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Synthesis and Spectral Properties of the Metallophthalocyanines with the Fragments of Substituted Pyrazoles

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Abstract—By the reaction of 4-bromphthalonitrile with corresponding 1-phenyl-3-methyl-5-hydroxy- and 1-*p*-sulfophenyl-3-methyl-5-oxypyrazolaes the substituted phthalonitriles were synthesized and converted into metallophthalocyanines with the fragments of substituted pyrazoles. The compounds obtained were identified using the data of elemental analysis, gas chromatography–mass spectrometry, IR, ^{1}H NMR, and electronic spectroscopy. The influence of the peripheral environment of the phthalocyanine ligand in the resulting metal complexes on the spectral and other properties of the latter was revealed.

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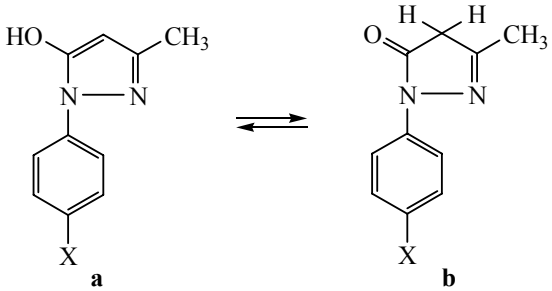
Among the multitude of substituted phthalocyanines, of special interest are the compounds containing biophoric fragments on the periphery of the macrocycle, in particular, the fragmrnts of substituted pyrazoles. It is known that a pyrazole heterocycle is a part of many drug molecules exhibiting anti-inflammatory, sedative, and bacteriostatic effect [1], as well as of high-performance dyes with pronounced fungicidal activity against specific fungi growing on textiles and causing destruction of the latter [2].

This paper presents the data on the synthesis and study of metallophthalocyanines containing methylphenylhydroxypyrazole residues as substituents.

An effective method for preparing substituted phthalocyanines is based on nitriles [3], and therefore our first task was to obtain the corresponding phthalonitriles with pyrazole substituents. As starting compound for this synthesis we used 4-bromphthalonitrile (**I**). The electron-withdrawing groups (CN) at the benzene ring of compound **I** provide sufficiently effective positive charge on the carbon atom bound to the bromine, which facilitates replacement of the latter at the action of nucleophilic reagents [4]. As the reagents we used mainly 1-phenyl-3-methyl-5-hydroxy (oxo)-pyrazole (**II**) and 1-*p*-sulfophenyl-3-methyl-5-hydroxy(oxo)-pyrazole (**III**).

According to [1], compounds **II** and **III** exist in two tautomeric forms: hydroxy- (**a**) and oxo- (**b**) (Scheme 1).

Scheme 1.

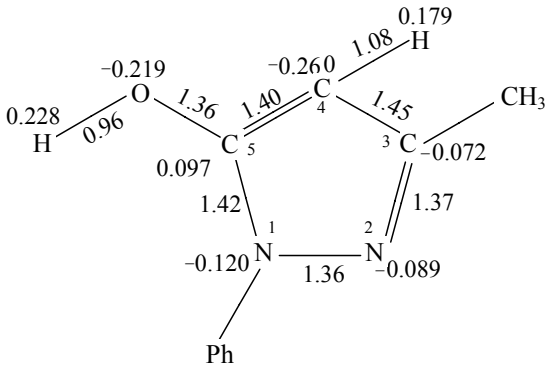


X = H (**IIa, IIb**); SO_3H (**IIIa, IIIb**).

The tautomeric equilibrium can be shifted in one or another direction, depending on the process conditions. In particular, bases, including potassium carbonate used by us, catalyze enolization [5, 6]. In addition, it was noted [7] that the keto ↔ enol equilibrium in polar solvents is shifted to the right. Based on the above, we assume that in the process conditions used by us (DMF, K_2CO_3) the most likely nucleophilic agents are compounds **IIa** and **IIIa.** As will be shown below, this assumption was experimentally confirmed in the study

of the synthesized nitriles **IV, V** and respective metallophthalocyanines **VI–IX**.

Quantum-chemical calculations performed by us showed that the highest values of the effective negative charges in the molecule of 1-phenyl-3-methyl-5-oxypyrazole are on the oxygen atom of the hydroxy group (–0.219) and the carbon atom in the position *4* of the pyrazole ring (–0.260).



Accordingly, the substituted pyrazoles **IIa** and **IIIa** can act as both O- and C-nucleophiles, in particular, their reaction with the nitrile **I** can occur in two ways (Scheme 2, routes *a* and *b*). However, the above reaction conditions, in which the hydroxy group is activated, suggests that the substitution of bromine in nitrile **I** takes mainly the route A. In particular, the reaction is carried out in DMF medium in the presence of potassium carbonate, which serves as deprotonating agent [8] with respect to the hydroxy groups of compounds **IIa, IIIa**.

