TETRASUBSTITUTED (4-CHLOROPHENOXY)- AND (2,4,5-TRICHLOROPHENOXY)PHTHALOCYANINE METAL(II) COMPLEXES AND THEIR SULPHONATED DERIVATIVES: SYNTHESIS AND PROPERTIES

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By template condensation of 4-(4-chlorophenoxy)- and 4-(2,4,5-trichlorophenoxy)phthalonitriles with cobalt(II), copper(II) and zinc(II) acetates, the corresponding metal(II) phthalocyaninates were synthesized, and some of their sulfonic acid derivatives were also isolated after sulphonation reactions. The spectroscopic characteristics and some physicochemical properties of the synthesized compounds were also given.

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INTRODUCTION

In modern chemistry, phthalocyanine derivatives have a great interest in the creation of novel functional materials.[1-3] Due to modification of metal complexing agent within the macrocycle or introduction of various peripheral substituents, it is possible to fine-tune the properties of the compound obtained and, correspondingly, of the material or devices based on them.[4-6]

Among the substituted phthalocyanines, aryloxy substituted were found to be antioxidants, substances exhibiting photoelectric and antimicrobial properties, photosensitizers for the photodynamic therapy of cancer, and catalysts for desulfurization, are very promising materials. The presence of aryloxy-substituents in the phthalocyanine ring allows good solubility in organic solvents, which facilitates the process of isolation and purification of the target products.

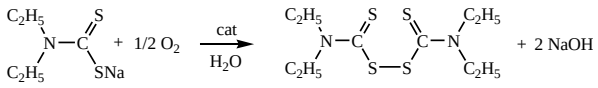
The literature presents data on phenoxy-substituted zinc phthalocyaninates containing halogen atom substituents (F, Cl, Br) as photosensitizers[7,8] and it was shown that the introduction of halogen atoms into the phthalocyanine molecule leads to an increase in their activity. In addition, aryloxy-substituted phthalocyanines containing halogen atoms are promising for use as an information storage devices[9-10] and sensors.[11-12]

Based on the foregoing, the aim of this work was to the synthesis of tetra(4-chlorophenoxy) and tetra(2,4,5-trichlorophenoxy)phthalocyaninates of copper(II), cobalt(II) or zinc(II) and sulfonic acids based on them, as well as to study of their properties.

EXPERIMENTAL

Elemental analysis of the synthesized compounds was carried out on a CHNS-O-Flash-EA 1112 analyzer. Before elemental analysis, the samples of the studied compounds were subjected to heat treatment at 110 °C for 2 hours. Electronic absorption spectra were recorded on a HITACHI-2001 spectrophotometer in organic solvents, in water, and sulfuric acid at room temperature in the wavelength range of 350-900 nm. IR spectra were recorded on an Avatar 360 FT-IR ESP spectrometer in the region of 400–4000 cm^{-1} in a potassium bromide matrix and thin films (chloroform).MALDI-TOF mass spectra were obtained on a Shimadzu Biotech Axima Confidence mass spectrometer in positive ion mode as a matrix 2,5-dihydroxybenzoic acid was used. Samples were prepared by dissolving the compounds in chloroform (10^{-4}-10^{-5} mol L^{-1}), then mixed in a 1:1 ratio (v/v) with a solution of the matrix (30 mg mL^{-1}) in THF.

The catalytic activity of cobalt phthalocyanines was measured by a known method[13-14] using the oxidation reaction of sodium N,N-diethyldithiocarbamate. The process proceeds according to Scheme 1.



Scheme 1. Oxidation of sodium N, N-diethyldithiocarbamate.

General synthetic process of 4-(4-chlorophenoxy)- and 4-(2,4,5-trichlorophenoxy)phthalonitriles

4-Nitrophthalonitrile (1.73 g, 0.01 mol) and 0.01 mol of the corresponding substituted phenol were dissolved in 30 mL of DMF. A solution of 2.76 g (0.02 mol) of K_2CO_3 in 5 mL of water was added to the resulting solution and stirred at 100 ° C for 3 h. The precipitate obtained was filtered off, washed with water to pH 7 and dried in air at 70-80 ºC. (Scheme 2).

4-(4-Chlorophenoxy)phthalonitrile (2)

Yield: 2.05 g (80.7 %). FT-IR: 2229 (C≡N), 1278 (Ar-O-Ar), 1085 (C-Cl) cm^{-1}. Anal. Calcd. for $C_{14}H_7ClN_2O$; C 66.03, H 2.77, N 11.00. Found: C 65.98, H 2.79, N 10.97.

