then becomes typical of the corresponding dication (Fig. 1). The step protonation constants $K_1$ and $K_2$ were estimated at $(4 \pm 1) \times 10^{-9}$ and $(4 \pm 3) \times 10^{-10}$ l mol$^{-1}$, respectively, using Eq. (3) which takes into account the proportionality between the concentration and optical density ($A_0$, $A_\infty$, and $A_e$) of the neutral and protonated forms of the complex and their equilibrium mixtures.

$$K = (A_e - A_0)/(A_\infty - A_0)/[1 - (A_e - A_0)/(A_\infty - A_0)] \times 1/[a_{H^+} - c^0_{MPc}(A_e - A_0)/(A_\infty - A_0)]. \qquad (3)$$

**Table 2.** Total energies *E*, heats of formation Δ*Q*, step protonation energies *E*' and heats Δ*Q*', and interatomic distances in the coordination entity of the complexes $(X)AlPc(4\text{-}Cl)_4(5\text{-}NO_2)_4$ and their protonated forms, calculated by the ZINDO1 method

| Complex | *E*, kcal/mol | Δ*Q*, kcal/mol | *E*', kcal/mol | Δ*Q*', kcal/mol | Distance, Å | | | | | | |
|---|---|---|---|---|---|---|---|---|---|---|---|
| | | | | | $N^1$–Al | $N^2$–Al | $N^3$–Al | $N^4$–Al | N–$H^+$ | N–$H^+$ | Al–X |
| $(Cl)AlPc(4\text{-}Cl)_4(5\text{-}NO_2)_4$ | | | – | – | 2.1684 | 2.1689 | 2.1698 | 2.1692 | – | – | 2.3825 |
| $(Cl)AlPc(4\text{-}Cl)_4\cdot(5\text{-}NO_2)4H^+$ | –24406.3 | –16411.9 | –179.7 | –127.7 | 2.1709 | 2.1622 | 2.1747 | 2.1933 | 1.0529 | – | 2.3675 |
| $(Cl)AlPc(4\text{-}Cl)_4(5\text{-}NO_2)_4\cdot H_2^{2+}$ | –24401.0 | –16354.6 | –179.1 | –127.0 | 2.1793 | 2.1790 | 2.1792 | 2.1791 | 1.0538 | 1.0539 | 2.3564 |
| $(OH)AlPc(4\text{-}Cl)_4(5\text{-}NO_2)_4$ | | | – | – | 2.1758 | 2.1744 | 2.1758 | 2.1781 | – | – | 2.1819 |
| $(OH)AlPc(4\text{-}Cl)_4\cdot(5\text{-}NO_2)_4H^+$ | –24482.6 | –16405.6 | –180.9 | –128.8 | 2.1963 | 2.1712 | 2.1722 | 2.1971 | 1.0542 | – | 2.1960 |
| $(OH)AlPc(4\text{-}Cl)_4\cdot(5\text{-}NO_2)_4H_2^{2+}$ | –24480.0 | –16350.9 | –180.2 | –128.1 | 2.1914 | 2.1789 | 2.1815 | 2.1937 | 1.0538 | 1.0535 | 2.1718 |

The number of protons added at the first and second protonation steps was determined from the slopes of straight lines plotted in the $\log I$—$a_{H^+}$ coordinates, where *I* is the reference ratio $(A_e - A_0)/(A_\infty - A_0)$, and $a_{H^+}$ is the activity of protons [6]. In both cases values close to unity were obtained.

It is seen that the shifts of the long-wave absorption maximum on first protonation are similar for all four complexes. However, the latter differ strongly in their basicities: Complexes **I** and **IV** can be protonated further to give dications, and the corresponding shifts $\Delta\lambda_{max}$ are also strongly different (Table 1). Increase in the equilibrium constant for compound **IV** by an order of magnitude in going from the first equilibrium stage to the second is well consistent with the results of quantum-chemical calculations given in Table 2. Table 2 contains the calculated energy and geometric parameters of complexes **IV** and its mono- and diprotonated forms. First, the calculations confirm the possibility of formation of two protonated forms of compound **IV**; second, the energy of addition of the first proton is greater by 2.9 kJ/mol than the energy of the second protonation. As follows from Table 1, the basicites of Cu(II) and Al(III) complexes change in the opposite directions on replacement by halogen (cf. complexes **I**, **II** and **III**, **IV**). It will be clear from the kinetic data on dissociation of complexes **I**–**IV** that such variations are the result of participation of $d_\pi$ orbitals of Cu in electron density redistribution and the lack of population of such orbitals in Al(III) complexes.

