ISSN 1070-3632, Russian Journal of General Chemistry, 2014, Vol. 84, No. 9, pp. 1777–1781. © Pleiades Publishing, Ltd., 2014.
Original Russian Text © A.A. Voronina, I.A. Kuzmin, A.S. Vashurin, G.P. Shaposhnikov, S.G. Pukhovskaya, O.A. Golubchikov, 2014, published in Zhurnal Obshchei Khimii, 2014, Vol. 84, No. 9, pp. 1540–1545.

Self-Association of Sulfo Derivatives of Cobalt Phthalocyanine in Aqueous Solution

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Received March 24, 2014

Abstract—Sulfo derivatives of cobalt phthalocyanine containing naphthalene fragments have been synthesized, and their self-association and molecular complexation with pyridine in aqueous solution have been studied by spectrophotometry. The dissociation constants of the dimeric associates have been determined. The effects of the number of functional groups in the peripheral substituents and of the axial ligand on the phthalocyanine dimerization process have been revealed.

Keywords: cobalt sulfophthalocyanine, dimerization, molecular complex, spectrophotometry

DOI: 10.1134/S1070363214090230

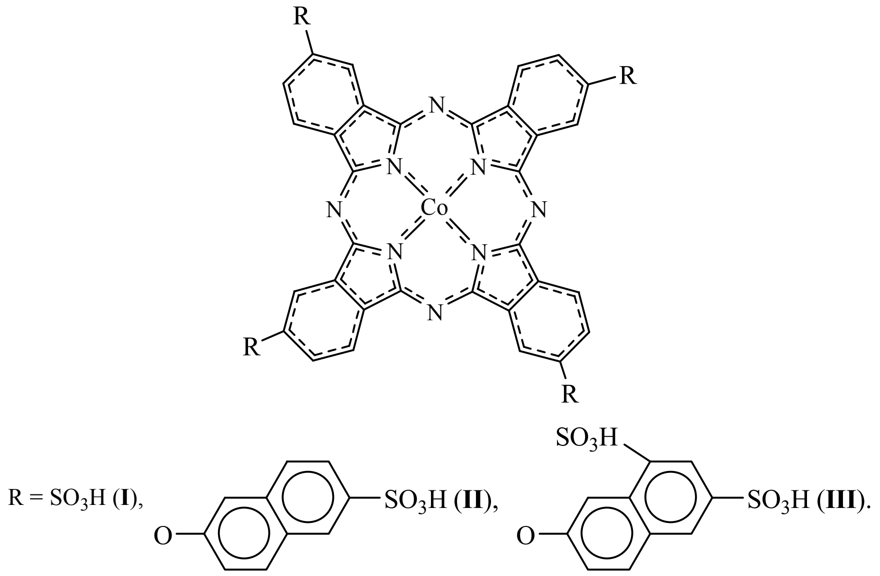
Selective oxidation of hydrocarbons and sulfur-containing compounds with molecular oxygen constitutes now a priority line in catalysis and implies the use of metal complex catalysts. Extensively developing studies in this field are concerned with catalysis by coordination compounds which simulate the action of enzymes. From this viewpoint, promising are metal complexes of water-soluble phthalocyanines [1–5].

Catalytic activity of metal phthalocyanines is largely determined by their ability to extra coordination of one or two neutral ligands by the central metal ion [6–9]. However, association of phthalocyanine metal complexes in solution creates some problems in their use as catalysts [10–12]. It is known that metal phthalocyanines in solution form dimers and other associates [13, 14]. Dimerization considerably reduces their catalytic activity [15, 16] since the formation of some dimeric structures, e.g., π–π dimers, leads to shielding of the reaction center, which hampers interaction with a substrate. Introduction of some activating additives, such as axial ligands, often enhances the catalytic activity. Examples of catalytic reactions have been reported, where addition of a small amount of some compounds dramatically changed the reaction rate [17–19].