4-(2,4,5-Trichlorophenoxy)phthalonitrile (3)

Yield: 2.43 g (75 %). FT-IR: 2231 (C≡N), 1250 (Ar-O-Ar), 1088 (C-Cl) cm^{-1}. ^{1}H NMR ($CDCl_3$) δ = 7.81 (d, 1H, H^3, J_{HH}10.89 Hz), 7.69 (s, 1H, H^4), 7.33 (s, 1H, H^1), 7.29-7.28 (m, 1H, H^2), 7.24-7.22 (m, 1H, H^5). MALDI-TOF: *m/z* = 362 $[M+K]^+$. Anal. Calcd. for $C_{14}H_5Cl_3N_2O$: C51.97; H 1.56; N 8.66. Found: C C 51.89; H 1.60; N 8.64.

Synthesis of tetra(4-chlorophenoxy)phthalocyanine metal complexes

A thoroughly ground mixture of 1 mmol of the corresponding substituted phthalonitrile (**2** or **3**) and 0.3 mmol of the acetate of the corresponding metal was heated at 185-190 °C until it solidified. The resulting complexes were reprecipitated from concentrated sulfuric acid on ice. The precipitate was filtered off and washed with water to pH 7, then dried. The final purification was performed by column chromatography on silica gel M60 using chloroform as eluent.

Tetra(4-chlorophenoxy)phthalocyaninatocobalt(II) (4a)

Yield: 0.21 g (78.1 %). MALDI-TOF: *m/z* = 1077 $[M]^+$. FT-IR: 1249 (Ar-O-Ar), 1080 (C-Cl) cm^{-1}. Anal. Calcd. for $C_{56}H_{28}Cl_4CoN_8O_4$; C 62.42; H 2.62; N 10.40. Found: C 62.40; H 2.70; N 10.38.

Tetra(4-chlorophenoxy)phthalocyaninatocopper(II) (4b)

Yield: 0.19 g (70.3 %). MALDI-TOF: *m/z*= 1082 $[M]^+$. FT-IR: 1248 (Ar-O-Ar), 1081 (C-Cl) cm^{-1}. Anal. Calcd. for $C_{56}H_{28}Cl_4CuN_8O_4$: C 62.15; H 2.61; N 10.35. Found: C 62.11; H 2.65; N 10.30.

Tetra(4-chlorophenoxy)phthalocyaninatozinc(II) (4c)

Yield: 0.20 g (74.1 %). MALDI-TOF: m/z = 1084 $[M]^+$. FT-IR: 1246 (Ar-O-Ar), 1080 (C-Cl) cm^{-1}. Anal. Calcd. for $C_{56}H_{28}Cl_4CoN_8O_4$: C 62.04; H 2.60; N 10.34. Found: C 61.99; H 2.62; N 10.31.

Tetra(2,4,5-trichlorophenoxy)phthalocyaninatocobalt(II) (5a)

Yield: 0.22 g (65.0 %). MALDI-TOF: m/z = 1352 $[M-H]^+$. FT-IR: 1246 (Ar-O-Ar), 1080 (C-Cl) cm^{-1}. Anal. Calcd. for $C_{56}H_{20}Cl_{12}CoN_8O_4$: C 49.71; H 1.49; N 8.28. Found: C ; 49.69; H 1.51; N 8.26.

Tetra(2,4,5-trichlorophenoxy)phthalocyaninatocopper(II) (5b)

Yield: 0.21 g (61.9 %). ^{1}HNMR ($CDCl_3$) δ = 7.80 (d, 1H, H^3, J_{HH} 8.70 Hz), 7.69 (s, 1H, H^4), 7.33 (s, 1H, H^1), 7.29-7.28 (m, 1H, H^2), 7.22 (dd, 1H, H^5 $^2J_{HH}$ 8.70, $^3J_{HH}$ 2.6 Hz). MALDI-TOF: *m/z* = 1358 $[M+H]^+$, 1374 $[M+Na]^+$. FT-IR: 1244 (Ar-O-Ar), 1084 (C-Cl) cm^{-1}. Anal.Calcd. for $C_{56}H_{20}Cl_{12}CuN_8O_4$: C 49.54; H 1.48; N 8.25. Found: C 49.52, H 1.51; N 8.23.