Decomposition of complexes **I**–**IV** in hot concentrated sulfuric acid is accompanied by gradual decrease in the intensity of absorption of the initial protonated forms (Fig. 2) while other absorbing species (including metall-free substituted phthalocyanine) do not appear. This means that the rate-determining stage is decomposition of the coordination entity, which is followed by fast decomposition of the metal-free macroring to weakly colored products [reactions (4) and (5)]. The dissociation of compounds **I**–**III** is satisfactorily described by formally first-order kinetic equation (6) (with respect to the concentration of the complex). The rate constants $k_{app}$ are given in Table 3.

$$MPc(R)_nH_m^{m+} + 2H_3O^+_{solv} \rightarrow H_2Pc(R)_nH_m^{m+} + M^{2+}_{aq}, \quad (4)$$

$$H_2Pc(R)_nH_m^{m+} \longrightarrow \text{Weakly colored products}, \quad (5)$$

$$dc_{MPc(R)_nH_m^{m+}}/d\tau = k_{app}–c_{MPc(R)_nH_m^{m+}}. \quad (6)$$

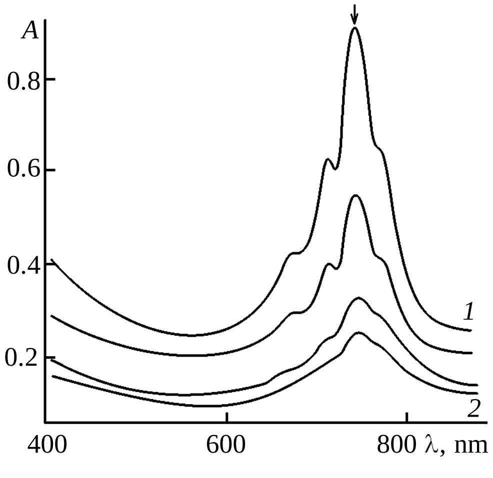


**Fig. 2.** Variation of the absorption spectrum of the complex $(OH)AlPc(4\text{-}NO_2)_4$ in 17.15 M $H_2SO_4$ at 410 K: (*1*) initial spectrum and (*2*) after 1920 s.

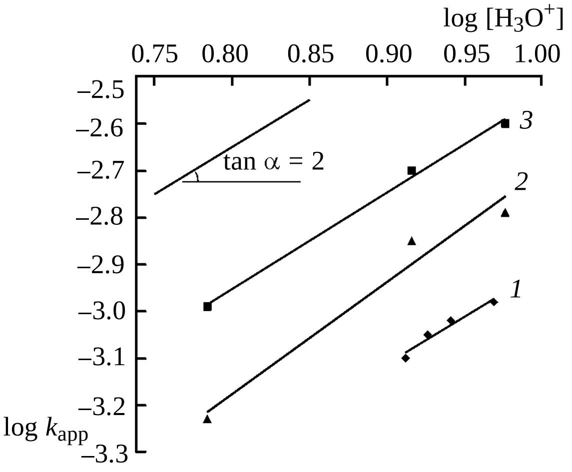


**Fig. 3.** Plots of $\log k_{\mathrm{app}}$ vs. $\log[\mathrm{H_3O^+}]$ at 410 K: (*1*) $\mathrm{(OH)AlPc(4\text{-}NO_2)_4}$, (*2*) $\mathrm{CuPc(4\text{-}NO_2)_4}$, (*3*) $\mathrm{CuPc \cdot (4\text{-}Br)_4(5\text{-}NO_2)_4}$.

The rate constants $k_{\mathrm{app}}$ decrease in a nonlinear mode as the initial acid concentration $c^0_{\mathrm{H_2SO_4}}$ rises, giving rise to a smooth curve complexes **I** and **III**. The $k_{\mathrm{app}}$–$c^0_{\mathrm{H_2SO_4}}$ dependence for complex **II** at 410 K shows a jump at a sulfuric acid concentration corresponding to the maximum on the $[\mathrm{H_3O^+}]$–$c^0_{\mathrm{H_2SO_4}}$ dependence [7, 8]. The equilibrium concentration of $\mathrm{H_3O^+}$ ions, calculated for elevated temperatures on the basis of published data [9] decreases together with the reaction rate as the concentration of sulfuric acid increases. Therefore, a linear correlation between $k_{\mathrm{app}}$ and $\mathrm{H_3O^+}$ could be expected.