The present work was aimed at studying association of octa- and tetrasulfo derivatives of cobalt phthalocyanines in aqueous solution and water–pyridine mixtures. The substrates were (3,10,17,24-tetrasulfophthtalocyaninato)cobalt(II) (**I**), [3,10,17,24-tetrakis-(6-sulfonaphthalen-2-yloxy)phthalocyaninato]cobalt(II) (**II**), and [3,10,17,24-tetrakis(6,8-disulfonaphthalen-2-yloxy)phthalocyaninato]cobalt(II) (**III**) (Scheme 1).

Dissolution of cobalt phthalocyanines **I**–**III** in weakly alkaline aqueous solution (pH 7.1–8.1) involves formation of the corresponding salts at the sulfo groups. The concentration dependence of the electronic absorption spectra shows that complex **I** in the concentration range from 2×10^{-5} to 2×10^{-4} M exists mainly as dimer (Fig. 1). The latter absorbs at λ 615–630 nm against λ 670–675 nm for the monomeric species. The molar absorption coefficient of the dimer at λ 630 is 15 200±50 L mol^{-1} cm^{-1}, which is consistent with published data [13, 20–22]. No relaxation effects (which are commonly related to change of the aggregate state of the macrocycle) were observed in the electronic absorption spectra [16, 20]; this provides an additional proof for the prevalence of dimeric species in solution. Some red shift of the *Q* band upon dilution is most likely to result from formation of unstable molecular complexes with oxygen [23].

Scheme 1.



It is known [20] that the ability of phthalocyanines to undergo association decreases as the number of sulfo groups in the molecules increases. The electronic absorption spectra of phthalocyanines **II** [λ_{max} 615 nm, $\varepsilon = 4800 \pm 50$ L mol^{-1} cm^{-1}] and **III** [λ_{max} 630 nm, $\varepsilon = 800 \pm 20$ L mol^{-1} cm^{-1}] in the concentration range 5×10^{-5} to 6×10^{-4} M conform to the Beer–Lambert–Bouguer law (Fig. 2). Judging by the position of the absorption maxima, these phthalocyanines also exist mainly as dimers. The structure of **II** and **III** suggests preferential formation of π–π or μ-oxo dimers.

In order to determine the mode of dimerization of compounds **I**–**III**, we examined the temperature dependences of their electronic absorption spectra and molecular complexation with pyridine. Raising the temperature from 25 to 60°C led to different changes in the spectrs of cobalt phthalocyanines **I**–**III**.

In the spectrum of **I** we observed reduction of the absorbance at λ 630 nm (dimer band) and increase of the *Q* band intensity; in addition a new band appeared with its maximum at λ 975 nm. In keeping with published data [24, 25], the latter band corresponds to so-called columnar aggregates. An isosbestic point was observed. In the spectra of complexes **II** and **III**, only a new band appeared at λ 965–975 nm.

Presumably, rise in temperature leads to displacement of the equilibrium toward monomeric phthalocyanine **I**, while the remaining dimeric species are transformed into columnar aggregates. Phthalocyanines **II** and **III** containing naphthalene fragments

