Russian Journal of General Chemistry, Vol. 74, No. 3, 2004, pp. 446–450. Translated from Zhurnal Obshchei Khimii, Vol. 74, No. 3, 2004, pp. 491–495.

Synthesis and Properties of Sulfophenyl-Substituted Metal Phthalocyanine Complexes

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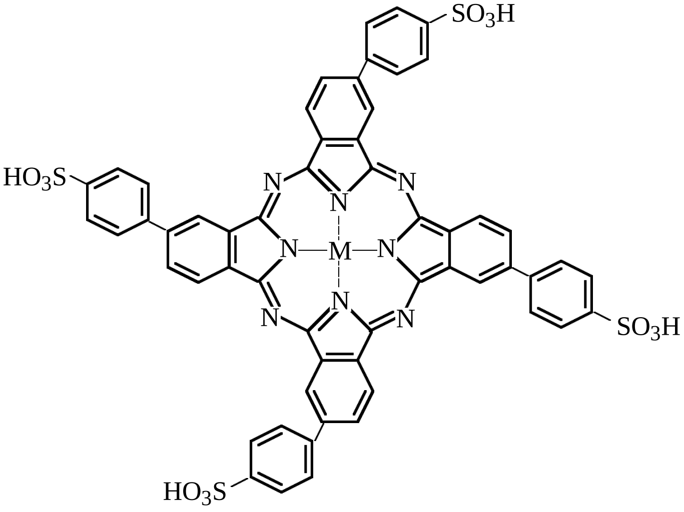
Received December 5, 2001

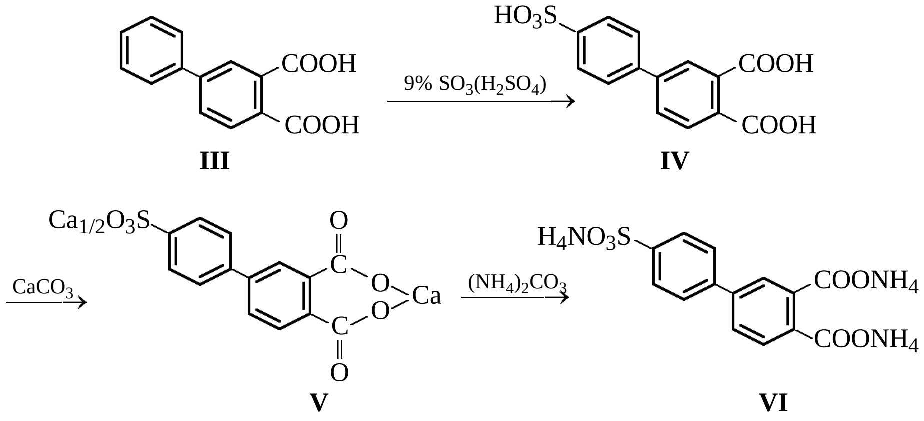
Abstract—Sulfonation of 4-phenylphthalic acid gave 4-(*p*-sulfophenyl)phthalic acid triammonium salt which was used in the synthesis of tetra[4-(*p*-sulfophenyl)]phthalocyanine copper and cobalt complexes by the urea method. The products were characterized by elemental analyses and ^{13}C NMR, IR, and electronic spectra. Some specific features of the electronic spectra of sulfophenyl-substituted metal phthalocyanines were revealed, depending on the central metal atom, solvent nature, and concentration.

Metal phthalocyanines containing sulfo groups attract interest as potential dyes, catalysts of various processes, photosensitizers, etc. [1–3]. The available published data on sulfonated phthalocyanines concern mainly those in which the sulfo group is attached directly to the benzene rings of the phthalocyanine ligand. However, derivatives having a sulfo group in the existing substituents, e.g., phenyl groups, also deserve attention. Such compounds may be interesting as models for studying the effect of the number and position of the sulfo groups on physical and chemical properties, as well as from the viewpoint of possible practical application. It is also promising to convert sulfo groups in phthalocyanine molecules into sulfonyl chloride with a view to synthesize numerous derivatives and thus considerably extend the series of available substituted phthalocyanines.