$$k_{\mathrm{app}} = k\,[\mathrm{H_3O^+}]^n. \qquad (7)$$

Complexes **I**–**III** give rise to satisfactory linear correlations between $\log k_{\mathrm{app}}$ and $\log[\mathrm{H_3O^+}]$; the correlation coefficient is 0.95 to 0.99 (Fig. 3), and the slope is close to 2. Hence the overall kinetic equation of reaction (4) is as follows [Eq. (8)].

$$dc_{\mathrm{MPc(R)}_n\mathrm{H}_m^{m+}}/d\tau = k\,c_{\mathrm{MPc(R)}_n\mathrm{H}_m^{m+}}[\mathrm{H_3O^+}]^2. \qquad (8)$$

Table 4 contains the true values of rate constants and activation energies of reaction (4), which were determined by treatment of Eq. (8) and temperature dependence of *k*, respectively, by the least-squares procedure. The entropies of activation were calculated using the main equation of the transition state theory. It should be noted that the above relations refer to dissociation of monoprotonated complexes **II** and **III** [$m = 1$ in Eqs. (4)–(6) and (8)] and diprotonated form of **I** ($m = 2$). The latter gives monoprotonated species at a sulfuric acid concentration below 14.0 M. Complex **IV** takes one proton in sulfuric acid solutions with a concentration of 12 to 17 M and two protons at higher $\mathrm{H_2SO_4}$ concentration. Thus in the Brand region, where the dissociation of complex **IV** was studied (Table 3), the state of the complex changes at $c_{\mathrm{H_2SO_4}} = 17$ M. This leads to deviation of the $\log k_{\mathrm{app}}$–$\log[\mathrm{H_3O^+}]$ correlation from linearity: The rate of reac-

**Table 3.** Apparent dissociation rate constants of complexes **I**–**IV** in sulfuric acid

| Comp. no. | $c^0_{\mathrm{H_2SO_4}}$, M | $k_{\mathrm{app}} \times 10^4$, s$^{-1}$ | | |
|---|---|---|---|---|
| | | 379 K | 410 K | 423 K |
| **I** | 15.85 | 12.2 ± 0.9 | 36 ± 2 | 58 ± 2 |
| | 16.67 | 1.7 ± 0.1 | 24 ± 2 | 45 ± 3 |
| | 17.08 | 1.4 ± 0.2 | 20.3 ± 1.5 | 29 ± 3 |
| | 17.68 | 0.54 ± 0.04 | 10.3 ± 0.9 | 23 ± 2 |
| **II** | 15.85 | 3.7 ± 0.4 | 10.2 ± 0.7 | 33.2 ± 0.2 |
| | 16.67 | 4.0 ± 0.2 | 16.1 ± 0.4 | 24 ± 2 |
| | 17.08 | 1.13 ± 0.07 | 14.0 ± 0.9 | 19.8 ± 0.6 |
| | 17.68 | 0.67 ± 0.03 | 5.8 ± 0.7 | 16.4 ± 0.9 |
| **III** | 16.0 | 1.7 ± 0.1 | | 20 ± 2$^a$ |
| | 16.67 | 1.7 ± 0.1 | 10.5 ± 0.3 | 19.6 ± 0.2$^a$ |
| | 16.92 | 1.6 ± 0.1 | 9.5 ± 0.5 | 16 ± 1$^a$ |
| | 17.02 | 1.24 ± 0.06 | 9 ± 1 | 16.0 ± 0.5$^a$ |
| | 17.15 | 0.856 ± 0.004 | 7.9 ± 0.3 | 14 ± 1$^a$ |
| | 17.62 | 0.74 ± 0.05 | | |
| | 17.67 | 0.55 ± 0.05 | | 13.0 ± 0.9$^a$ |
| | 17.88 | 0.50 ± 0.06 | | |
| **IV** | 16.67 | 0.74 ± 0.02$^b$ | 7.0 ± 0.2 | |
| | 17.02 | 0.46 ± 0.03$^b$ | 7.8 ± 0.2 | 16 ± 1$^a$ |
| | 17.62 | 0.60 ± 0.02$^b$ | 8.1 ± 0.4 | 13 ± 1$^a$ |
| | 17.67 | 0.58 ± 0.01$^b$ | 5.7 ± 0.3 | 14 ± 1$^a$ |
| | 17.88 | 0.52 ± 0.02$^b$ | 6.0 ± 0.1 | 12 ± 1$^a$ |

[a] At 419 K. [b] At 376 K.

