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Synthesis and Properties of Metal Phthalocyanines Based on Disulfophthalic Acid

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Abstract—Octasulfo-substituted cobalt phthalocyaninate was synthesized from 3,5-disulfophthalic acid, and its ammonium salt was converted into the corresponding sulfonyl chloride by the action of chlorosulfonic acid. Treatment of the chlorosulfonyl-substituted phthalocyanine complex with aliphatic amines gave octaalkyl-sulfamoyl derivatives. The products were characterized by IR and electronic absorption spectra. **DOI:** 10.1134/S1070363206080317

Sulfo derivatives constitute a large group of substituted phthalocyanines; these compounds have already found application as dyes and redox catalysts [1]. In the recent years, sulfo-substituted phthalocyanines are extensively studied as photosensitizers in the diagnostics and therapy of malignant tumors [2, 3].

Most generally, sulfo derivatives of phthalocyanines are synthesized by sulfonation of unsubstituted metal phthalocyaninates. Depending on the conditions, one to four sulfo groups can be introduced. Published data on phthalocyanine metal complexes containing more than four sulfo groups are very limited [4]. In addition, further transformations of sulfo groups into other substituents, in particular al-kylsulfamoyl, attract interest from the viewpoint of obtaining water-soluble phthalocyanines [5].

Here we report on the synthesis and properties of sulfo-substituted metal phthalocyaninates based on 3,5-disulfophthalic acid (IV). Compound II was obtained by oxidation of dipotassium 2-hydroxy-naphthalene-6,8-disulfonate (I) with potassium permanganate (KMnO₄) in aqueous–alkaline medium.



The oxidation occurs primarily at the aromatic ring containing electron-donor OH group which is known [6, 7] to destroy its aromaticity. We have found optimal conditions for the oxidation process; these conditions implied a constant amount of water in the reaction mixture, temperature not exceeding 90– 95°C, and portion-wise addition of the oxidant as it was consumed. If the reaction mixture was overheated and strong evolution of oxygen was observed, the second (sulfo-substituted) benzene ring was also oxidized. As a result, the yield of compound **II** decreased, and the concentration of inorganic impurities increased. When the oxidation was complete, target product II was precipitated by acidification to pH 3–4 with hydrochloric acid and cooled. In this case, the precipitate of compound II contained inorganic impurities. Salt II was obtained with higher purity by precipitation of impurities from water–ethanol (2:2.5), followed by isolation of II from the filtrate.

Compound **II** was treated with chlorosulfonic acid to obtain acid chloride **III** which was extracted into acetone. After removal of the solvent, water was added to the dry residue, and chloride **III** was thus converted into 3,5-disulfophthalic acid **IV**. Compound **IV** is a light yellow powder, which is readily soluble in water and aqueous alcohol. It was identified on the basis of its elemental composition and IR spectral data. The IR spectrum of **IV** contained absorption bands in the region 1050–1200 cm⁻¹ due to stretching vibrations of the S=O bond. Carboxy carbonyl groups gave rise to absorption at 1740 cm⁻¹ [8].



Octasulfo-substituted metal phthalocyaninates were synthesized by the "urea" method, i.e., by heating a mixture of the initial phthalic acid derivative, cobalt or copper salt, urea, and a catalytic amount of ammonium molybdate. However, we succeeded in obtaining only the complex CoPc(3,5-SO₃H)₈ (**V**) in this way; it was synthesized in a high yield using preliminarily dehydrated cobalt acetate. Complex **V** was purified by washing with an 80% aqueous solution of acetic acid until colorless washings and was dried at 90–100°C until disappearance of the odor of acetic acid; it was then extracted with water, the aqueous extract was evaporated, and the dry residue was washed with methanol.

Complex V is a dark blue powder, which is readily soluble in water and aqueous alkalis, sparingly soluble in DMF and other polar organic solvents, and insoluble in weakly polar organic solvents. It was identified by the analytical data and IR and electronic absorption spectra. In the IR spectrum of V we observed absorption bands in the regions 1000–1100 and 1150–1210 cm⁻¹, typical of symmetric and asymmetric stretching vibrations of S=O bond in aromatic sulfonic acids and their salts. Poor resolution of some absorption bands in the IR spectrum of that complex, as compared to unsubstituted phthalocyanine metal complexes [9], may be due to enhanced intermolecular interactions.