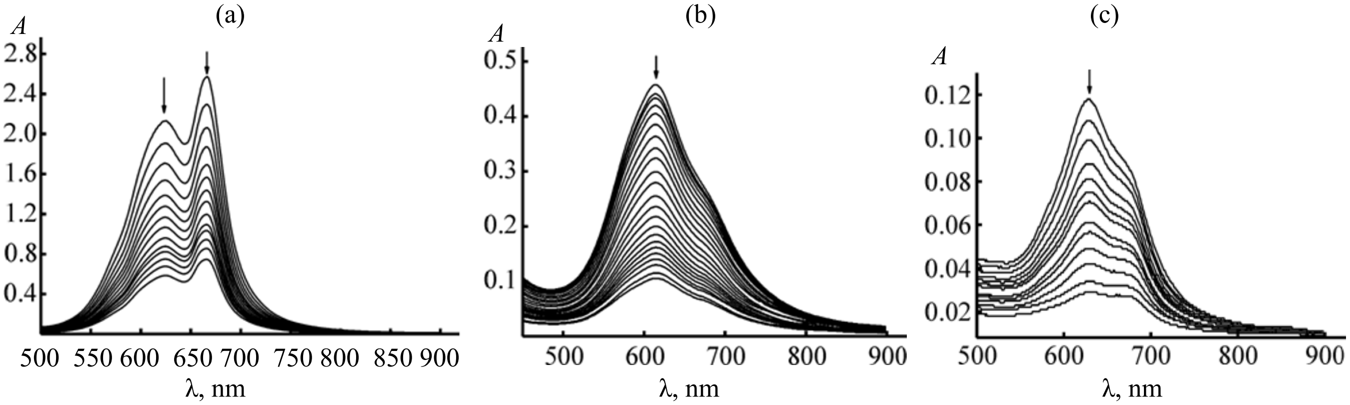


Fig. 1. Variation of the electronic absorption spectra upon dilution of aqueous solutions of phthalocyanines (a) **I**, (b), **II**, and (c) **III** in the concentration range from 2×10^{-4} to 2×10^{-7} M.

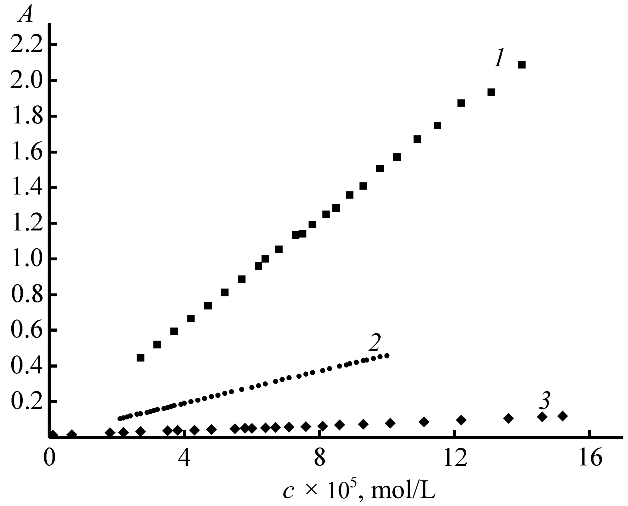


Fig. 2. Concentration dependences of the optical density of solutions of phthalocyanines (*1*) **I**, (*2*) **II**, and (*3*) **III** at 298.15 K.

give rise to only less ordered columnar aggregates at elevated temperature.

In order to refine the mode of dimerization, aqueous solutions of phthalocyanines **I**–**III** were titrated with pyridine. Addition of pyridine to solutions of **II** and **III** resulted in successive increase of the *Q* band intensity and decrease of the absorbance at λ 615–640 nm (Fig. 3) corresponding to the dimer; i.e., equilibrium (1) was displaced toward the monomeric species. Pyridine can affect the association equilibrium via extra coordination to the central metal ion (2), which rules out the possibility for π–π interaction between two macrocycles.

$$2\text{MPc} \overset{K_{\text{eq1}}}{\rightleftharpoons} (\text{MPc})_2, \quad (1)$$

$$\text{MPc} + \text{L} \overset{K_{\text{eq2}}}{\rightleftharpoons} \text{MPc·L}. \quad (2)$$

The complex formation constants of cobalt phthalocyanines with pyridine were determined by measuring the optical density at two wavelengths (descending and ascending) [26–29] using formula (3).

$$K_{\text{eq2}} = [\text{MPc·L}]/([\text{MPc}]\cdot[\text{L}]) = (1/[\text{L}])\cdot[(\Delta A_{i,\lambda 1}\cdot\Delta A_{0,\lambda 2})/(\Delta A_{0,\lambda 1}\cdot\Delta A_{i,\lambda 2})]. \quad (3)$$

Here, λ_1 is the descending wavelength, λ_2 is the ascending wavelength, [L] is the equilibrium concentration of the ligand (pyridine), ΔA_0 is the maximum variation of the optical density at a given wavelength, ΔA_i is the change of the optical density at a given wavelength at a given concentration. The error in the determination of K_{eq2} was 5–7%.

