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# Preparation and Properties of Copper Tetra-4-[(4'-carboxy)phenylamino]phthalocyanine

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**Abstract—**Interaction of 4-nitrophthalonitrile with 4-aminobenzoic acid in dimethylsulfoxide in the presence of potassium carbonate has led to 4-[(4'-carboxy)phenylamino]phthalonitrile. From the latter, copper tetra-4-[(4'-carboxy)phenylamino]phthalocyanine has been prepared via the template synthesis. The spectral properties of the product have been studied. It has been demonstrated that in aqueous alkaline solutions the complex associates, whereas in dimethylformamide it predominantly exists in the monomeric form.

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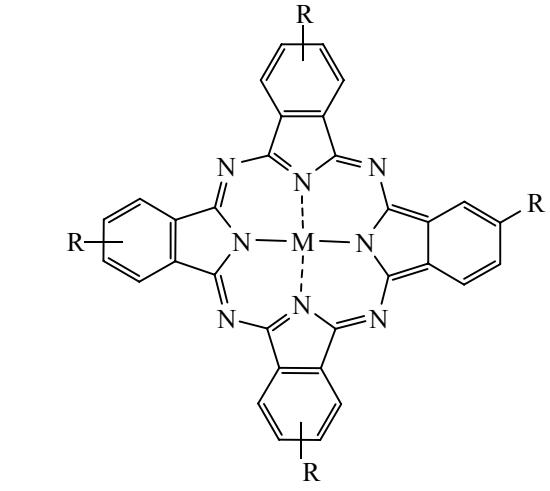
Phthalocyanine $H_2Pc$ and its metal complexes MPc have been popular recently due to unique properties and wide possibilities of chemical modification leading to novel compounds and materials with peculiar utilitarian characteristics [1–10]. Various phthalocyanines Pc are synthetic analogs of widely spread natural porphyrins, this has added to the interest to Pc growing over the recent decades.

Phthalocyanines have been applied as high-class blue, green, and mixed blue-green dyes and pigments [11], efficient catalysts of thiols for oil refining [12, 13], molecular semiconductors for microelectronics devices [14], liquid crystalline materials [15–19], and in other fields of science and technology [20–29].

Up to now, many Pc derivatives have been prepared and characterized, differing in the nature, number, and location of the substituents. Carboxylic acids derived from Pc form a class of special interest; such compounds can be used as dyes, catalysts, photosensibilizers in photodynamic cancer therapy, precursors of thermally stable polymers, and for further modification of Pc into amides or esters [6, 14, 16, 19, 25, 30–35].

Metal phthalocyanine complexes based on Pc derivatives with carboxylic group bound to the isoindole fragment, either directly or via the phenoxy or phenylsulfanyl moieties, have been described in the literature.

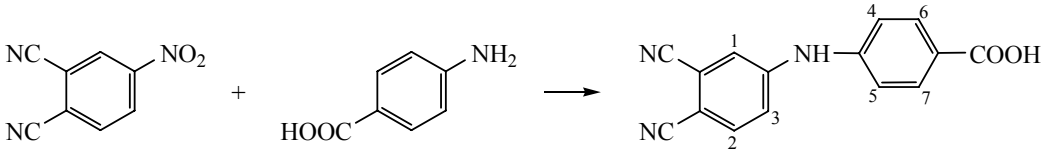



This work aimed at preparation and evaluation of physico-chemical parameters of the novel metal complexes, copper tetra-4-[(4'-carboxy)phenylamino]phthalocyanine.

That complex was prepared via “nitrilic” method; there-fore, the first problem to be solved was to synthesize the corresponding precursor.

The key precursor for the target complex preparation was 4-nitrophthalonitrile **I** that was prepared according to the known procedures [36, 37],

in particular, via phthalimide nitration with mixture of sulfuric and nitric acids, subsequent amidation of 4-nitrophthalimide with concentrated aqueous ammonia, and dehydration of the so prepared diamide with thionyl chloride in DMF.