The electronic absorption spectra of complex V in aqueous and organic media (Fig. 1, Table 1) are characterized by the presence of one strong band in the long-wave region with its maximum located at λ 658–670 nm, depending on the substituent. The short-wave slope of this band has a shoulder at λ 605–612 nm. The observed spectral pattern suggests lesser degree of association of molecules V in solution, as compared to known di- and tetrasulfo-substituted phthalocyanine cobalt complexes [10].

We failed to isolate analogous octasulfo-substituted phthalocyanine copper complex by the "urea fusion" technique. Presumably, the different results obtained by fusion of copper and cobalt salts with disulfophthalic acid **IV** originate from different coordinating abilities and sizes of ions of these metals. We believe that the presence of a bulky SO₃H group in position 3 of molecule **IV** creates steric hindrances to cyclocondensation in the template synthesis. On the other hand, joint "urea fusion" of CuCl, compound



Fig. 1. Electronic absorption spectra of complex V in (1) water, (2) 1% aqueous ammonia, and (3) DMF.

IV, and phthalic anhydride at a ratio of 2:2 or 1:3 gave complexes readily soluble in aqueous alkalis, and their electronic absorption spectra were typical of CuPc sulfonic acids (Fig. 2, Table 1). Taking into



Fig. 2. Electronic absorption spectra of complex VI in (1) water and (2) 1% aqueous ammonia.

account published data on joint fusion of sulfosubstituted and unsubstituted phthalic acid derivatives [11], we believe that the formation of complexes **VI** and **VII** is the most probable.





The formation of phthalocyanine copper complex having three disulfo-substituted and one unsubstituted isoindole fragments, as well as of isomeric complex with *cis*-arranged substituted fragments, seems to be improbable for steric reasons.

The electronic absorption spectrum of complex VI in water and 1% aqueous ammonia contains a broadened band with its maximum at λ 610–616 nm and a weakly expressed shoulder at λ 680 nm. This pattern suggests that molecules VI in aqueous medium are mostly associated.

Aromatic sulfonic acids are known to be readily converted into the corresponding sulfonyl chlorides which are used as acylating agents in reactions with amines. Taking into account the data of [12] and that each of the benzene rings in complex V contains two sulfo groups, in the synthesis of sulfonyl chloride **VIII** we used a large excess of chlorosulfonic acid,

 Table 1. Positions of absorption maxima in the electronic spectra of compounds V-VII

Comp. no.	H ₂ O	H ₂ O/NH ₄ OH (1%)	DMF
V	658, 605 sh	670, 612 sh	669, 606 sh
VI	610, 680 sh	616, 680 sh	680, 620 w
VII	–	612, 675 sh	678, 618 w

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Comp. no.	Chloroform	DMF	
IX	668, 605 sh	663, 605 sh	
X	671, 607 sh	667, 607 sh	
XI	677, 610 sh	674, 630 inf	

 Table 2. Positions of absorption maxima in the electronic spectra of compounds IX-XI

and the substrate (octasulfo-substituted complex V) was preliminarily converted into ammonium salt Va.

$$CoPc(3,5-SO_3NH_4)_8 + 8HOSO_2Cl$$

$$Va$$

$$\longrightarrow CoPc(3,5-SO_2Cl)_8 + 8NH_4HSO_4.$$
VIII

Sulfonyl chloride **VIII** was then used as acylating agent in reactions with aliphatic amines to obtain octaalkylsulfamoyl-substituted phthalocyanine cobalt complexes. Interest in these compounds is explained by the fact that introduction of alkylsulfamoyl groups into molecules of phthalocyanine metal complexes is known to considerably improve the solubility in organic solvents, so that alkylsulfamoyl derivatives can be used as dyes for polyamide fibers, fat-soluble pigments, homogeneous catalysts, and components of optical materials [5].

We performed reactions of sulfonyl chloride **VIII** with alkylamines (1.5 equiv) in acetone at 30–55°C.

When the reaction was complete, the solvent was distilled off, and products **IX**–**XI** were purified by column chromatography. Compounds **IX**–**XI** are blue–green powders, which are insoluble in water,



Fig. 3. Electronic absorption spectra of complex **X** in (1) chloroform and (2) DMF.



IX, Alk =
$$C_2H_5$$
; **X**, Alk = C_8H_{17} .

sparingly soluble in polar (DMF, DMSO, etc.), and readily soluble in a wide series of weakly polar solvents such as benzene, chloroform, etc. The products were identified on the basis of their elemental compositions and IR and electronic absorption spectra.