The required duration for the reaction with 1-*p*-sulfophenyl-3-methyl-5-oxypyrazol **III** as a nucleophile was monitored by the total consumption of phthalonitrile **I** in the reaction mixture: the sample of the reaction mixture becomes almost completely soluble in water. The same reaction duration (2 h) was applied in the synthesis of the phthalonitrile **IVa**. The dimethylformamide solution of the obtained phthalonitrile was separated from the inorganic impurities (KBr, K_2CO_3) by filtration, DMF was removed in a vacuum at a temperature of 90–100°C. Final purification of the phthalonitriles was performed using chromatography on alumina, while eluting with DMF (nitrile **IV**) or a mixture of DMF and water in a ratio 1: 1, v/v (nitrile **V**). Difference in mobility of nitriles **IVa, Va,** and **IVb**, **Vb** allowed us to isolate them in individual form at the chromatographic purification. The proportion of nitriles **IVb** and **Vb** did not exceed 3%.

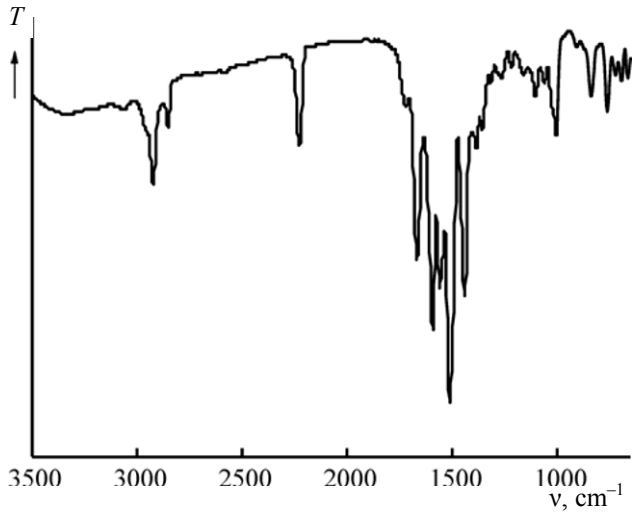
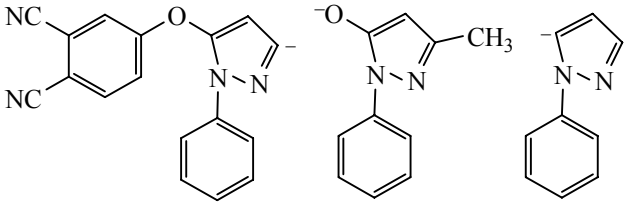


Fig. 1. IR spectrum of nitrile **IVa**.

To confirm the structure of the synthesized phthalonitriles **IVa and Va** we used the data of the elemental analysis, gas chromatography–mass spectrometry, IR and ^{1}H NMR spectroscopy.