Tetra(2,4,5-trichlorophenoxy)phthalocyaninatozinc(II) (5c)

Yield: 0.24 g (74 %). FT-IR: 1246 (Ar-O-Ar), 1080 (C-Cl) cm^{-1}. MALDI-TOF: *m/z* = 1359 $[M]^+$. Anal. Calcd. for $C_{56}H_{20}Cl_{12}ZnN_8O_4$: C 49.43; H 1.32; N 8.23. Found: C 49.39; H 1.40; N 8.20.

Synthesis of sulfonic acid derivatives of tetra(4-chlorophenoxy) and tetra(2,4,5-trichlorophenoxy)phthalocyaninatometal(II) complexes

Sulfonic acid derivatives were synthesized by the interaction of 0.1 mmol of the corresponding phthalocyanine metal complex and 15 mL of 26 % oleum at 70 °C for 2 h and 10 h for chlorophenoxy- and trichlorophenoxy-derivatives, respectively. The reaction mixture f was poured into the mixture of ice and NaCl. The precipitate was filtered off, washed with cc. HCl and dried in air. The desired product was extracted with water and the water was removed from the solution by evaporation. The final purification step was carried out by column chromatography on silica gel M 60, DMS was selected as eluent.

Tetra(2,3,5,6-tetrasulfo-4-chlorophenoxy)phthanocyaninato-copper(II) (6b)

Yield: 0.13 g (56.5 %). ^{1}HNMR δ = 7.34 (s, H3, 4H), 7.23 (s, H1, 4H), 7.13 (s, H2, 4H). FT-IR (KBr): 1249 (Ar-O-Ar), 1167, 1042 (S=O), 1086 (C-Cl), 1069 (C-S) cm^{-1}.

Tetra(2,3,5,6-tetrasulfo-4-chlorophenoxy)phthalocyaninato-zinc(II) (6c)

Yield: 0.14 g (60.9 %). FT-IR (KBr): 1248 (Ar-O-Ar), 1160, 1048 (S=O), 1081 (C-Cl), 1069 (C-S) cm^{-1}.

Tetra(3,6-disulfo-2,4,5-trichlorophenoxy)phthalocyaninatoco-balt(II) (7a)

Yield: 0.14 g (70.3 %). FT-IR (KBr): 1240 (Ar-O-Ar), 1045 (C-Cl), 1167, 1042 (S=O), 1069 (C-S) cm^{-1}.

Tetra[(3,6-disulfo-2,4,5–trichlorophenoxy)phthalocyaninato-copper(II) (7b)

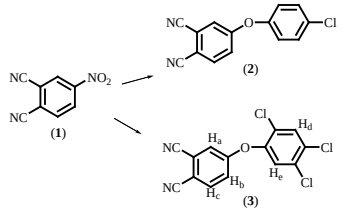
Yield: 0.15 g (75.3 %). ^{1}HNMR δ = 7.23 (s, H3, 4H), 7.13 (s, H1, 4H), 7.03 (s, H2; 4H). FT-IR (KBr): 1249 (Ar-O-Ar), 1123, 1052 (S=O), 1082 (C-Cl), 1069 (C-S) cm^{-1}.

Tetra(3,6-disulfo-2,4,5–trichlorophenoxy)phthalocyaninato-zinc(II) (7c)

Yield: 0.14 g (70.0 %). FT-IR (KBr): 1248 (Ar-O-Ar), 1120, 1048 (S=O), 1083 (C-Cl), 1067 (C-S) cm^{-1}.

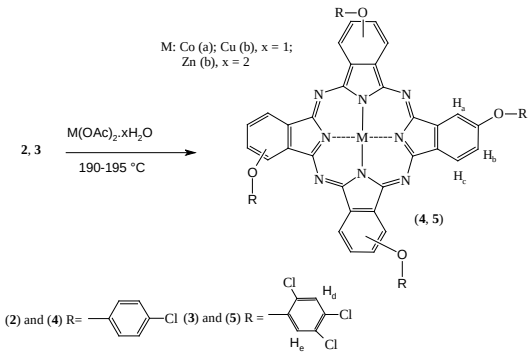
RESULTS AND DISCUSSION

For the synthesis of the target phthalocyanines in the first stage, the initial 4-chlorophenoxy- (**2**)[15] and 4-(2,4,5-trichlorophenoxy)phthalonitriles (**3**) were obtained by means of the interaction of 4-nitrophthalonitrile (**1**) and the corresponding phenols (Scheme 2) in DMF in the presence of potassium carbonate.



