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Nucleophilic Substitution in 4-Bromo-5-nitrophthalodinitrile: IV.[1] 5-Nitro-4-(phenylthio)phthalodinitrile and Octa-substituted Metal Phthalocyanines Based Thereon

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Abstract—5-Nitro-4-(phenylthio)phthalodinitrile was obtained by nucleophilic substitution of the bromine atom in 4-bromo-5-nitrophthalodinitrile. The product was used to prepare copper(II) and cobalt tetra(5-nitro-4-phenylthio)phthalocyanines, and their spectral properties were studied.

The present work is a continuation of studies in the field of disubstituted phthalodinitriles with peripheral substituents of various nature ((R^1, R^2) and of the corresponding octasubstituted metal phthalocyanines $MPc(4\text{-}R^1)_4(5\text{-}R^2)_4$ [1–5] and deals with synthesis and properties of (5-nitro-4-phenylthio)-substituted phthalodinitrile and metal phthalocyanines based thereon.

5-Nitro-4-(phenylthio)phthalodinitrile (**II**) was prepared by nucleophilic substitution of the halogen in 4-bromo-5-nitrophthalodinitrile (**I**). Compound **I** was obtained by the procedure in [2].

It is known that phenyl substitution in metal phthalocyanines endows the latter with solubility in organic solvents, thus making them convenient objects for studying various properties in solutions, including reactivity and catalytic activity in homogeneous reactions [6].

We earlier showed [1, 3, 4] that the halogen atom in compound **I** is more mobile than the nitro group, and thus it is the first target for nucleophilic substitution.

Attempted synthesis of 5-nitro-4-(phenylthio)phthalodinitrile under the conditions we used earlier for preparing 5-nitro-4-phenoxyphthalodinitrile [1], i.e. by the reaction of phthalodinitrile **I** with a nucleophilic agent (thiophenol) in the presence of lithium hydroxide in DMSO has not met with success.

It is known that a halogen substituent in phthalodinitrile can be substituted by a phenylthio group in DMF in the presence of triethylamine [7]. The synthesis of 5-nitro-4-(phenylthio)phthalodinitrile (**II**) was performed by the latter procedure but with another reactant ratio (thiophenol and triethylamine were taken in a double excess; otherwise, complete bromine substitution could not be attained.

Copper and cobalt tetra(5-nitro-4-phenylthio)phthalocyanines (**III, IV**) were synthesized by the reactions of phthalodinitrile (**II**) with the corresponding metal acetates at 220–225°C.

Complexes **III** and **IV** were extracted with benzene and purified by column chromatography on silica gel (eluent chloroform). Metal phthalocyanines and their derivatives are frequently purified by reprecipitation from concentrated sulfuric acid; therewith, however, metal tetra(4-phenoxy)phthalocyanines [6], as well as metal tetra(5-nitro-4-phenoxy)phthalocyanines $MPc(5\text{-}NO_2)_4(4\text{-}OPh)_4$ [8] underwent sulfonation. The same proved also true of metal complexes **III** and **IV**, and thus we could prepare sulfonic acid **V**. We suppose that the sulfo group enters the *para* position of the phenyl substituents, as with octaphenyl-substituted tetraazaporphines [9].

The purity of the synthesized compounds was confirmed by elemental analysis, as well as by IR and electronic spectroscopy. The IR spectrum of nitrile **II** shows, along with bands characteristic of substituted phthalodinitriles [10], bands at 1528 and 1344 cm^{-1} due to NO_2 stretching absorption and bands at 1088–1112 cm^{-1} due to Ar–S–Ar absorption [11]. The IR spectra of metal phthalocyanines **III** and **IV** show, like with phthalodinitrile **II**, bands due to Ar–S–Ar and NO_2 absorption.

The presence of phenylthio substituents endows phthalocyanines **III, IV** with solublity in benzene, chlorobenzene, and chloroform. The compounds are also soluble in DMF and concentrated sulfuric acid

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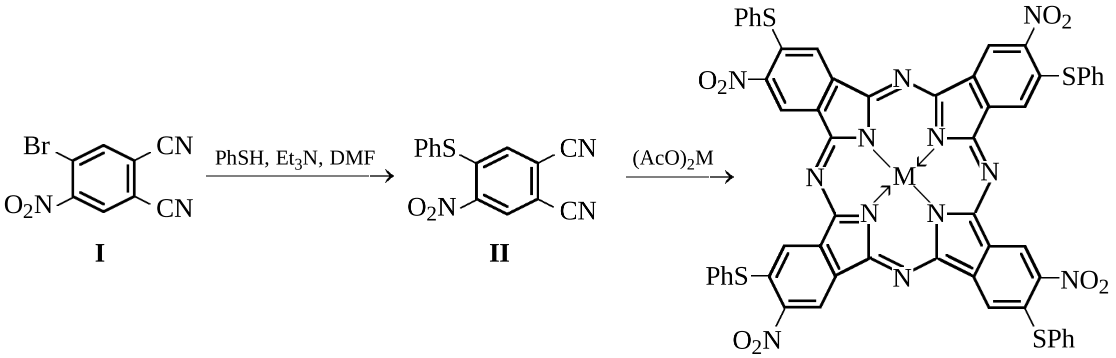
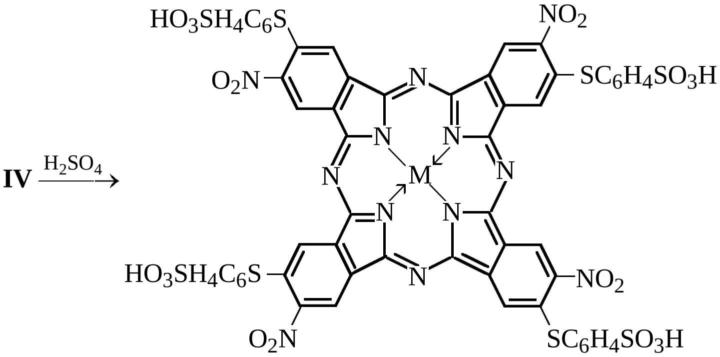
[1] For communication III, see [1].



