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5-Acylamino-4-phenoxyphthalodinitriles and Metal Phthalocyanines Based Thereon

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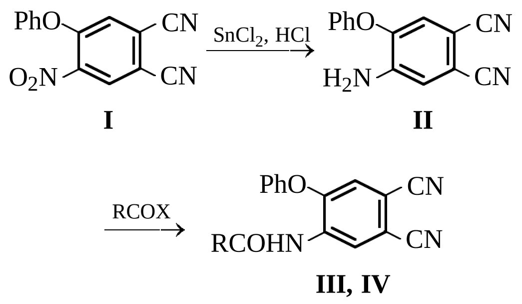
Abstract — Tetra(5-acetylamino-4-phenoxy)-, tetra(5-benzoylamino-4-phenoxy)-, and tetra(5-octanoylamino-4-phenoxy)phthalocyanines are synthesized, and their electronic absorption spectra are studied.

There is some information in literature concerning the synthesis and properties of hydroxy-substituted phthalocyanines, including alkoxy-, aryloxy-, aryleneoxy-, and other derivatives [1–5], that are soluble in organic solvents and find application as pH-sensitive dyes [1, 2], photosensitizers in photodynamic therapy of cancer [3], catalysts for fuel elements, solar batteries [4, 5], etc. They all contain from 4 to 8 identical substituents. The only reported phthalocyanines with the benzene rings bearing both aryloxy and other substituents are tetra(4-aryloxy-5-nitro)phthalocyanines [6].

In the present paper we report the synthesis and properties of cobalt and copper(II) tetra(5-acylamino-4-phenoxy)phthalocyanines. The synthesis was performed by the nitrile procedure from 5-acylamino-4-phenoxyphthalodinitriles and the corresponding metal acetates.

The starting phthalodinitriles were prepared in two ways. The first started from 5-nitro-4-phenoxyphthalodinitrile (**I**) [6].



R = Me (**III**), C_7H_{15} (**IV**); X = AcO, Cl.

5-Amino-4-phenoxyphthalodinitrile (**II**) was obtained by reduction of dinitrile **I** with tin dichloride in hydrochloric acid. It was found that up to 45°C compound **I** undergoes no transformations, while above 80°C it decomposes. The IR spectrum of product **II** lacks absorption bands characteristic of C≡N stretching vibrations. The reaction performed at 60°C (2 h) at the **I**:$SnCl_2$ ratio of 1:4 gave compound **II** in a fairly high yield. The product was identified by elemental analysis, IR spectroscopy, and by a comparison of its physicochemical characteristics with those of authentic samples.

5-Amino-4-phenoxyphthalodinitrile (**II**) is a beige-colored powder with a well-defined melting point. Above 80°C it darkens and above 102°C, melts with decomposition. The presence of a primary amino group in the phthalodinitrile was confirmed by qualitative reaction.

The IR spectra of dinitriles **I** and **II** contain a series of common absorption bands [7]. In particular, at 2232 cm^{-1} there is a C≡N absorption band [8]. A band at 1256 cm^{-1} is observed, belonging to the phenoxy group [8]. The band near 1544 cm^{-1} due to symmetrical stretching virations of the nitro group, characteristic of dinitrile **I**, disappears from the IR spectrum of compound **II**, while new bands at 1632 and 3416 cm^{-1} appear, characteristic respectively of bending and stretching vibrations of the amino group [8].

Dinitrile **II** was acylated with acetic anhydride and octanoyl chloride to obtain 5-acetylamino and 5-octanoylamino-4-phenoxyphthalodinitriles (**III, IV**), respectively.

The synthesis of compound **III** was performed at 100–110°C in the presence of freshly calcined sodium acetate. In the absence of the additive and at a higher temperature (to 150°C), the reaction mixture gets dark, and the target reaction product is difficult to isolate.

The synthesis of compound **IV** was performed at 120°C using a double excess of octanoyl chloride. After neutralization of the reaction mixture, nitrile **IV** was extracted with diethyl ether.