**I** **II**

The presence of two electron-accepting groups in 4-nitrophthalonitrile favored the nucleophilic substitution, in particular, the substitution of the labile nitro group with the (4'-carboxy)phtnylamine, thus giving 4-[(4'-carboxy)phenylamino]phthalonitrile **II**.

The reaction was performed in DMSO medium in the presence of calcined potassium carbonate similarly to the preparation of 4-[(4'-carboxy)phenoxy]phthalonitrile reported in [19].

The prepared phthalonitrile **II** was a powder soluble in aqueous alkaline solutions and in some organic solvents (for instance, ethanol and acetone). The attempts to convert it into the corresponding esters or amides (following the procedure reported in the cases of 4-[(4'-carboxy)phenoxy]phthalonitrile [19] and 4-[(4'-carboxy)phenylsulfanyl]phthalonitrile [35]) failed.

The prepared phthalonitrile **II** was identified with the elemental analysis, IR and $^1$H NMR data.

Under conditions of EI ionization, no molecular ion peak of the target compound **II** was found in the mass spectrum. In the literature, the instability of the similar structures under EI conditions has been noted [38].

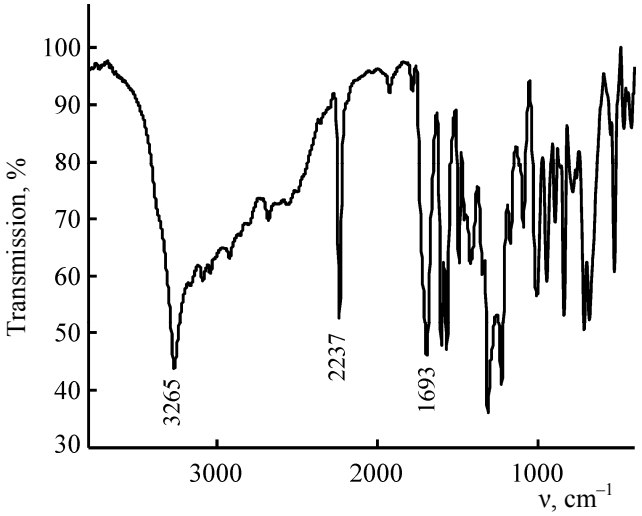



**Fig. 1.** IR spectrum of 4-[(4'-carboxy)phenylamino]phthalonitrile (**II**).

In the IR spectrum, the absorption bands due to vibrations of cyano group (2237 cm$^{-1}$), carboxylic group (1693 cm$^{-1}$), and bridging NH group (1313 and 3265 cm$^{-1}$) [39] were found (Fig. 1). No bands of nitro group deformations (located at 1355 and 1537 cm$^{-1}$ in the precursor **I**) were found.

The cyano group stretching band of **II** was somewhat shifted towards higher frequency as compared to that of 4-[(4'-carboxy)phenylsulfanyl]phthalonitrile [35], whereas the bands assigned to the carboxylic groups were shifted towards lower frequencies. As compared with the cyano group stretching in **I** (2242 cm$^{-1}$), that in **II** was found at lower frequency. The above-mentioned observations confirmed the completeness of **I**→**II** nucleophilic substitution.