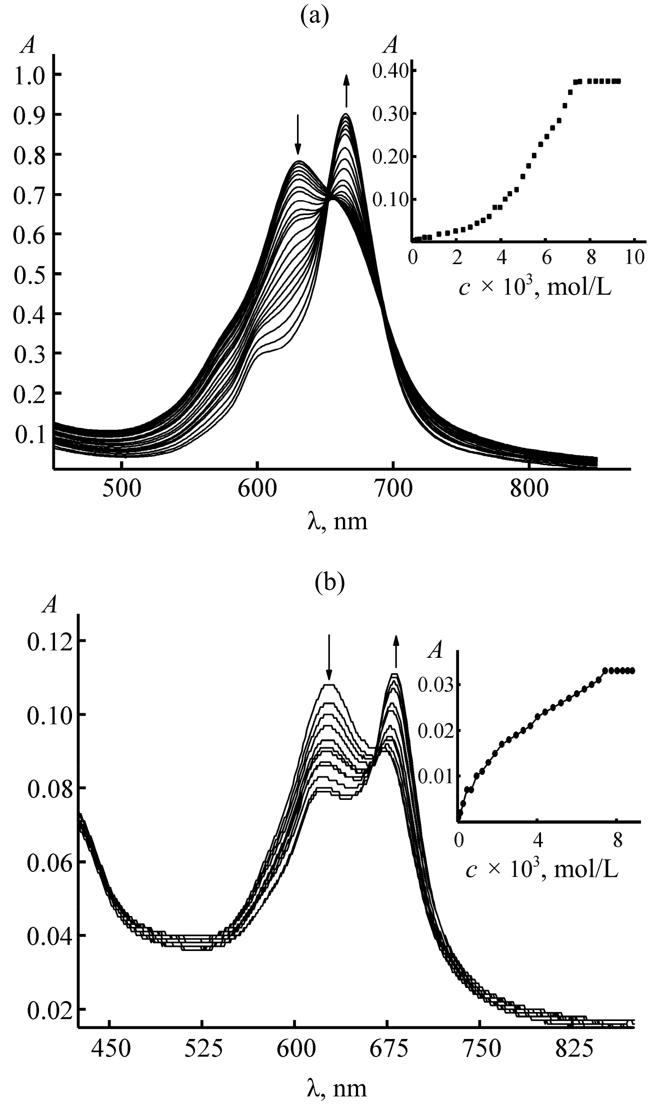


Fig. 3. Spectrophotometric titration of aqueous solutions of phthalocyanines (a) **II** and (b) **III** (c = 2×10^{-5} M) with pyridine at 298.15 K.

It is known that coordination of one extra ligand to macrocyclic tetrapyrrole complexes leads to deviation of the metal ion from the macrocycle plane toward the extra ligand, which induces red shift of the *Q* band. Addition of the second extra ligand is accompanied by blue shift of the *Q* band, so that the overall shift may be small [30]. In our experiments, addition of pyridine to solutions of **I**–**III** resulted in red shift of the *Q* band by 20–30 nm. Therefore, we assumed coordination of only one pyridine molecule as extra ligand with formation of 1 : 1 complex.

Two linear parts corresponding to equilibria (1) and (2) can be distinguished on the spectrophotometric titration curves obtained for all the examined systems (Fig. 3). Presumably, the second linear part of the titration curve reflects only the formation of molecular complex. In keeping with the equilibrium constants, the stability of the pyridine complexes decreases in the series **III** (K = 2500 L/mol) > **II** (1600 L/mol) > **I** (17 L/mol [13, 20]). These data may be interpreted in favor of π–π dimers of **I**–**III**. Had the dimeric structures been formed through hydrogen bonding between the peripheral substituents or had μ-oxo dimers been formed, extra coordination of pyridine would not favor monomerization of cobalt phthalocyanines **I**–**III**.

π–π Dimers are formed via π–σ-attraction and π–π repulsion of electronic systems of the two macrocyclic molecules. Coordination of pyridine increases polarizattion of the π-system, which in turn leads to domination of π–π repulsion over π–σ attraction and displacement of equilibrium (1) toward monomeric species. Taking into account that the electronic absorption spectra of the dimers in the concentration range 5×10^{-5} to 2×10^{-4} M fit the Beer–Lamberta–Bouguer law, the dissociation constants of the dimers of **I**–**III** were calculated by Eqs. (4) and (5) from the molar absorption coefficients of the monomer and dimer according to [20, 31–34].

$$K_{\text{diss}} = 1/K_{\text{dim}}, \tag{4}$$

$$(A_0 - A_i) = \{(2\varepsilon_M - \varepsilon_D)(1 + 4K_{\text{dim}}[\text{MPc}]) - (1 + 8K_{\text{dim}}[\text{MPc}]^{1/2})\}/8K_{\text{dim}}. \tag{5}$$

Here, A_0 is the optical density of the initial solution, A_i is the optical density at a current concentration, K_{dim} is the dimerization constant, ε_{M} is the molar absorption coefficient of the monomer, abd ε_{D} is the molar absorption coefficient of the dimer.