Compounds **IX–XI** characteristically showed in the IR spectra absorption bands at 2900–3000 cm⁻¹, corresponding to stretching vibrations of alkyl C–H bonds; bands at 1300–1400 cm⁻¹ were assigned to vibrations of the S=O group in the alkylsulfamoyl moieties. The IR spectrum of **XI** contained a broad band at 3150–3330 cm⁻¹ due to stretching vibrations of the NH bond. It should be noted that the IR bands become more clearly resolved in going from compound **V** to **IX–XI** due to weakening of intermolecular interactions.

The electronic absorption spectra of complexes IX-XI in chloroform and DMF (Fig. 3, Table 2) suggest that the presence of eight bulky alkylsulfamoyl groups does not change the character of spectral curves to an appreciable extent. In the region λ 663–677 nm we observed a strong Q band corresponding to $\pi - \pi^*$ transition in the phthalocyanine macroring and a weakly expressed shoulder on the short-wave side of that band (605–610 nm). The position of the Q band changes depending on the solvent and on the length and degree of branching of the alkyl residue. Unlike tetraalkylsulfamoyl-substituted phthalocyanine metal complexes [13], the Q band in the electronic spectra of complexes **IX**-XI is defined more clearly, presumably due to weak association of their molecules in solution.

EXPERIMENTAL

The IR spectra were recorded on an Avatar-360FTIR spectrometer. The electronic absorption spectra were measured in the spectral range from λ 400 to 800 nm from solutions in water, 1% aqueous ammonia, DMF, and chloroform on a Specord M-80 spectrophotometer at room temperature.

3,5-Disulfophthalic acid (IV). A hot solution of 0.1 mol of 2-hydroxynaphthalene-6,8-disulfonic acid (preliminarily recrystallized from water) in 400 ml of water was made alkaline (pH 8–9) by adding potas-

sium hydroxide. The solution was heated to 70°C, 170 g of potassium permanganate (KMnO₄) was added in ~2.5-g portions until persistent magenta color (test on a filter paper), and the mixture was heated to 90-95°C and stirred for 30 min at that temperature. Excess KMnO₄ was quenched by treatment with ethanol. The hot suspension was filtered, and the precipitate was washed with hot water $(2 \times$ 30 ml) on a filter. The filtrate was combined with the washings, evaporated to 1/3 of the initial volume, and acidified with hydrochloric acid to a weakly acidic reaction (pH 4–5). After cooling, the precipitate was filtered off, dried at 90°C to constant weight, and dissolved in 200 ml of water on heating to 40-50°C. Mineral salts were precipitated by adding ethanol to the aqueous solution. The mixture was cooled, and the precipitate was filtered off and washed with cold ethanol $(3 \times 20 \text{ ml})$. The ethanolic filtrate was evaporated on a water bath, and the dry residue was treated with 1.6 mol of chlorosulfonic acid for 3 h at 130-135°C. The mixture was cooled and poured imto a saturated solution of sodium chloride. The precipitate (light yellow flakes) was filtered off and dried in a desiccator over concentrated sulfuric acid. Acid chloride **III** was extracted into anhydrous acetone, the extract was evaporated, 100 ml of water was added to the residue, and the mixture was heated until it became homogeneous. The solution was evaporated, and the residue was dried to obtain 8.8 g (27%) of compound IV as a light yellow substance, which was soluble in water, methanol, and ethanol. Decomposition point ~210°C. IR spectrum, v, cm⁻¹: 1740 (C=O), 1050-1200, 1200 (S=O). Found, %: C 29.4; H 2.0; S 19.2. C₈H₆O₁₀S₂. Calculated, %: C 29.4; H 1.8; S 19.6.

(2,4,9,11,16,18,23,25-Octasulfophthalocyaninato)cobalt(II) (V). Compound IV, 1 mmol, was thoroughly mixed with 8 mmol of urea, 0.3 mmol of cobalt(II) acetate, and 0.03 mmol of ammonium molybdate. The mixture was transferred into a test tube which was mounted vertically in an electric furnace and heated under stirring for 90 min at 140-150°C, 50 min at 170–180°C, 75 min at 190–200°C, and 120 min at 210-220°C. After cooling, the mixture was pounded and washed with a mixture of acetic acid with water (10:3) until weakly colored washings. The target product was extracted into water, the extract was evaporated on a water bath, and the dry residue was washed with acetone until colorless washings and dried at 90–100°C. Yield 0.045 g (15%). IR spectrum, v, cm⁻¹: 1000–1110 [v_s (S=O)], 1150–1210 [v_{as} (S=O)]. Found, %: C 32.0; H 1.25; Co 5.0; N 9.7; S 20.8. C₃₂H₁₆CoN₈O₂₄S₈. Calculated, %: C 31.7; H 1.3; Co 4.8; N 9.2; S 21.1.