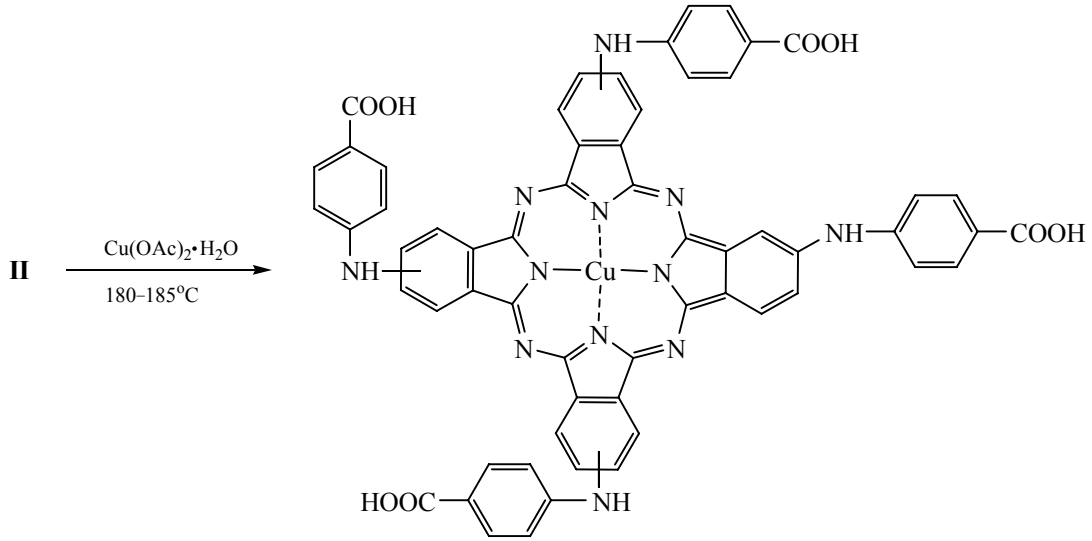
In $^1$H NMR spectrum of **II** in deuterated pyridine, several groups of the aromatic proton signals were observed at 7.29–8.54 ppm. From the comparison of the recorded spectrum with that of the similar 4-[(4'-carboxy)phenylsulfanyl]phthalonitrile [35] it followed that the nature of the bridging heteroatoms did not influence the chemical shifts of $H^{1,2}$, whereas the signals of $H^{4-7}$ were shifted upfield and the $H^3$ signal was shifted downfield in the case of **II**.

The next part of this work was consisted in preparation of copper tetra-4-[(4'-carboxy)-phenylamino]phthalocyanine via "nitrilic" method, the interaction of **II** with copper acetate in the presence of urea at 180–185°C. In the absence of urea, the target complex yield was too low, of <15%. The prepared complex was purified by recrystallization from sulfuric acid (see Scheme 1).

The complex **III** was soluble in aqueous alkali solutions, in DMF, and in concentrated sulfuric acid.

The structure of **III** was identified by means of elemental analysis, electronic and IR spectroscopy.

**Scheme 1.**




In the IR spectrum, the absorption bands at 1715–734 $cm^{-1}$ were found, typical of phthalocyanines [40, 41]. Besides those, the absorption bands assigned to the carboxylic and Ar–NH–Ar groups in **II** were preserved in the spectrum of **III**.

The comparative analysis of electronic spectrum of **III** and of copper tetra-4-[(4'-carboxy)phenylsulfanyl] phthalocyanine [35] revealed that in the case of aqueous alkaline solutions of the studied compounds the Beer–Lambert law was not held; therefore, the complexes were associated, similarly to other metal complexes of carboxylated phthalocyanines [33]. In the case of DMF solutions, **III** existed predominantly in the monomeric form, in contrast with copper tetra-4-[(4'-carboxy)phenylsulfanyl]phthalocyanine (Fig. 2).

Furthermore, the comparison of absorption spectra of **III** solution in DMF with those of copper tetra-4-[(4'-carboxy)phenylsulfanyl]phthalocyanine [35] and copper tetra-4-[(4'-carboxy)phenoxy]phthalocyanine [19] revealed that the change of O-bridge to S- or NH-bridge was accompanied with the red shift of the long-wavelength band (the shift being more significant in the case of NH), and the association was suppressed simultaneously.

The geometry of copper tetra-4-[(4'-carboxy)phenylamino]phthalocyanine and tetra-4-[(4'-carboxy)phenylsulfanyl]phthalocyanine was simulated by quantum chemistry methods [42, 43], and the theoretical electronic absorption spectra were calculated. The results demonstrated that the complexes molecules were planar (Fig. 3); the absorption band red shift was confirmed as well.

