3-Bromo-5-sulfobenzene-1,2,4-tricarboxylic Acid and Cobalt Phthalocyanine Based Thereon

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Abstract — 3-Bromo-5-sulfobenzene-1,2,4-tricarboxylic acid and cobalt(II) phthalocyanine based thereon were synthesized.

Among a great variety of substituted phthalocyanines, of particular interest are sulfo, carboxy, and halo derivatives. Sulfo- and carboxy-substituted phthalocyanines are characteristically readily soluble in aqueous media and polar organic solvents, which extends the field of their investigation and practical application, Halogenation in benzene rings of the phthalocyanine ligand serves to improve coloristic and other properties.

At present sufficient evidence has been accumulated concerning separately halo-, sulfo-, and carboxysubstituted phthalocyanines [1–6]. Certain of such derivatives have found practical application as dyes and pigments [7], catalysts for redox reactions [8], and biologically active substances [9]. Other scientific and technical applications have also been reported [8]. At the same time, the information on phthalocynines containing the above substituents together is very scarce, even though they present undeniable interest as objects for studying combined effects of different substituents on the properties of the substrate and as candidates for practical applications.

Proceeding with our research into phthalocyanines [10–12], in the present work we synthesized 3-bromo-5-sulfobenzene-1,2,4-tricarboxylic acid and cobalt(II) phthalocyanine on its basis.

In the first stage, starting from 1,2,4-trimethylbenzene (I) via intermediates II–IV, we synthesized dipotassium salt of 3-bromo-5-sulfobenzene-1,2,4-tricarboxylic acid (V).



Sulfonation of compound I and isolation of the sulfonation product as potassium salt III were performed by known procedures [13]. Based on the negative charge distribution in I, obtained by quantum-chemical calculations, as well as thermodynamic characteristics of possible σ complexes, we showed [10] that the sulfo group most probably enters into the 5 position.

Further on compound **III** was dissolved in water and treated with ethanolic bromine at room temperature. To determine the most probable direction of bromine attack on molecule **III**, we calculated the enthalpies (ΔH^0) of σ complexes **A** and **B** of the bromination reaction.

The resulting ΔH^0 values led us to conclude that

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bromination most probably involves formation of the $3-\sigma$ complex and, consequently, the most probable reaction product is 3-bromo-2,4,5-trimethyl-1-sulfobenzene (**IV**).



Treatment of compound **IV** with potassium permanganate in boiling aqueous alkali in the presence of pyridine resulted in the oxidation of the three methyl groups to carboxyls.

The progress of substitution in compounds IV and V and oxidation of the methyl groups into carboxyls during conversion of compound IV into compound V was followed by IR spectroscopy. The spectrum of compound V contains two stretching vibration bands

of the S=O (1000–1100 cm⁻¹) and C–Br (600– 680 cm⁻¹) bonds. As compound **IV** converted into compound **V**, we observed disappearance of the C–H stretching vibration bands at 2850–3000 cm⁻¹ and appearance of bands at 1720 cm⁻¹, belonging to stretching vibrations of carboxy C=O groups, and of two bands at 1620 and 1350 cm⁻¹, that, according to data in [14], relate to stretching vibrations of C–O bonds in resonantly stabilized carboxylate anions.

The synthesis of cobalt tetra(3-bromo-4-carboxy-5sulfo)phthalocyanine (VI) was performed by the "urea" procedure, specifically, by heating a muxture of phthalocyanogen V, urea, dry cobalt(II) acetate, and a catalytic amount of ammonium molybdate.

Complex **VI** is a dark violet powder with a metallic shine. It is readily soluble in aqueous media and polar organic solvents. Its composition and structure were proved by elemental analysis and IR and electronic spectroscopy.



The IR spectrum of complex VI preserves the C=O (in COOH), S=O (in SO₃H), and C-Br stretching absorption bands, characteristic of compound V. At the same time, unlike was is observed with unsubstituted metal phthalocyanines [15], the spectrum is poorly resolved, implying intermolecular interactions possible due to the presence in the benzene rings of polar functional groups (SO₃H and COOH), as well as bromine atoms.

The electronic absorption spectra of complex VI (see figure) contain a strong long-wave band (Q band), formed by π - π -electron transitions in the principal conjugation contour of the phathalocyanine macroring.

The shape and position of this band depend on the nature of the solvent. According to [6], the electronic absorption spectra are much affected by intermolecular interactions leading to formation of dimers and other associates or aggregates. The strong Q band with maxima at 682–688 nm, that is well defined in solutions of complex VI in DMF and 1% ammonia solutions, relates to the monomeric form. The long-wave absorption in aqueous solution appears as broadened bands, providing evidence for association that results in coupling of π -conjugated systems of neighboring molecules. Therewith, it should be noted that the tendency of complex VI for association in aqueous

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Electronic absorption spectra of cobalt(IV) tetra(3-bromo-4-carboxy-5-sulfo)phthalocyanine in (1) DMF, (2) 1% aqueous ammonia, and (3) water.

alkaline solutions is weaker than in aqueous. As follows from a comparison of the spectra of complex **VI** in water and aqueous alkalis with the spectra of tetrasulfo- or tetra(4-bromo-5-sulfo)-substituted cobalt phthalocyanines, the former complex is weaker associated. Probably, the combination in the benzene rings of the phthalocyanine ligand of carboxy and sulfo groups arranged *ortho* to each other attenuates the tendency for intermolecular interaction in favor of intramolecular interaction.