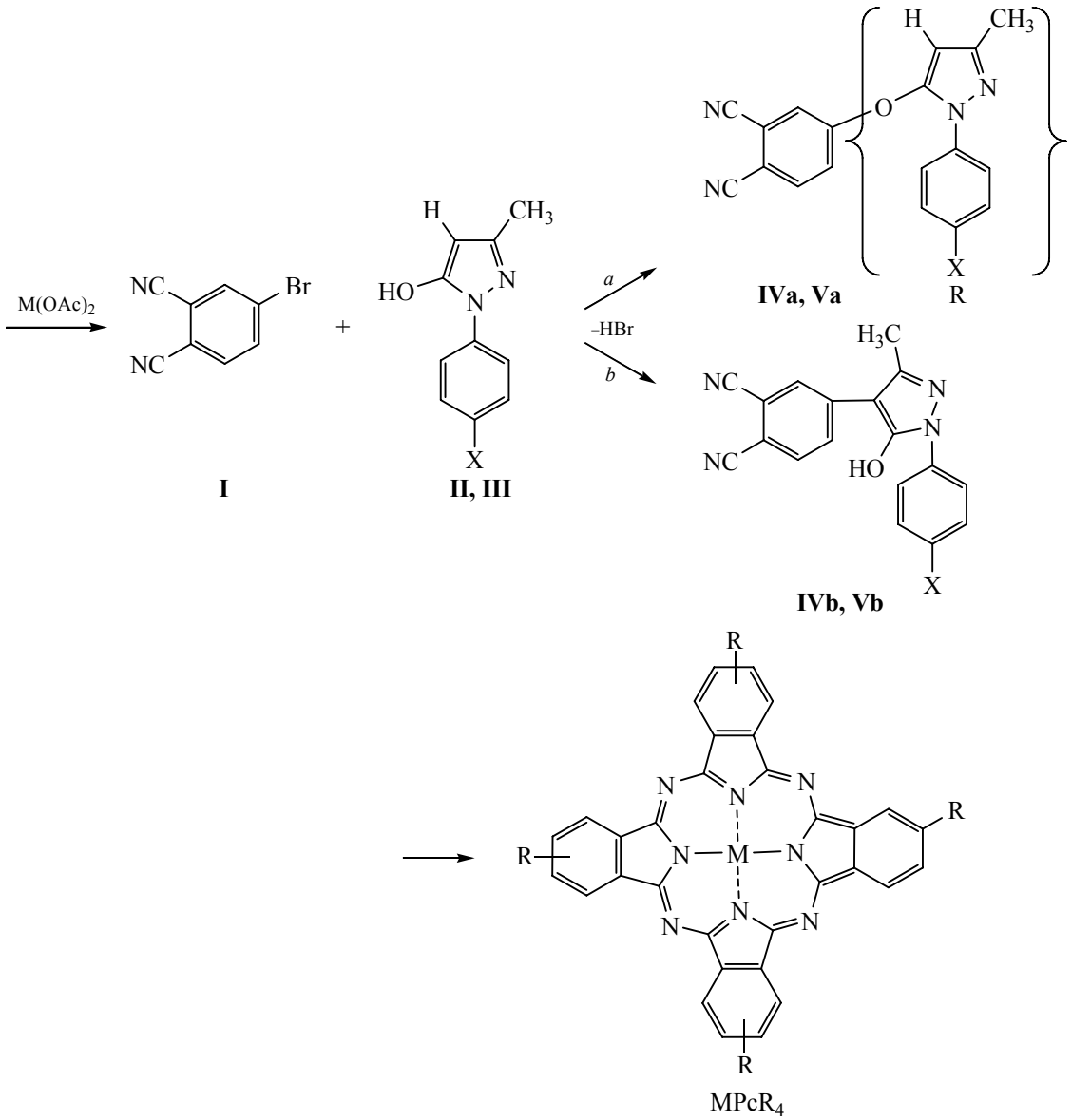
Thus, in the chromatogram of nitrile **IVa** a strong single peak was recorded. The mass spectrum of this compound has a peak at *m*/*z* 300 corresponding to the main molecular ion, as well as several weak signals of fragmentation products.



m/*z* 285 *m*/*z* 173 *m*/*z* 157

Analysing the IR spectrum of nitrile **IVa** (Fig. 1), we should note retention of the stretching vibration band (2230 cm^{-1}) of the cyano group which is slightly displaced ($\Delta\nu$ = 6 cm^{-1}) in the low-frequency region compared to the spectrum of parent 4-bromophthalonitrile **I**. The substitution of bromine resulted in the disappearance in the IR spectrum of the band of stretching vibrations C_{Ar}–Br (645 cm^{-1}), and appearance of new bands, among which these at 2852 and 2923 cm^{-1}, related to the symmetric and asymmetric stretching vibrations of CH in methyl groups, and the band at 1668 cm^{-1}, corresponding to the N–N stretching vibrations in the pyrazole [9] are the most clear. In the IR spectrum of nitrile **Va** containing sulfo group,

Scheme 2.

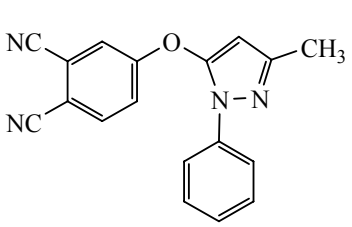


X = H (**II**), SO_3H (**III**); X = H, M = Co (**VI**), Cu (**VII**), Ni (**VIII**); X = SO_3H, M = Co (**IX**).

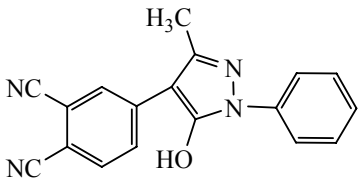
besides the above bands are the bands at 1035 cm^{-1} related to the S=O symmetric stretching vibrations and at 1130 cm^{-1} of the asymmetric stretching vibrations. The IR spectra of the synthesized nitriles **IVa** and **Va** practically do not contain absorption bands corresponding to the carbonyl and hydroxyl groups, which confirm the above assumption of participation in nucleophilic substitution predominantly of enol forms of the substituted pyrazoles **IIa** and **IIIa** and the reaction proceeding by the route *a* (Scheme 2).