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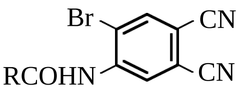
Yields, positions of the first band in the electronic absorption spectra, and elemental analyses of copper(II) and cobalt tetra(5-acylamino-4-phenoxy)phthalocyanines **VIII**–**XII**

Comp. no.	Yield, %	Electronic spectrum, λ_{max}, nm			Found, %			Formula	Calculated, %		
		H_2SO_4	DMF	chloroform	C	H	N		C	H	N
VIII	44	825	687	690	66.1	3.6	14.6	$C_{64}H_{44}CuN_{12}O_8$	65.6	3.8	14.3
IX	35	794	681	685	71.4	3.9	11.5	$C_{84}H_{52}CuN_{12}O_8$	71.0	3.7	11.8
X	37	789	685	683	71.5	3.6	11.5	$C_{84}H_{52}CoN_{12}O_8$	71.2	3.7	11.9
XI	48	757, 776	687	633, 689	70.5	6.3	11.5	$C_{88}H_{92}CuN_{12}O_8$	70.0	6.1	11.1
XII	46	760	681	690	70.4	6.3	11.6	$C_{88}H_{92}CoN_{12}O_8$	70.2	6.2	11.2

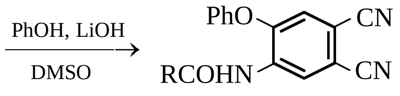
Nitriles **III, IV** recrystallized from benzene are clream-colored powders with well-defined melting points. Therewith, the melting point markedly decreases with increasing alkyl chain length. Thus, the melting points of **III** and **IV** are respectively 120–122 and 74–76°C. The test for primary amino group was negative.

The IR spectra of compounds **III** and **IV** preserve most absorption bands characteristic of nitrile **II**, including that at 2232 cm^{-1}. At the same time, the band at 1632 cm^{-1} due to the free amino group disappers, and a band at 1724–1712 cm^{-1} appears, characteristic of acylamino carbonyl vibrations [8].

It is known that the bromine atom in bromine-substituted phthalodinitriles can be subject to nucleophilic substitution [6, 9]. We attempted to use this reaction for preparing acylaminophenoxyphthalodinitriles from nitriles **V, VI**. The latter were obtained by the procedure in [10].



V, VI



III, VII

R = Me (**III**), Ph (**VII**).

As the nucleophilic agent we used phenol in the presence of lithium hydroxide. The synthesis was performed in DMSO under conditions similar to those for preparing nitrile **I** [6]. However, only mixtures of the starting and target dinitriles could be isolated, which proved impossible to separate.

Nitriles **III, IV**, and **VII** were reacted with Cu(II) and cobalt acetates at 175–180°C (30 min) to obtain metal phthalocyanines **VIII**–**XII** (see table).

Complexes **VIII**–**XII** are dark green powders. They are insoluble in water and aqueous alkalis and readily soluble in DMF, chloroform, acetone, benzene, pyridine, and concentrated sulfuric acid.

The solubility in organic solvents allowed the complexes to be extracted with chloroform and then purified by column chromatography (sorbent silica gel, eluent chloroform–benzene, 2 : 1).

It should be noted that the elemental analyses of the complexes synthesized from mixtures of dinitriles **III, V** and **VI, VII** and isolated as described above show that the products contain no admixtures of bromides derived from **V, VI**. Copper tetra(5-acetylmino-4-phenoxy)phthalocyanine (**VIII**) obtained both from nitrile **III** and a mixture of nitriles **III** and **V** had similar electronic absorption spectra.

Compounds **VIII**–**XII** were identified by elemental analysis and electronic spectroscopy.

Analysis of the electronic absorption spectra in organic solvents (see table and Figs. 1 and 2) shows the following. The complexes all exhibit strong absorption in the range 633–690 nm. But complex **XII** in chloroform gives a diffuse band with a maximum at 690 nm and an inflection at 645 nm, whereas the related copper complex **XI**, two absorption bands at 689 and 633 nm. The same spectrum (λ_{max} 689 and 630 nm) is also characteristic of the latter complex in benzene, implying aggregation of the compounds in organic solvents. Replacement of the acetyl residue by octanoyl has almost no effect on the position of the *Q* band. As would be expected, in going from organic solvents to concentrated sulfuric acid the first band undergoes a bathochromic shift. It should be noted that the long-wave band of complex **XI** is split into two bands, which is probably associated with the presence of positional isomers (randomers).