(2,4,16,18-Tetrasulfophthalocyaninato)copper(II) (VI). A mixture of 0.5 mmol of 3,5-disulfophthalic acid dipotassium salt, 0.5 mmol of phthalic anhydride, 8 mmol of urea, 0.3 mmol of copper(I) chloride, and 0.3 mmol of ammonium molybdate was placed in a vertical test tube and heated for 50 min at 140–145°C, 50 min at 165–170°C, 30 min at 185– 190°C, and 120 min at 200–205°C. After cooling, the mixture was pounded and washed on a filter first with 17% and then with 5% hydrochloric acid until colorless washings. The residue was dissolved in 0.5% aqueous sodium hydroxide and filtered. The filtrate was acidified with dilute hydrochloric acid, and the precipitate of complex VI was washed with 5% hydrochloric acid and centrifuged. The washingcentrifugation sequence was repeated several times until evaporation of a drop of the washings (applied to a slide) left no solid residue. The product was dried at 90–100°C. Yield 0.175 g (21%). Found, %: C 43.1; H 1.7; Cu 6.9; S 15.0. C₃₂H₁₆CuN₈O₁₂S₄. Calculated, %: C 42.8; H 1.8; Cu 7.1; S 14.3.

(2,4-Disulfophthalocyaninato)copper(II) (VII) was synthesized as described above for compound VI from 0.25 mmol of compound IV and 0.75 mmol of phthalic anhydride. Yield 0.176 g (24%). Found, %: C 52.7; H 2.1; Cu 8.6; N 14.8; S 9.0. $C_{32}H_{16}CuN_8 \cdot O_6S_2$. Calculated, %: C 52.2; H 2.2; Cu 8.7; N 15.2; S 8.7.

[2,4,9,11,16,18,23,25-Octakis(diethylaminosulfonyl)phthalocyaninato]cobalt(II) (IX). Complex V was preliminarily converted into octaammonium salt **Va** by treatment with aqueous ammonia, evaporation of the solution on a water bath, and drying of the residue at 90–100°C. A flask equipped with a sulfuric acid seal was charged with 1 mmol of octaammonium salt Va, 10 ml of chlorosulfonic acid was added, and the mixture was heated for 3 h at 140°C. The mixture was cooled and poured into a saturated solution of sodium chloride, cooled with ice. The precipitate was filtered off, washed with a solution of sodium chloride until the absence of acidic reaction (Congo Red), and dried in a desiccator over concentrated sulfuric acid. Octakis(sulfonyl chloride) VIII was extracted into acetone, and 24 mmol of diethylamine was added to the extract. The mixture was kept for 1 h at room temperature and filtered, the solvent and excess diethylamine were evaporated from the filtrate, and compound IX was purified by column chromatography on silica gel (Silicagel L, 40–100 µm) using chloroform-methanol (10:1) as eluent. Yield 1.52 g (92%). Found, %: C 47.2; H 4.9; Co 4.1; N 13.0; S 15.6. $C_{64}H_{88}CoN_{16}O_{16}S_8$. Calculated, %: C 46.5; H 5.3; Co 3.6; N 13.6; S 15.5.

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[2,4,9,11,16,18,23,25-Octakis(dioctylaminosulfonyl)phthalocyaninato]cobalt(II) (X) was synthesized as described above for compound IX using 24 mmol of dioctylamine; the mixture was kept at 30°C. Yield 2.84 g (95%). Found, %: C 64.7; H 9.8; Co 2.3; N 6.7; S 9.1. $C_{160}H_{280}CoN_{16}O_{16}S_8$. Calculated, %: C 64.1; H 9.3; Co 1.9; N 7.5; S 8.5.

[2,4,9,11,16,18,23,25-Octakis(octadecylaminosulfonyl)phthalocyaninato]cobalt(II) (XI). Octadecylamine, 12 mmol, was added to a solution of 1 mmol of complex VIII in 50 ml of acetone, and the mixture was heated for 2 h under reflux. The solvent was evaporated, the residue was extracted with chloroform, and the extract was subjected to column chromatography on silica gel (Silicagel L, 40–100 μ m) using chloroform–methanol (10:1) as eluent. Yield 3.02 g (94%). Found, %: C 66.1; H 10.0; Co 2.0; N 6.7; S 7.7. C₁₇₆H₃₁₂CoN₁₆S₈. Calculated, %: C 65.6; H 9.7; Co 1.8; N 6.9; S 7.9.

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