^{1}H NMR spectrum of the nitrile **IVa** (Fig. 2) was compared with the theoretically calculated spectra of nitriles with peripheral fragments **A, B,** and **C**.

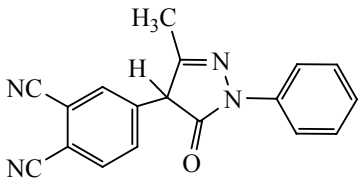
The comparison of the positions of the signals of aromatic and aliphatic protons leads to the following conclusions. The signals in the weak field 7.75, 7.92, and 7.31–7.54 ppm refer to the benzene ring protons of the phthalonitrile and phenyl substituent. In the high field there is a strong signal at 2.38 ppm of the protons



A



B



C

of methyl group. The positions of these signals are in good agreement with the theoretically calculated spectrum corresponding to the structure of **A**.

Structures **B** and **C** are excluded according to the following reasons:

(a) There are no signals in the spectrum of the protons of the hydroxyl group (4.24 ppm) (structure **B**), and the proton at the carbon atom C^4 of the pyrazole ring matching structure **C.**

(b) The signals of the protons of the methyl group in structure **C** theoretically should appear at 1.90 ppm, while they are fixed at 2.38 ppm (Fig. 2), which is closer to the structure of **A** (2.22 ppm).

(c) The signal of the proton at the carbon atom C^4 of the pyrazole ring (5.88 ppm) is close to the theoretical value for the structure **A** (6.04 ppm).

Thus, the set of the experimental data confirms our assumption that in the synthesis of the phthalonitriles with pyrazole substituent the major products are phenylmethyl pyrazolyloxy-substituted compounds **IVa** and **Va**.

Using the obtained nitriles **IVa** and **Va** we synthesized the corresponding substituted metallophthalocyanines **VI–IX** in accordance with the Scheme 2 (route *a*). The synthesis of metallophthalocyanines **VI–VIII** not containing sulfo group was performed by heating the corresponding substituted nitrile **IVa** with anhydrous copper, cobalt or nickel acetate at a temperature of 190–195°C for 45–60 min.

A solid reaction mixture isolated after the synthesis was thoroughly crushed, washed first with 18% aqueous solution of HCl, then with water to neutral filtrates. The residue was dried and the target complexes were extracted from it with chloroform in a Soxhlet apparatus.

When using sulfophthalonitrile **Va**, we succeeded to get only cobalt complex **IX** by fusing **Va** with anhydrous cobalt acetate and urea at 190–195°C for 1 h. The urea is required to create a melt, and the ammonia evolved at the urea decomposition is known [10] to be involved in the formation of phthalocyanine. Complexes of copper and nickel in these conditions formed in trace amounts. This feature (that is, only the formation of the cobalt complexes) was observed earlier for other sulfophthalocyanine precursors [8], but it is not explained so far. The cobalt complex **IX** containing sulfo group after synthesis was washed with hydrochloric acid at gradually decreased concentration from 18 to 5% to colorless filtrates. The residue was dried and the target product was extracted with water, the aqueous solution was then evaporated to dryness.

Final purification of the synthesized complexes **VI–IX** was performed by chromatography on alumina, eluting with chloroform (**VI–VIII**) or 1-propanol with 1% solution of aqueous ammonia in a volume ratio of 1: 2 (**IX**).

The **i**solated metallophthalocyanines **VI–IX** are dark blue crystalline substances. Complexes **VI–VIII** not containing sulfo group are readily soluble in organic solvents of low polarity. Complex **IX** containing sulfo group is soluble in DMF, water, and aqueous alkali. To identify them we used elemental

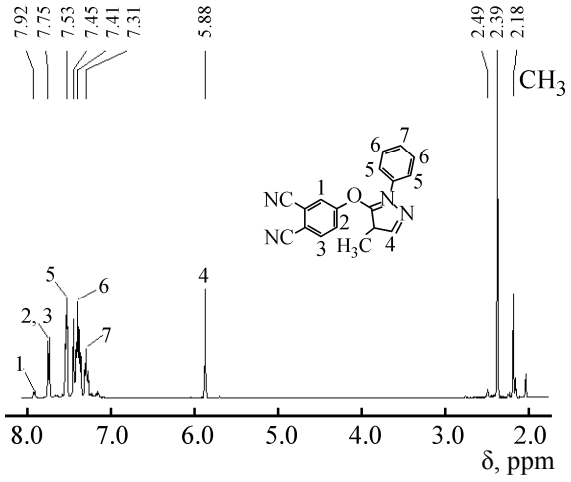


Fig. 2. ^{1}H NMR spectrum of nitrile **IVa**.