I **II** **III, IV**



V

M = Cu (**III**), Co (**IV**).

Position of the first band in the electronic absorption spectra of cobalt phthalocyanines

Compound	λ_{max}, nm		Reference
	DMF	H_2SO_4	
CoPc	660	790	[13]
$CoPc(4\text{-}Br)_4(5\text{-}NO_2)_4$	680	773	[5]
$CoPc(5\text{-}NO_2)_4(4\text{-}OPh)_4$	678	786	[8]
$CoPc(5\text{-}NO_2)_4(4\text{-}SPh)_4$ (**IV**)	698	846	
$CoPc(5\text{-}NO_2)_4(4\text{-}SC_6H_4SO_3H)_4$ (**V**)	694		

and insoluble in water, alcohols, and aqueous alkalis. Sulfonation of compound **IV** makes it soluble in water and aqueous alkalis and reduces its solubility in DMF.

The electronic absorption spectra of complxes **III, IV** in organic solvents contain a *Q* band at 698–718 nm. In going from DMF to chloroform (benzene, chloroform), the *Q* band shifts slightly red in the order: benzene, chlorobenzene, chloroform.

Compared with the corresponding unsubstituted [12] and tetra(4-bromo-5-nitro)phthalocyanines [5], the *Q* band is shifted red both in organic solvents and in concentrated sulfuric acid (see table).

Comparison of the electronic absorption spectra of complexes **III** and **IV** and the corresponding metal tetra(5-nitro-4-phenoxy)phthalocyanines reveals a bathochromic shift of the *Q* band. The same was earlier observed with metal tetra(phenoxy)- and tetra-(phenylthio)phthalocyanines [6]. The possible reason is the lower electronegativity of S compared with O (2.5 and 3.5, respectively) [14].

As evident from the electronic absorption spectrum of complex **V** in DMF, sulfo substitution in the bulky phenyl substituent, like with the tetrasulfonic acid derived from cobalt tetra(5-nitro-4-phenoxy)phthalocyanine, produces a slight bathochromic shift of the *Q* band compared with the parent compound **IV**. In aqueous solution, the *Q* band is broadened because of molecular aggregation.

EXPERIMENTAL

The electronic absorption spectra were measured in DMF, chloroform, benzene, chlorobenzene, and concentrated sulfuric acid on a Specord M-40 spectrometer at room temperature in the range 300–900 nm.

The IR spectra were obtained on a Specord M-80 spectrophotometer in the range 4000–400 cm^{-1} in KBr.

The melting point was determined on a Boetius hot stage with an RNMK-05 observation device (Boetius microscope).

5-Nitro-4-(phenylthio)phthalodinitrile (II). Thiophenol, 0.7 ml, and 0.78 ml of triethylamine were added to a solution of 0.6 g of nitrile **I** in 20 ml of DMF. The mixture was vigorously stirred at 20–25°C for 4 h and then poured into 50 ml of water. The precipitate was filtered off, washed with 5% aqueous sodium bicarbonate, and then with distilled water to neutral medium. The reaction product was dried in air. Yield 0.42 g (62%), mp 130–132°C. Found, %: C 57.9; H 2.7; N 14.7. $C_{14}H_7N_3O_2S$. Calculated, %: C 59.8; H 2.49; N 14.9.

Metal tetra(5-nitro-4-phenylthio)phthalocyanines III, IV. Nitrile **I**, 0.9 mmol, was thoroughly ground and mixed with 0.25 mmol of corresponding metal acetate. The mixture was heated in a quartz ampule at 220–225°C for 1.5 h and then cooled, thoroughly ground, and treated with benzene. The products were purified by column chromatography on silica gel (eluent chloroform).

Copper tetra(5-nitro-4-phenylthio)phthalocyanine, yield 0.12 g (42%). Electronic absorption spectrum, λ_{max}, nm (log ε): DMF 710 (4.81), 334 (4.86); chloroform 718 (4.82), 342 (4.97); benzene 716 (4.82), 334 (4.99); concentrated sulfuric acid 853 (4.74), 334 (4.64). Found, %: C 54.8; H 2.5; N 13.9. $C_{56}H_{28}CuN_{12}O_8S_4$. Calculated, %: C 56.6; H 2.38; N 14.2.

Cobalt tetra(5-nitro-4-phenylthio)phthalocyanine (IV), yield 0.11 g (42%). Electronic absorption spectrum, λ_{max}, nm (log ε): DMF 698 (4.52), 334 (4.48); chloroform 704 (4.81), 327 (4.64); benzene 706 (4.83), 317 (4.81); concentrated sulfuric acid 846 (4.99), 321 (4.90). Found, %: C 54.9; H 2.5; N 14.0. $C_{56}H_{28}CoN_{12}O_8S_4$. Calculated, %: C 56.8; H 2.4; N 14.2.

Complex **IV** was reacted with concentrated sulfuric acid to obtain tetrasulfonic acid **V**. Electronic absorption spectrum, λ_{max}, nm: water 670, 319; DMF 694, 341.

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