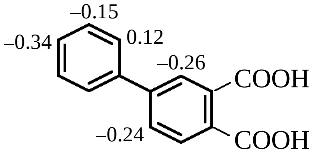
M = Cu (**I**), Co (**II**).

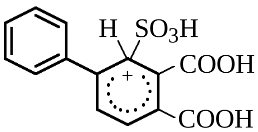
In the present work we have synthesized sulfophenyl-substituted metal phthalocyanines **I** and **II** and examined their properties. As starting compounds for the synthesis of complexes **I** and **II** we used 4-phenylphthalic acid triammonium salt which was prepared according to the following scheme.



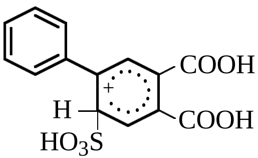
Compound **III** was sulfonated with 8% oleum at 90–100°C. In order to determine the most probable direction of attack on molecule **III** by electrophilic species, we calculated the orbital coefficients of the carbon atoms in the highest occupied molecular orbital of 4-phenylphthalic acid. The calculations were performed with full geometry optimization using AM-1 Hamiltonian (MOPAC 7).

In addition, we calculated thermodynamic parameters (enthalpies ΔH, entropies ΔS, and Gibbs energies ΔG) of different σ complexes which could be formed in the sulfonation of **III** (Table 1). Here, it was assumed that the reactive electrophilic species is HSO_3^+ ion which is readily formed by protonation of sulfuric anhydride in sulfuric acid [4].

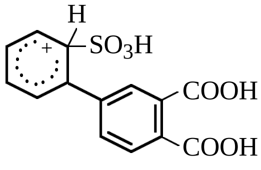




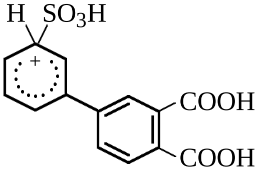
3-σ



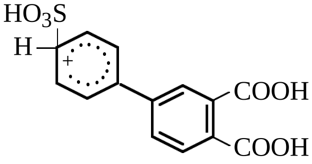
5-σ



o-σ



m-σ



p-σ

The calculated orbital coefficients and thermodynamic parameters of possible σ complexes suggest that in the sulfonation of **III** the most probable is intermediate formation of the *p*-σ complex and hence isolation of 4-(*p*-sulfophenyl)phthalic acid (**IV**) as final product. Introduction of a sulfo group into the para position of phenyl ring was also observed in the sulfonation of octaphenyl-substituted tetraazaporphyrins [5].

By neutralization of the reaction mixture with calcium carbonate we initially obtained 4-(*p*-sulfo-

Table 1. Thermodynamic parameters of intermediate σ complexes in the sulfonation of 4-phenylphthalic acid (**III**)

σ-Complex	$-\Delta H$, kJ mol^{-1}	$-\Delta S$, J mol^{-1} K^{-1}	$-\Delta G$ kJ mol^{-1}
3-σ	165.782	637	355.589
5-σ	159.287	645	351.449
o-σ	179.206	649	373.241
m-σ	171.803	654	367.453
p-σ	194.571	658	390.353

Table 2. Position of bands in the electronic absorption spectra of metal phthalocyanines **I** and **II**, λ_{max}, nm (log ε)

Complex	DMF	Water	0.5% NaOH
I	690 (5.04), 621 (4.46), 356 (4.72)	627	608
II	682 (5.14), 621 w, 334 (4.99)	694 w, 638	680 w, 649

phenyl)phthalic acid calcium salt (**V**) which was converted into the corresponding ammonium salt **VI** by treatment with ammonium carbonate. Salt **VI** is a beige powder which is readily distilled in water. It was identified by the data of elemental analysis and IR and ^{13}C NMR spectroscopy. The IR spectrum of **VI** contains two bands at 1420 and 1500 cm^{-1}, which belong to symmetric and antisymmetric stretching vibrations of the C=O bond in carboxylate ion. The band at 1060 cm^{-1} corresponds to stretching vibrations of the S=O bond, and N–H in ammonium ions give rise to a broad band in the region 3100–3300 cm^{-1} [6].