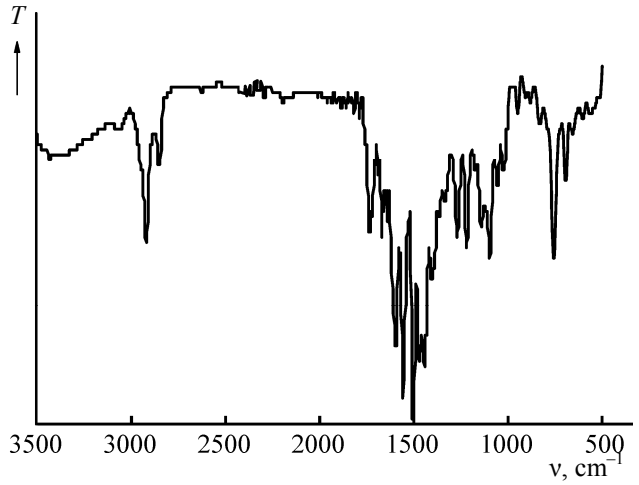


Fig. 3. IR spectrum of copper phthalocyanine **VII**.

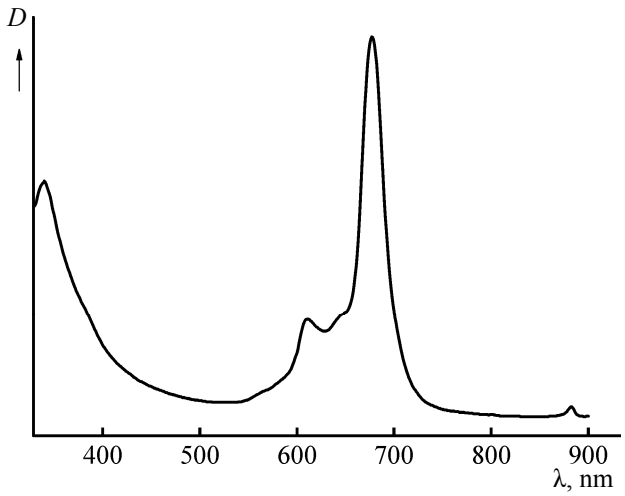


Fig. 4. EAS of copper complex **VII** in chloroform.

analysis, vibration, electronic, and ^{1}H NMR spectroscopy.

In the IR spectrum of complex **VII** (Fig. 3) we must first identify the bands of stretching vibrations of the CH methyl groups mentioned above in the analyzis of phthalonitriles **IVa** and **Va**; N–N bonds of pyrazole heterocycle, and N–C_{Ph} bond; in the spectrum of the complex **IX** containing sulfo group r additional bands appea of symmetric and asymmetric stretching vibrations of the S=O in aromatic sulfonic acids.

In the ^{1}H NMR spectrum of the nickel complex **VIII** the signals in the weak field at 7.87 and 7.73 ppm refer to the protons of benzene ring of the phthalocyanine ligand, and at 7.55 and 7.46 ppm, to the protons of the phenyl substituent at the pyrazole heterocycle. The signals in the strong field at 2.20 and 2.39 ppm belong to the protons of the methyl groups.

The good solubility of the synthesized complexes **VI–IX** allowed us to analyze the electron absorption spectra (EAS) of their solutions in a wide range of solvents (see the table). As can be seen from the table and Figs. 4 and 5, the EAS in organic solvents (chloroform, DMF) are characterized by an intense band (*Q*-band) in the wavelength region of 660–677 nm due to π–π* electron transition in the phthalocyanine macroring. In addition to the main peak, there is a shoulder or a low-intensity band at 600–645 nm on the short-wavelength slope of the spectral curve.

We succeeded to record the Soret band in the ultraviolet region (340 and 352 nm) for the copper complex **VII** in chloroform (Fig. 4) and cobalt complex **IX** in DMF (Fig. 5). This band is known [11] to be genetically linked with the absorption of isoindole fragments. The position of the *Q*-band