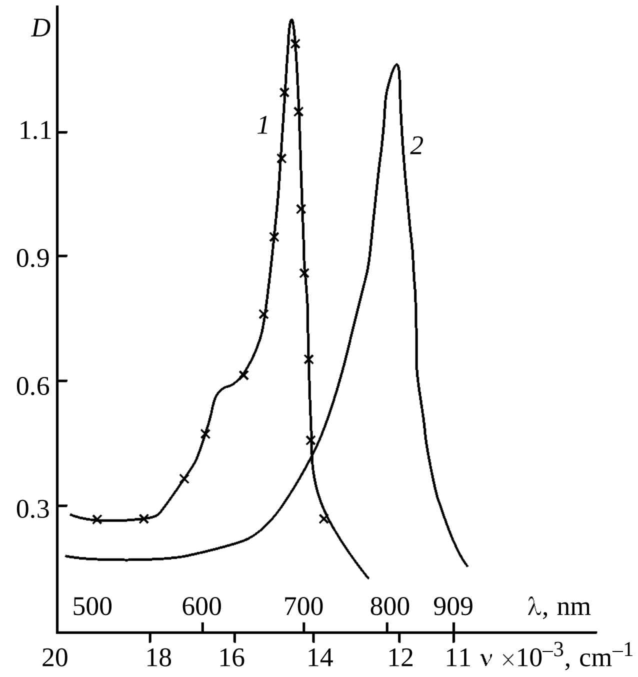


Fig. 1. Electronic absorption spectra of solutions (*c* 1.1 × 10^{-5} M) of copper tetra(5-acetylamino-4-phenoxy)phthalocyanine (**VIII**) in (*1*) DMF and (*2*) H_2SO_4.

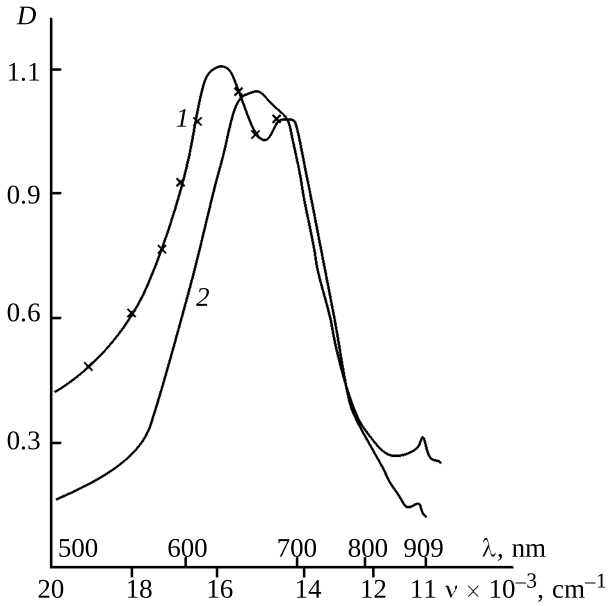
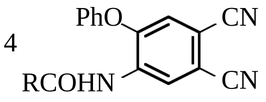
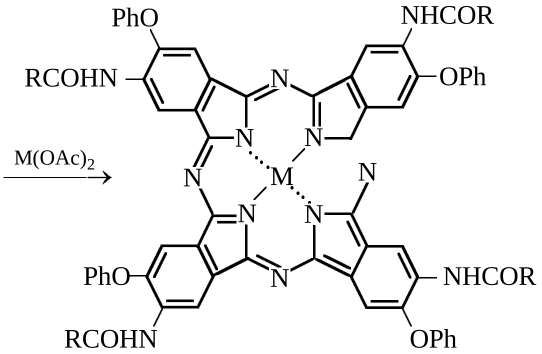


Fig. 2. Electronic absorption spectra of solutions (*c* 10^{-5} M) of (*1*) copper tetra(5-octanoylamino-4-phenoxy)phthalocyanine (**XI**) and (*2*) cobalt tetra(5-octanoylamino-4-phenoxy)phthalocyanine (**XII**) in DMF.



III, IV, VII



VIII–XII

R = Me (**VIII**), Ph (**IX, X**), C_7H_{15} (**XI, XII**); M = Cu (**VIII, IX, XI**), Co (**X, XII**).

As follows from a comparion of the electronic absorption spectra of known metal tetra(5-nitro-4-phenoxy)phthalocyanines and synthesized *N*-acylamino derivatives **VIII**–**XII**, the position of the *Q* band depends the nature of alkyl in the acylamino group. With **VIII**, a bathochromic shift is observed, while with **XI, XII**, hypsochromic (see table). This difference is apparently explained by the different size of the alkyl substituents, which, in its turn, leads to a different depth of protonation of the porphyrazine cycle.