The studied complex **III** (as well as copper tetra-4-[(4'-carboxy)phenylsulfanyl]phthalocanine [35]) did not form the lyotropic mesophase, in contrast to copper tetra-4-carboxyphthalocyanine [15] and copper tetra-4-[(4'-carboxy)phenoxy]phthalocyanine [19].

The prepared complex **III** revealed significant affinity to the cellulose and regenerated protein fibers; therefore, it might be used as direct or acid dye [44].

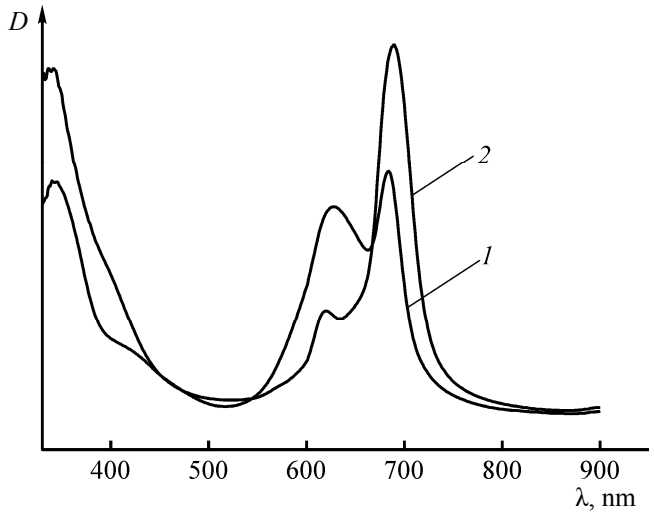



**Fig. 2.** Electron absorption spectra of copper tetra-4-[(4'-carboxy)phenylsulfanyl]phthalocyanine (*1*) and of complex **III** (*2*) in DMF.

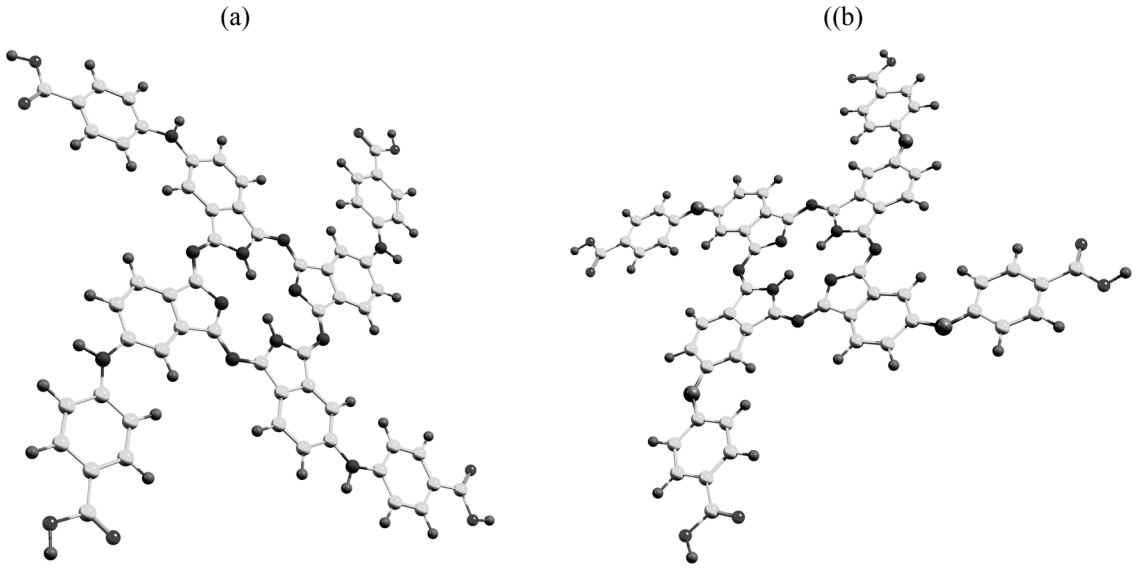



**Fig. 3.** Optimized geometry of copper tetra-4-[(4'-carboxy)phenylamino]phthalocyanine (a) and copper tetra-4-[(4'-carboxy)phenylsulfanyl]phthalocyanine (b) molecules.