Position of the bands in the electron absorption spectra of complexes **VI–IX**

Comp. no.	λ_{max}, nm (I_{rel})				
	chloroform	DMF	H_2O	0.5% NaOH	H_2SO_4
VI	670:607 w (1.00:0.31)	663:600 w (1.00:0.33)	–	–	777:690 sh:415 w (1.00:0.52:0.57)
VII	677:645 sh:611 w:340 (1.00:0.29:0.29:0.64)	673:640 inf:610 sh (1.00:0.41:0.36)	–	–	788:745 sh:700 w:420 w (1.00:0.46:0.32:0.36)
VIII	660:640 sh:605 w (1.00:0.37:0.33)	669:640 (1.00:0.80)	–	–	776:690 sh:420 (1.00:0.28:0.31)
IX	–	668:608 sh:352 (1.00:0.35:0.50)	628:679 inf (1.00:0.80)	640:690 w (1.00:0.93)	772:690 sh:412 (1.00:0.43:0.31)

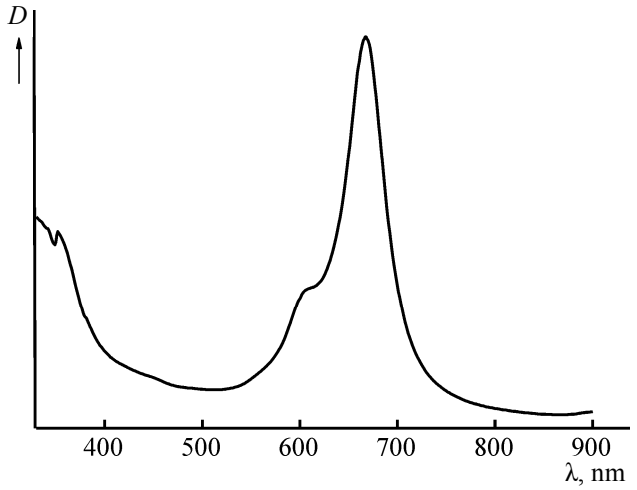


Fig. 5. EAS of cobalt complex **IX** in DMF.

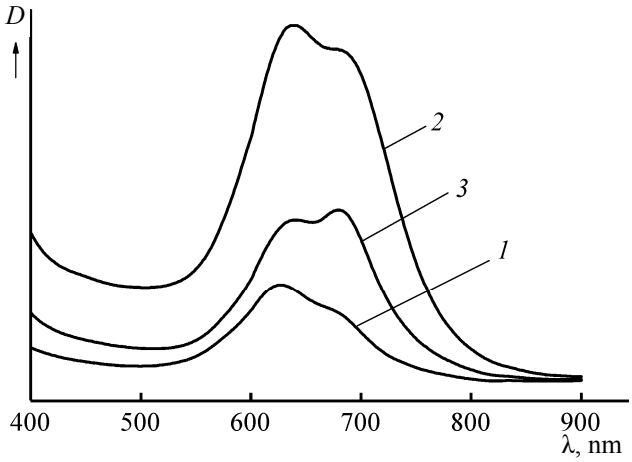


Fig. 6. EAS of complex **IX**: (*1*) in water, (*2*) in 0.5% NaOH, (*3*) in 0.25% NaOH.

depends on the nature of the metal. In the spectrum of the copper complex **VII** the *Q*-band is shifted red by 4–17 nm in comparison with the cobalt (**VI**) and nickel (**VIII**) complexes (see the table). Compared to the corresponding unsubstituted complexes [12], this band in DMF has a small red shift (up to 5 nm).

The sulfo groups in the molecules of the complex **IX** are responsible for the good solubility of the complex in water and aqueous alkali medium, so it was possible to record the EAS in these solvents. As with most well-known sulfo-substituted phthalocyanines [13], at the replacement of dimethylformamide by water and water-alkaline solutions the nature of the spectrum of complex **IX** changes significantly (see the table and Fig. 6).

The EAS have broad absorption bands with peaks at 628–640 and 679–690 nm. As noted, the ratio of the intensities of the long-wave and short-wave components of the *Q*-band depends on the concentration of the studied complex and the medium pH. In particular, the higher the concentration of the complex, the more pronounced short-wavelength component of the *Q*-band. The observed features of the spectrum are due to the presence in the solution of a mixture of associated and non-associated molecules [14].

The replacemen of organic or aqueous solvent by concentrated sulfuric acid results in a red shift of the *Q*-band in the EAS by 104–116 nm (see the table and Fig. 7). A similar change in the spectra is typical of the majority of known phthalocyanine compounds and is explainable by the process of protonation of the nitrogen mesoatoms of the macro ring [15]. The characteristic property of the synthesized metal complexes is that the value of this displacement is smaller (by 13–16 nm) than in the spectra of the non-substituted complexes. This is due to the presence of nitrogen atoms in the pyrazole ring, which may add protons,and the degree of protonation of the nitrogen meso-atoms in the phthalocyanine macrocycle is reduced.