Comparing the electronic absorption spectra of complex VI with the spectra of tetracarboxy-, -sulfo-, or -bromo-substituted cobalt phthalocyanines in the same solvent [16], one can see that the Q band is shifted bathochromically by 10–12 nm.

To assess practical use of complex **VI**, we dyed cotton fibers with it. Test dyeings showed that complex **VI** exhibits a fairly strong affinity to such fibers and dyes cotton fabrics into a bluish green color.

EXPERIMENTAL

The IR spectra were measured on a Specord M-80 instrument at 500–4000 cm^{-1} in KBr. The electronic absorption spectra of complex **VI** in DMF, water, and 1% aqueous ammonia were taken on a Specord M-40 spectrophotometer at room temperature at concentrations of complex **VI** of 10–5 M in the range 400–900 nm.

3-Bromo-2,4,5-trimethyl-1-sulfobenzene (IV). A solution of 0.081 mol of bromine in 33 ml of absolute ethanol was slowly added (20 drops min⁻¹) to a vigorously stirred solution of 0.073 mol of calcium salt **III** in 300 ml; therewith, the temperature of the reaction mixture warmed up to 30°C. During bromination

the mixture changed from colorless to yellow. After completion of the reaction, a colorless precipitate dropped. The reaction mixture was stirred at 30°C until it decolorized. The precipitate was filtered off, washed with a little cold water, and dried to obtain compound **IV** as a colorless water-insoluble powder, yield 6.12 g (30%). IR spectrum, v, cm⁻¹: 3000 (C–CH₃), 1100 (S=O), 600 (C–Br). Found, %: Br 28.1; S 11.1. C₉H₁₁BrO₃S. Calculated, %: Br 28.7; S 11.5.

Dipotassium salt of 3-bromo-5-sulfobenzene-1,2,4-tricarboxylic acid (V). Compound IV, 0.03 mol, was suspended in 200 ml of water. The suspension was made weakly alkaline with KOH, diluted with 100 ml of pyridine, and heated to 70°C, after which potassium permanganate was added in portions of 0.019 mol. Each successive portion was added when the preceding portion decolorized. After addition of three first portions, the reaction mixture was heated to boiling. The addition took 4 h until potassium permanganate no longer decolorized (test on filter paper). The suspension was filtered while hot. The manganese dioxide precipitate was washed with hot water. The filtrate and washings were combined, pyridine was distilled off with water until the distillate no longer smelled of pyridine. The solution was reduced to 1/3 the initial volume and made weakly acidic (pH 4-5) with HCl. After cooling, a precipiate dropped and was filtered off. The filtrate was again reduced to 1/3 the initial volume and acidified to pH 4-5 with HCl. After cooling, compound V precipitated. Yield 4 g (30%), colorless powder readily soluble in water. IR spectrum, v, cm⁻¹: 1720 (C=O in COOH), 1624, 1384 (C-O in COO-), 1100 (S=O), 600 (C-Br). Found, %: Br 17.3; S 7.8. C₉H₃BrK₂O₉S. Calculated, %: Br 18.0; S 7.2.

Cobalt tetra(3-bromo-4-carboxy-5-sulfo)phthalocyanine (VI). Compound V, 4.5 mol, urea, 36 mmol, anhydrous cobalt(II) acetate, 0.3 mmol, and 0.15 mmol of ammonium molybdate were thoroughly mixed. The mixture was placed into a tube fixed vertically in an electric resistance oven and heated with stirring in the following program: 140–150°C (90 min), 170-180°C (35 min), 190°C (15 min), and 200°C (60 min). After cooling, the resulting material was ground, washed first with 17% and than 5% HCl to colorless washings. The solid material on the filter was dissolved in aqueous ammonia, the solution was filtered, and the solvent was evaporated on a water bath. The solid residue was again treated with 17% HCl and purified in a Soxhlet apparatus with methanol. Yield 0.36 g (23%), dark violet powder with a metallic shine, readily soluble in water and aqueous acids and alkalis and moderately soluble in DMF and

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other polar organic solvents. IR spectrum, v, cm⁻¹: 1700 (C=O in COOH), 1100 (S=O), 600 (C-Br). Electronic absorption spectrum, λ_{max} , nm: 682.2 (DMF), 688.1 (1% NH₄OH), 684.3 (H₂O). Found, %: C 30.8; Br 24.8; Co 4.0; N 7.4; S 8.6. C₃₆H₁₂Br₄· CoN₈O₂₀S₄. Calculated, %: C 30.4; Br 25.3; Co 4.3; N 7.9; S 9.0.

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