Scheme 2. Synthesis of substituted phthalonitriles.

Next, the synthesis of phthalocyanines by the "nitrile" method was carried out by fusing phthalonitriles (**2**, **3**) with acetates of copper, cobalt and zinc at 180-200 °C until the reaction mixture solidified (Scheme 3).



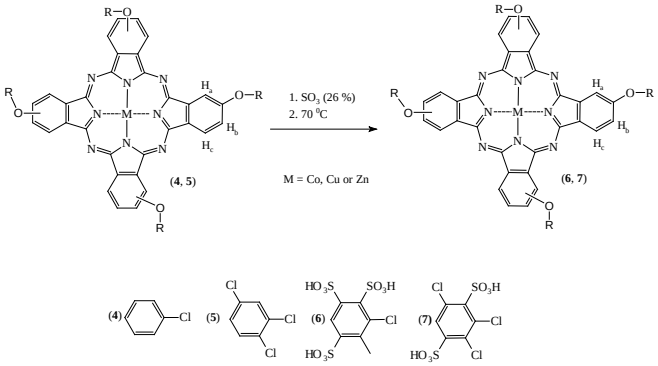
Scheme 3. Synthesis of metal complexes of phthalocyanines

The synthesized complexes were reprecipitated from concentrated sulfuric acid. The final purification was carried out by column chromatography on silica gel M60 using chloroform as eluent.

The composition and structure of the obtained compounds were established using data from MALDI-TOF spectrometry, 1H NMR, IR and electron spectroscopy.

In the FT-IR spectra of the synthesized phthalocyanines (**4-5a,b**), there are no absorption bands in the region of 2228-2231 cm^{-1}, corresponding to stretching vibrations of the nitrile group, which indicates the absence of the initial phthalonitrile as an impurity. Absorption bands characteristic of compounds of the phthalocyanine series are observed.[16] In addition, there are bands in the region of 1244-1246 cm^{-1} (C-O-C) and the region of 1080-1084 cm^{-1} (C-Hal).[17-18]

To obtain water-soluble complexes, sulfonation of the above-described phthalocyanines (**4b,c, 5a-c**) was carried out. Chlorosulfonic acid did not lead to expected products; therefore, oleum was used for the sulfonation reactions (Scheme 4).



Scheme 4. Sulfonation of phthalocyanine complexes.

Sulfonation reactions were carried out with 26 % oleum with constant stirring and a temperature of 70 °C for 2 h and 10 h, for complexes **4** and **5**, respectively. At the end of the reaction, the sulfonated mass was poured into a mixture of ice and sodium chloride, the precipitate formed was filtered off, washed with concentrated hydrochloric acid, then dried in the air, the target product was extracted with water, which was then evaporated. The final purification was carried out by column chromatography on silica gel M60. The eluent was DMF. The composition and structure of the obtained compounds were determined using ^{1}H NMR, IR, and electron spectroscopy.

The number and position of sulfonic acid groups in the phthalocyaninatozinc(II) complexes were studied by ^{1}H NMR spectroscopy (Figure 1). The NMR spectra of sulfonic acid complexess (**6b**, **7b**) showed proton signals as triplets at 7.03, 7.13 or 7.23 ppm and 7.13, 7.23 or 7.34 ppm for **7b** and **6b**, respectively. These signals relate to the protons in positions 2, 1 and 3 of the phthalocyanine nuclei. Since only these protons could be detected by ^{1}H NMR, the chlorophenyl rings are completely substituted with sulphonic acid groups, namely two and four sulfonic acid groups were introduced into the compounds **6b** and **7b**, respectively. It is noted that upon the introduction of new sulfonic acid groups into the phthalocyanine molecule, the signals of the ring protons are shifted into a weaker field, which is associated with the effect of the strong electron-acceptor sulfonic acid substituents.