EXPERIMENTAL

Electron absorption spectra were recorded in the region 330–900 nm on a Hitachi UV–2001 spectrophotometer at room temperature. The solvents used are chloroform, DMF, aqueous NaOH, sulfuric acid. The concentration of the complexes in these solvents was $\approx 10^{-5}$ mol l^{-1}. IR spectra were obtained on an Avatar 360 FT-IR ESP spectrophotometer in the range of 400–4000 cm^{-1}. Samples were prepared by the usual method in KBr tablet. Elemental analysis was performed on a Flash EA CHNS-O Analyzer. Chromato-mass spectra were taken on a Saturn 200 GC/MS instrument. ^{1}H NMR spectra were recorded on a Bruker DRX-500 instrument, solvent $CDCl_3$.

4-[(3-Methyl-1-*p*-sulfophenyl-1*H*-pyrazol-5-yl)-oxy]phthalonitrile (Va). A mixture of 1.04 g (5 mmol) of 4-bromophthalonitrile, 2.54 g (10 mmol) of 1-*p*-sulfophenyl-3-methyl-5-oxypyrazole, and 2.76 g (20 mmol) of potassium carbonate in 50 ml of DMF was heated with stirring to 125–130°C and kept for 2 h at this temperature. After cooling, the dimethylformamide solution was separated from the inorganic precipitate by filtration. The solvent was removed in a vacuum and the dry residue was dissolved in water. The saturated aqueous solution of the nitrile obtained

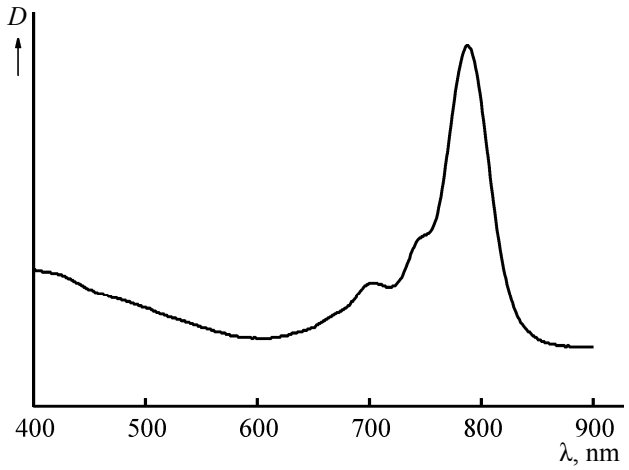


Fig. 7. EAS of copper complex **VII** in sulfuric acid.

was acidified with concentrated hydrochloric acid to pH 2–3. The resulting precipitate was filtered off, washed with 5% hydrochloric acid, and dried. Final purification was carried out by chromatography on alumina of I-st activity grade, eluent DMF–H_2O (1: 1). After removal of the eluent by vacuum distillation, the solid residue was kept in a vacuum drying cabinet at 70°C to constant weight. Yield 0.61 g (32%), light brown powder, decomp. point > 260°C, soluble in water and DMF. IR spectrum, ν, cm^{-1}: 2227 [ν(C≡N)], 1060 [ν_{as}(S=O)], 1270 [ν(Ar–O–$C_{pyrazole}$)], 2853, 2923 [ν(CH)]. Found, %: C 56.6, H 3.1, N 14.8, S 8.5. $C_{18}H_{12}N_4O_4S$. Calculated, %: C 56.8, H 3.2, N 14.7, S 8.4.

4-[(3-Methyl-1-phenyl-1*H*-pyrazol-5-yl)oxy]-phthalonitrile (IVa). Obtained by the above method using 1.74 g (10 mmol) of 1-phenyl-3-methyl-5-oxypyrazole. The dimethylformamide solution after separation from the inorganic precipitate was purified by chromatography on alumina of I-st grade activity eluting with DMF. Yield 0.63 g (42%), a beige powder, mp > 125°C, soluble in DMF and acetone. IR spectrum, ν, cm^{-1}: 2230 [ν(C≡N)], 1272 [ν(Ar–O–$C_{pyrazole}$)], 2852, 2923 [ν(CH)]. ^{1}H NMR spectrum ($CDCl_3$), δ, ppm: 7.75 (1H, H^1), 7.92 (2H, $H^{2,3}$), 7.31–7.54 (5H, Ph), 2.38 (3H, CH_3). Mass-spectrum (*m*/*z*): 300. Found, %: C 71.8, H 4.1, N 18.6. $C_{18}H_{12}N_4O$. Calculated, %: C 72.0, H 4.0, N 18.6.