The dissociation constants K_{dim} decrease in the series **III** > **II** > **I** ($K_{\text{diss}} = 2.2 \times 10^{-4}$, 1.54×10^{-4}, and 1.08×10^{-4} M [13, 21], respectively), which characterizes the effect of peripheral substitution on the aggregation of sulfo derivatives of cobalt phthalocyanines in aqueous solution.

In summary, we have found that sulfo-substituted cobalt phthalocyanines in aqueous solution exist mainly as π–π dimers. Remoteness of sulfo groups from the conjugated macrocycle and increase in their number destabilize the π–π dimers. Addition of a small amount of bases, in particular pyridine, also favors dissociation of the dimers and shift the association equilibrium toward the monomeric species.

EXPERIMENTAL

The solvents were purified according to standard procedures [35]. Association of cobalt phthalocyanines in aqueous solution was studied by spectrophotometry. The electronic absorption spectra were measured on a Shimadzu UV 1800 spectrophotometer. The IR spectra (400–4000 cm^{-1}) were recorded in KBr on a Bruker Vertex 80v spectrometer.

Cobalt phthalocyanines were synthesized, purified, and identified as described in [36]. (3,10,17,24-Tetrasulfophthalocyaninato)cobalt(II) (**I**) was commercial product (purity 99.9%; Sigma–Aldrich).

[3,10,17,24-Tetrakis(6-sulfonaphthalen-2-yloxy)-phthalocyaninato]cobalt(II) (II). A mixture of 0.78 g of potassium 6-(1,3-dioxo-2,3-dihydro-1*H*-isoindol-2-yloxy)naphthalene-2-sulfonic acid and 0.065 g of anhydrous cobalt(II) chloride was heated for 60 min at 190–195°C under stirring. The resulting cobalt phthalocyanine was extracted into dimethyl sulfoxide and precipitated from the extract with anhydrous ethanol. The precipitate was filtered off and washed with ethanol in a Soxhlet extractor. The product was additionally purified by chromatography on silica gel M 60 using aqueous DMF (1 : 1 by volume) as eluent. Yield 0.39 g (54%); blue–green powder, readily soluble in water, aqueous DMF, DMSO, and aqueous alkali. IR spectrum, ν, cm^{-1}: 1045 (S=O, sym.), 1103 (S=O, asym.), 1205 (C–O–C). Found, %: C 58.42; H 2.70; N 7.62; S 8.80. $C_{72}H_{40}CoN_8O_{16}S_4$. Calculated, %: C 59.22; N 2.74; N 7.68; S 8.80.

[3,10,17,24-Tetrakis(6,8-disulfonaphthalen-2-yl-oxy)phthalocyaninato]cobalt(II) (III) was synthesized in a similar way from 1.01 g of dipotassium 7-(1,3-dioxo-2,3-dihydro-1*H*-isoindol-2-yloxy)naphthalene-1,3-disulfonate. Yield 0.53 g (59%); blue–green powder, readily soluble in water, aqueous DMF, DMSO, and aqueous alkali. IR spectrum, ν, cm^{-1}: 1039 (S=O, sym.), 1103 (S=O, asym.), 1210 (C–O–C). Found, %: C 48.32; H 2.20; N 6.23; S 14.43. $C_{72}H_{40}CoN_8O_{28}S_8$. Calculated, %: C 48.57; H 2.25; N 6.30; S 14.39.

ACKNOWLEDGMENTS

This study was performed under financial support by the Russian Foundation for Basic Research (project no. 13-03-00 615_a) and partially supported by the state task Ministry of Education and Science of the Russian Federation.

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