EXPERIMENTAL

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

The electronic absorption spectra were measued in DMF, chloroform, and concentrated suluric acid on a Specord M-40 spectrophotometer at room temperature in the range 500–900 nm.

5-Amino-4-phenoxyphthalodinitrile (II). 5-Nitro-4-phenoxyphthalodinitrile, 0.3 g, was slowly added to a solution of 0.7 g of tin(II) chloride in 2.1 ml of conc. HCl. The reaction mixture was stirred at 60°C for 2 h and then poured into 50 ml of ice water. The precipitate that formed was filtered off, washed with water to neutral washings free of chloride ions, and dried at 60°C to obtain the reaction product as a yellow powder soluble in acetone, chloroform, DMF and insoluble in water and aqueous alkalis. Yield 0.2 g (79%), decomp. point 102–106°C. Found, %: C 72.1; H 4.1; N 18.1. $C_{14}H_9N_3O$. Calculated, %: C 71.5; H 3.9; N 17.9.

5-Acetylamino-4-phenoxyphthalodinitrile (III). *a*. A mixture of 0.1 g of nitrile **II**, 0.05 g of sodium acetate, and 0.1 ml of acetic anhydride was heated at 110°C for 2 h, after which it was diluted with water, the precipitate was filtered off, washed with water to neutral washings, and dried at 50°C. Nitrile **III** is a cream-colored powder insoluble in water and aqueous alkalis and soluble in acetone, chloroform, and DMF. Yield 0.05 g (38 %), mp 120–122°C. Found, %: C 70.5; H 4.2; N 15.4. $C_{16}H_{11}N_3O_2$. Calculated, %: C 69.3; H 4.0; N 15.2.

b. Phenol, 0.27 g, was added to a solution of 0.5 g of nitrile **V** in 30 ml DMSO, after which 0.11 g of lithium hydroxide was added to the mixture over the course of 2 h. The reaction mixture was stirred for 7 days at room temperature and then poured into 300 ml of 10% aqueous sodium chloride. The precipitate that formed was filtered off and washed with 5% aqueous sodium hydroxide to neutral washings free of bromide ions. Purification was performed by recrystallization from benzene.

5-Octanoylamino-4-phenoxyphthalodinitrile (IV). A mixture of 0.1 g of nitrile **II** and 0.2 ml of octanoyl chloride was heated at 120°C for 1.5 h, after which it was diluted with 5 ml of 10% aqueous sodium bicarbonate, the precipitate was filtered off, washed with water to neutral washings, dried at 50°C, and recrystallized from benzene to obtain compound **IV** as a cream-colored powder insoluble in water and aqueous alkalis and soluble in acetone, chloroform, and DMF. Yield 0.09 g (63%), mp 74–76°C. Found, %: C 72.9; H 6.7; N 11.9. $C_{22}H_{23}N_3O_2$. Calculated, %: C 73.1; H 6.4; N 11.6.

5-Benzoylamino-4-phenoxyphthalodinitrile (VII). A mixture of 0.38 g of nitrile **VI**, 0.16 g of phenol, and 0.07 g of lithium hydroxide in 30 ml of DMSO was stirred for 7 days at room temperature, after which it was poured into 300 ml of 10% aqueous sodium chloride. The precipitate formed was filtered off, and washed with 5% aqueous sodium hydroxide and then with water to neutral washings free of bromide ions.

Tetra(5-acylamino-4-phenoxy)phthalocyanines VIII–XII. Disubstituted phthalodinitrile, 0.9 mmol, and 0.25 mmol of corresponding metal acetate were melted in a quartz ampule at 175–180°C for 30 min. The resulting melt was ground, washed successively with 3% HCl to colorless filtrates and water to remove chloride ions. The reaction products were dried at 50°C and purified first by extraction with chloroform in a Soxhlet apparatus and then by column chromatography on silica gel (eluent chloroform–benzene, 2 : 1). Phthalocyanines **VIII**–**XII** are dark green powders insoluble in water and aqueous alkalis and soluble in DMF, chloroform, benzene, pyridine, and concentrated sulfuric acid, and compounds **X**–**XII**, in acetone.

ACKNOWLEDGMENTS

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