Cobalt tetra-{4-[(3-Methyl-1-phenyl-1*H*-pyrazol-5-yl)oxy]}phthalocyanine (VI). A mixture of 0.6 g (2 mmol), of nitrile **IVa** and 0.18 g (1 mmol) of anhydrous cobalt acetate was heated to 190–195°C and maintained at that temperature for 45–60 min to reach solidification of the reaction mixture. After cooling to room temperature, the reaction mixture was thoroughly crushed, washed on a glass frit filter with 18% hydrochloric acid to colorless filtrate, and then with water to neutral medium. The filtered off solid was dried at 80°C. The resulting complex **VI** was extracted with chloroform in a Soxhlet apparatus. Final purification was carried out by chromatography on alumina of Ist activity grade, using chloroform as an eluent. After distillation of the eluent, the residue was dried at 70°C to constant weight. Yield 0.28 g (44%), a dark blue powder, soluble in chloroform, DMF, and concentrated sulfuric acid. IR spectrum, ν, cm^{-1}: 1668 [ν(N–N)], 1265 [ν(Ar–O–$C_{pyrazole}$)], 2852, 2923 [ν(CH)]. Found, %: C 68.4, H 3.7, N 18.0. $C_{72}H_{48}CoN_{16}O_4$. Calculated, %: C 68.8, H 3.8; N 17.8.

Copper tetra-{4-[(3-Methyl-1-phenyl-1*H*-pyrazol-5-yl)oxy]}phthalocyanine (VII) was prepared by the same method using 0.18 g (1 mmol) of copper acetate. Yield 0.20 g (32%), dark blue powder, soluble in chloroform, DMF, and concentrated sulfuric acid. IR spectrum, ν, cm^{-1}: 1662 [ν(N–N)], 1230 [ν(Ar–O–$C_{pyrazole}$)], 2850, 2920 [ν(CH)]. Found, %: C 68.1, H 3.7, N 17.8. $C_{72}H_{48}CuN_{16}O_4$. Calculated, %: C 68.4, H 3.8, N 17.7.

Nickel tetra-{4-[(3-Methyl-1-phenyl-1*H*-pyrazol-5-yl)oxy]}phthalocyanine (VIII) was prepared similar to compound **VI** using 0.18 g (1 mmol) of nickel acetate. Yield 0.23 g (37%), dark blue powder, soluble in chloroform, DMF, and concentrated sulfuric acid. IR spectrum, ν, cm^{-1}: 1660 [ν(N–N)], 1258 [ν(Ar–O–$C_{pyrazole}$)], 2852, 2921 [ν(CH)]. ^{1}H NMR spectrum ($CDCl_3$), δ, ppm: 7.87, 7.73 (12H, H^{1-3}), 7.55, 7.46 (20H, Ph), 2.20, 2.39 (12H, CH_3). Found, %: C 68.7, H 3.6, N 17.9. $C_{72}H_{48}N_{16}NiO_4$. Calculated, %: C 68.6, H 3.8; N 17.8.

Cobalt tetra-{4-[(3-Methyl-1-*p*-sulfophenyl-1*H*-pyrazol-5-yl)oxy]}phthalocyanine (IX). A mixture of 0.76 g (2 mmol) of nitrile **Va** and 0.18 g (1 mmol) of anhydrous cobalt acetate was heated to 160°C and 0.30 g (5 mmol) of urea was added. The temperature was raised to 190–195°C and maintained for 40–45 min to solidification of the reaction mixture. After cooling to room temperature, the reaction mixture was thoroughly crushed, washed on a glass frit filter in succession with 18% and 5% hydrochloric acid to colorless filtrate. The solid residue was dried at 70°C to constant weight. The resulting complex was extracted with water and the aqueous solution was evaporated to dryness on a water bath. Final purification was carried out by

chromatography on alumina of I-st activity grade, using as eluent 1-propanol–1% aqueous ammonia in 1:2 ratio. After distilling off the eluent, the residue was dried in a vacuum drying cabinet at 70 ° C to constant weight. Yield 0.43 g (54%), dark blue powder, soluble in water, DMF, aqueous alkali solutions, and concentrated sulfuric acid. The substance crystallizes from an aqueous solution as needles. IR spectrum, ν, cm^{-1}: 1668 [ν(N–N)], 1260 [ν(Ar–O–$C_{pyrazole}$)], 2850, 2923 [ν(CH)], 1030, 1040 [ν(S=O)]. Found, %: C 54.6, H 3.0, N 14.3, S 8.1. $C_{72}H_{48}CoN_{16}O_{16}S_4$. Calculated, %: C 54.7, H 3.0; N 14.2; S 8.1.

Position of the bands in the electron absorption spectra of the synthesized complexes **VI–IX** and their relative intensities are listed in the table.

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