In the ^{13}C NMR spectrum of **VI** we observed a set of signals due to carbon atoms in the benzene rings. In keeping with published data [7, 8], the signals at δ_C 135.4 and 137.0 ppm were assigned to the carboxy-substituted carbon atoms, the signal at δ_C 143.1 ppm, to the carbon atom attached to the sulfo group, and those at δ_C 141.4 and 142.4 ppm, to the carbon atoms at the biphenyl bond. Signals from the carbonyl carbon atom were located in a weaker field (δ_C ~175 ppm). Several signals in the region δ_C 126.9–130.1 ppm were assigned to aromatic carbon atoms attached to hydrogen; a more detailed assignment of these signals was not performed.

Using compound **VI** we obtained sulfophenyl-substituted copper and cobalt phthalocyanines **I** and **II**. The synthesis was effected according to the urea procedure, i.e. by heating the initial phthalogen with metal salt, urea, and a catalytic amount of ammonium molybdate. Optimal conditions (temperature and reaction time) were found with a view to obtain the target products with a maximal yield.

Complexes **I** and **II** were purified by successive washing with hydrochloric acid solutions whose concentration was gradually reduced until the washings turned blue–green due to dissolution of metal phthalocyanine. The washed product was dissolved in distilled water, the solution was filtered, the filtrate was evaporated, and the product was extracted with acetone to remove impurities. Complexes **I** and **II** were isolated as dark blue powders. Unlike metal complexes of tetra(4-phenyl)phthalocyanine, compounds **I** and **II** are insoluble in weakly polar organic solvents (such as benzene, toluene, etc.) but are readily soluble in water, aqueous alkali, and polar organic solvents due to the presence of sulfo groups in their molecules. The solubility in water is typical of all sulfo-substituted phthalocyanines [9].

The IR spectra of compounds **I** and **II** in the range from 500 to 3600 cm^{-1} conform to their phthalocyanine structure [10]. Absorption bands at 1030 and 1200 cm^{-1} arise from vibrations of the sulfo groups [11]. The electronic absorption spectra of complexes **I** and **II** in DMF (Table 2, Fig. 1) contain a strong long-wave band (*Q*) due to π–π^* transition in the macroring and the Soret band related to the isoindole fragments. The position of these bands depends on the metal nature. In particular, the *Q* band in the spectra of copper complexes is displaced by 7–8 nm toward longer wavelengths relative to the corresponding band in the spectra of cobalt complexes. In going to more dilute solutions of the copper complex in DMF we observed reduction of the intensity of the vibrational satellite of the *Q* band and more distinct resolution in that region of the spectrum (Fig. 1). This fact together with the specific spectra of the complexes in water (Fig. 2) and dilute alkali (Table 2) indicates intermolecular interactions in solution with formation of associates. The degree of association of sulfo-substituted metal phthalocyanines strongly depends on their concentration [9].

EXPERIMENTAL

The IR spectra were recorded in the range from 400 to 4000 cm^{-1} on a Specord M-80 spectrometer. The electronic absorption spectra were measured in water, DMF, and 0.5% aqueous NaOH on a Specord

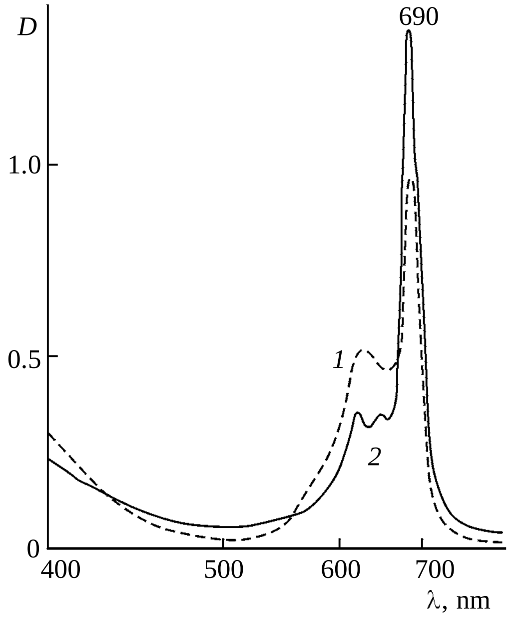


Fig. 1. Electronic absorption spectra of copper complex **I** in DMF. $c \times 10^{-5}$, M: (*1*) 7.5 and (*2*) 1.4.