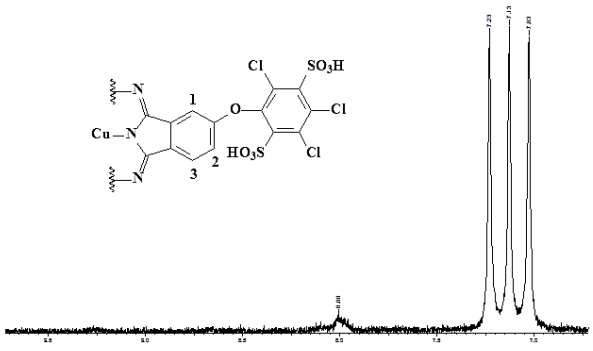


Figure 1. ^{1}H NMR spectrum of tetra(3,6-disulfo-2,4,5-trichlorophenoxy)phthalocyaninatocopper(II) (**7b**)

In the FT-IR spectra of the obtained sulphonated phthalocyanine complexes (**6-7**), the bands characteristic of phthalocyanine compounds, as well as of C-O-C and C-Hal bonds could be observed without important changes. In addition, bands appear in the regions 1210-1150 cm^{-1} and 1060-1030 cm^{-1}, characteristic of modes of sulfonic acid groups[19] appeared. It was also noted that FT-IR spectra of sulfonic acids are more diffuse compared to the initial ones, as was previously noted for phthalocyanines sulfonic acids.[20-21]

The solubility in the synthesized phthalocyanines (**4-7**) in organic solvents or aqueous-alkaline solutions allowed us to study their spectral characteristics. So, electronic absorbance spectra of all synthesized complexes are characterized by intense absorption in the wavelength region of 660-680 nm, caused by the π-π* electronic transition in the main conjugation circuit of the phthalocyanine ring. The position of the absorption bands is shown in Table 1.

Table 1. The position of the UV-VIS absorption bands of synthesized phthalocyanines.

No.	M	λ_{max}, nm			
		$CHCl_3$	DMF	H_2SO_4	H_2O
4a	Co	670	665	838	-
4b	Cu	681	676	860	-
4c	Zn	681	680	851	-
5a	Co	667	662	815	-
5b	Cu	678	621,	838	-
5c	Zn	677	678	831	-
6a	Cu	-	695	779	641, 682
6b	Zn	-	708	810	658, 698
7a	Co	-	685	759	673
7b	Cu	-	711	785	676
7c	Zn	-	714	792,81	718

Analyzing the effect of the nature of the substituent for complexes (**4-5**) soluble in organic solvents on the position of the Q-band, it was noted that the presence of additional chlorine atoms (**5a-c**) in the substituent leads to the hypsochromic shift of the main band compared to monochloro-substituted complexes (**4a-b**) (Table 1). The nature of the solvent also has an influence on the shape of the spectra for all complexes except zinc. Thus, a change in polar aprotic DMF to weakly polar aprotic chloroform leads to a bathochromic shift of the Q-band (Table 1).

It was noted that the position of the Q-band of cobalt complexes (**4a-7a**) both in chloroform and in DMF is shifted relative to the corresponding copper and zinc phthalocyanines (Table 1).

In the transition from organic solvents to concentrated sulfuric acid, a strong shift of the absorption bands to the long-wavelength region is observed due to protonation of the macro ring by the meso nitrogen atoms, the smallest shift observed for metal(II) tetra(2,4,5-trichlorophenoxy)-phthalocyaninates (Table 1). Depending on the nature of the metal, the position of the main band of the synthesized phthalocyanine complexes in concd. H_2SO_4 has a bathochromic shift in the following order Co < Zn < Cu (Figure 2, Table 1).

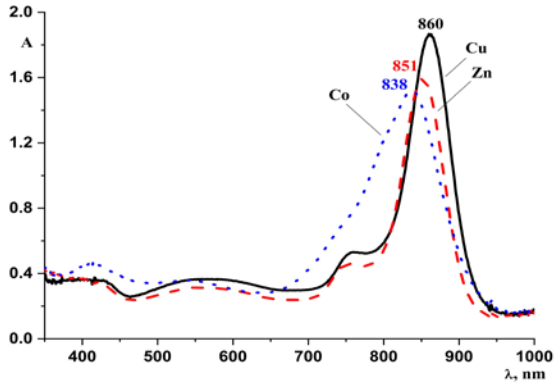


Figure 2. Electronic absorption spectra phthalocyanines **4a-c** in sulfuric acid.