**Table 4.** Rate constants *k* and activation energies *E* and entropies $\Delta S^{\neq}$ for dissociation of substituted metal phthalocyanines in sulfuric acid

| Comp. no. | $k \times 10^6$, s$^{-1}$ mol$^2$ l$^{-2}$ | | | | *E*, kJ/mol | $\Delta S^{\neq}$, J mol$^{-1}$ K$^{-1}$ |
|---|---|---|---|---|---|---|
| | 379 K | 410 K | 423 K | 298 K | | |
| **I** | 0.80 | 26.9 | 160 | $1.3 \times 10^{-6}$ | 172 | 79 |
| **II** | 0.62 | 8.1 | 300 | $1.05 \times 10^{-5}$ | 231 | 224 |
| **III** | 1.9 | 12 | 21$^a$ | $1.6 \times 10^{-3}$ | 82 | –148 |
| $\mathrm{CuPcH^+}$ [10] | | | | $1.4 \times 10^{-6}$ | 149 | 30 |
| $\mathrm{(X)AlPcH^+}$ [9] | | | | $3.9 \times 10^{-4}$ | 68 | –196 |

[a] At 419 K.

tion (4) initially decreases as $c^0_{H_2SO_4}$ rises, a positive jump is then observed, and the rate further decreases (Table 3).

The series of the true rate constants $k_{298}$ ($s^{-1}$ $mol^2 \times l^{-2}$) for unsubstituted and substituted Al and Cu complexes are as follows: $(OH)AlPc(4\text{-}NO_2)_4$ ($1.6 \times 10^{-9}$) > (X)AlPc ($0.39 \times 10^{-9}$ [10]) and $CuPc(4\text{-}Br)_4(5\text{-}NO_2)_4$ ($1.05 \times 10^{-11}$) > CuPc ($1.4 \times 10^{-12}$ [10]), $CuPc(4\text{-}NO_2)_4$ ($1.3 \times 10^{-12}$). Insofar as the true rate constant for complex **IV** was not determined, it may be compared with tetranitro-substituted aluminum complexes through the apparent constant $k^{298}_{app}$ ($s^{-1}$) at a fixed composition of the mixed solvent water–sulfuric acid: $(OH)AlPc(4\text{-}NO_2)_4$ ($2 \times 10^{-7}$) > $(OH)AlPc(4\text{-}Cl)_4(5\text{-}NO_2)_4$ ($2.2 \times 10^{-8}$) and $(OH)AlPc(4\text{-}NO_2)_4$ ($8 \times 10^{-8}$) > $(OH)AlPc(4\text{-}Cl)_4\text{-}(5\text{-}NO_2)_4$ ($8 \times 10^{-9}$) at $c^0_{H_2SO_4}$ 17.68 and 17.02, respectively. As follows from the above data, introduction of halogen (Cl, Br) into nitro-substituted metal phthalocyanines exerts the reverse effects on the stability of Al and Cu complexes. The same applies to their basicities (Table 1).

We previously showed [11] that halogen atom and nitro group in the *ortho*-position with respect to each other are not conjugated with the macroring of phthalocyanine copper complex. The negative inductive effect of bromine in complex **II** is reflected in the reduced strength of the Cu–N σ-bonds; as a result, complex **II** is an order of magnitude less stable than compound **I**. The effect of chlorine substitution in Al complexes is the reverse: The stability of chlorine-substituted complex **IV** is greater by a factor of 10 for the monoprotonated form and by a factor of 350 for the diprotonated form (17.68 and 17.02 M $H_2SO_4$, respectively). Presumably, the reason is the enhanced Al–O donor–acceptor interaction on introduction of chlorine. A strong effect of binding with anionic ligand on the electronic structure of the macroring is confirmed by quantum-chemical calculations (Table 2). In going from $(Cl)AlPc(4\text{-}Cl)_4(5\text{-}NO_2)_4H^+$ to $(OH)AlPc(4\text{-}Cl)_4(5\text{-}NO_2)_4H^+$ the energy $E'$ and heat $\Delta Q'$ of the first protonation decrease by 5.02 and 4.6 kJ/mol, respectively. A greater increase (by a factor of 35) in the stability in more concentrated sulfuric acid in going from $(OH)AlPc(4\text{-}NO_2)_4$ to its halogen-substituted analog suggests that protonation exerts a stabilizing effect. Obviously, the probability of effective collisions with the reagent ($H_3O^+$) decreases as the positive charge on the substrate rises.

## EXPERIMENTAL

Complexes **I**–**IV** were synthesized by the template procedure described in [12]. The thermodynamics of protonation and kinetics of dissociation of the complexes were studied by spectrophotometry using Specol-221, Specord M-400, and SF-26 instruments. Sulfuric acid of chemically pure grade was used; its concentration was determined by acid–base titration with an accuracy of ±0.09%.

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