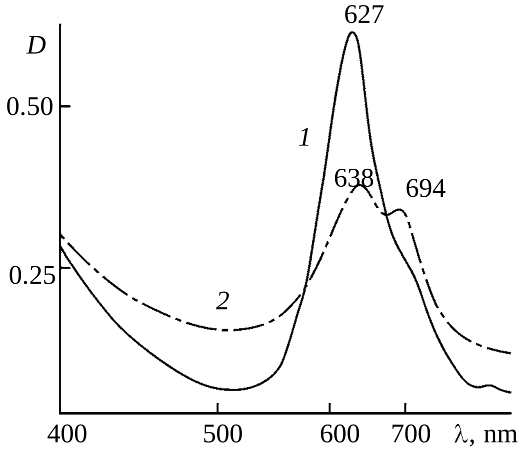


Fig. 2. Electronic absorption spectra of (*1*) copper complex **I** and (*2*) cobalt complex **II** in water.

M-40 spectrophotometer at room temperature (spectral range 400–800 nm). The ^{13}C NMR spectrum of triammonium salt **VI** was obtained on a Bruker WM-400 instrument from a solution in D_2O.

4-(*p*-Sulfophenyl)phthalic acid triammonium salt (VI). A mixture of 6 ml of 8% oleum and 8.3 mmol of 4-phenylphthalic acid was heated to 90–100°C and was kept for 4 h at that temperature. The mixture was cooled to room temperature and poured into an ice-water mixture (100 g). A solid precipitated and then dissolved almost completely as the mixture warmed up to room temperature. The acid solution was filtered through a glass filter, and the filtrate was neutralized with calcium carbonate. The precipitate of calcium sulfate was filtered off, and a required amount (0.02 mol) of ammonium carbonate was added to the filtrate. The precipitate of calcium carbonate was filtered off, and the filtrate was evaporated on a water bath. Yield 1.07 g (42%), decomposes above 240°C. Found, %: C 45.0; H 5.1; N 11.0. $C_{14}H_{19}O_7S$. Calculated, %: C 45.25; H 5.2; N 11.3.

Copper(II) tetra[4-(*p*-sulfophenyl)]phthalocyanine (I). A mixture of 1 mmol of salt **VI**, 4 mmol of urea, 0.3 mmol of copper acetate, and a catalytic amount of ammonium molybdate was thoroughly ground and was then fused for 90 min at 140–145°C, for 50 min at 170–175°C, for 75 min at 190–195°C, and for 90 min at 200–220°C. After cooling, the melt was ground and washed in succession with 17%, 8%, and 4% hydrochloric acid. The residue was dissolved in distilled water, the solution was filtered, and the filtrate was evaporated on a water bath. The product was purified by Soxhlet extraction with acetone. Yield 200 mg (67%). Found, %: C 55.9; H 2.6; N 9.3; S 10.7. $C_{56}H_{32}CuN_8O_{12}S_4$. Calculated, %: C 56.0; H 2.67; N 9.33; S 10.67.

Cobalt(II) tetra[4-(*p*-sulfophenyl)]phthalocyanine (II) was synthesized and purified in a similar way using 72 mg of cobalt(II) chloride. Yield 194 mg (65%). Found, %: C 65.1; H 2.53; N 8.95; S 10.2. $C_{56}H_{32}CoN_8O_{12}S_4$. Calculated, %: C 56.2; H 2.68; N 9.37; S 10.7.

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