## EXPERIMENTAL

The elemental analysis was performed with CHNS–O FlashEA (1112 series) analyzer. The electron absorption spectra of the solutions in DMF or in 0.5 wt % KOH were registered with Hitachi U-2001 spectrophotometer at 325–900 nm. The IR spectra were recorded with Avatar 360 FT-IR ESP spectrometer at 400–4000 $cm^{-1}$ (KBr). The melting point was determined with the Boetius type heated bench equipped with the RNMK 05 watching device. The $^1H$ spectrum of **II** was recorded with Bruker DRX-500 spectrometer relative to TMS standard.

The phase state of the specimens was probed with Leitz Labor-lux 12 Pol polarizing microscope equipped with the Mettler FP 82 heating table and the Wild MPS 51 photo attachment (24×36 $mm^2$). The lyotropic mesomorphism was studied by the contact specimen method.

The quantum-chemical calculations were performed with PC GAMESS v 7.1.E software package [42] taking advantage of the density field theory (hybrid B3LYP5 functional and 6–31G basis set, full symmetry-restricted geometry optimization). The results were visualized with the Chemcraft software [43].

**4-[(4'-Carboxy)phenylamino]phthalonitrile II.** Mixture of 1.73 g (10 mmol) of 4-nitrophthalonitrile, 1.37 g (10 mmol) of 4-aminobenzoic acid, 2.76 g (20 mmol) of potassium carbonate, and 20 mL of DMSO was incubated at 85–95°C during 5–6 h. After cooling the mixture down, it was poured into water and acidified with HCl till slightly acidic medium. The formed precipitate was filtered off, and the product was extracted from the mother liquor with chloroform. The product was then dried at 40°C in vacuum. Yield 1.15 g (75.6%), mp 172°C. IR spectrum (KBr), ν, $cm^{-1}$: 2237 (C≡N), 1693 (COOH), 1603 (ArCOO), 1313, 3265 (NH). $^1H$ NMR spectrum (Py-$d_6$), δ, ppm ($J$, Hz): 8.54 d ($1H^2$, $J$ 7.9), 7.90 d ($1H^3$, $J$ 8.2), 7.82 d ($1H^1$, $J$ 2.0), 7.71 d ($2H^{4,5}$, $J$ 8.8), 7.29 d ($2H^{6,7}$, $J$ 8.2). Found, %: C 68.25; H 3.61; N 15.85. $C_{30}H_{36}O_5N_2$. Calculated, %: C 68.44; H 3.45; N 15.96.

**Copper tetra-4-[(4'-carboxy)phenylamino]phthalocyanine III.** Mixture of 66 mg (0.25 mmol) of 4-[(4'-carboxy)phenylamino]phthalonitrile **II**, 14 mg (0.07 mmol) of copper acetate monohydrate, and 18 mg (0.3 mmol) of urea was thoroughly triturated, put into quartz tube, heated to 180–185°C, and incubated at that temperature during 1.5 h. The fusion cake was thoroughly triturated, washed with 10 wt % aqueous HCl, then washed with water till neutral pH, and dried. The crude complex **III** was purified as follows: washing with glacial acetic acid, washing with water till neutral pH, washing with acetone, drying, and recrystallization from concentrated sulfuric acid. Yield 38 mg (54%). Electronic absorption spectrum (DMF), $\lambda_{max}$, nm: 689. Found, %: C 63.76; H 3.37; N

14.82. $C_{60}H_{36}O_8N_{12}Cu$. Calculated, %: C 64.54; H 3.25; N 15.05.

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