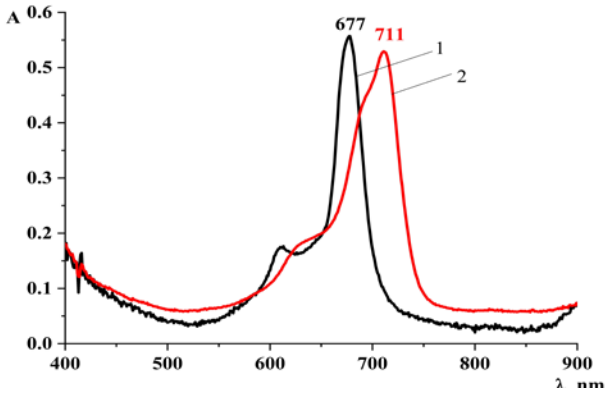


Figure 3. UV-vis spectra in DMF: 1 - copper phthalocyanine (**5b**), 2 – copper phthalocyanine (**7b**) complexes

The introduction of sulfonic acid groups into the molecules leads to a change in the spectra compared to the spectra of initial phthalocyanine derivatives. Thus, in DMF, the spectral curves become more diffuse, which indicates an increase in the tendency to the association in solutions (Figure 3). A bathochromic shift of the Q absorption band in DMF with respect to the corresponding non-sulfonated phthalocyanines was also noted (Table 1), with the most significant shift recorded for tetra(3,6-disulfo-2,4,5-trichlorophenoxy)phthalocyanines (Figure 3, Table 1).

The nature of metal in sulfonic acid derivatives has a strong influence on the absorption spectra in DMF. The bathochromic shift of absorption bands is observed in the following order: Co < Cu < Zn (Figure 4, Table 1). Thus, the presence of sulfonic acid groups in the substituents leads to an increase in the influence of the nature of the metal on the position of the Q-band.

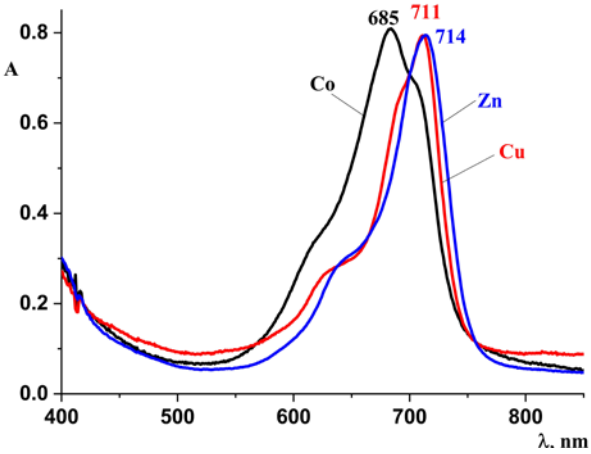


Figure 4. Electronic absorption spectra of tetra(3,6-disulfo-2,4,5-trichlorophenoxy)phthalocyanines (**7**) in DMF.

The spectral curves obtained for these complexes change on the transition from DMF to water. The absorption bands become more diffuse, and the hypsochromic shift is noted relative to those recorded in DMF, which indicates an increase in the tendency to associative processes. It was shown that the presence of three chlorine atoms in the compounds **7** prevents the association compared with mono-halogenated derivatives **6** (Figure 5).

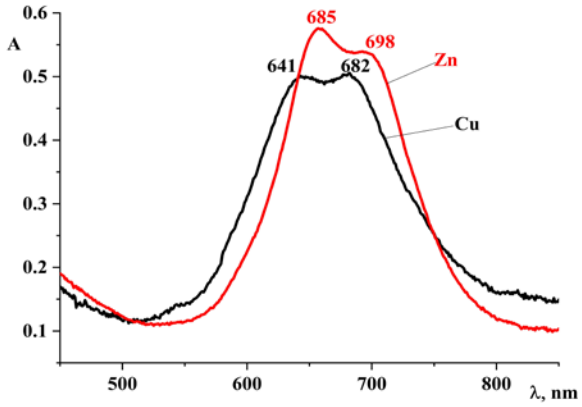


Figure 5. UV-VIS of tetra(2,3,5,6-tetrasulfo-4-chlorophenoxy)phthalocyanine complexes (**6**) in DMF.

It is important to note that cobalt complexes are the least prone to the association, which is due to the higher coordinating ability of cobalt (Figure 6). Cobalt phthalocyanine complexes in aprotic solvents form complexes with the solvent molecules as ligands, and intermolecular interactions[22] also complicate the spectral characteristics.

Change DMF and water to concentrated sulfuric acid, both the phthalocyanine sulfonic acid derivatives (**6-7**) and the non-sulfonated phthalocyanine complexes (**4-5**), show a bathochromic shift for all absorption bands. These are smaller in the case of **6** and **7** compounds than the values for the appropriate initial phthalocyanines (**4-5**) (Table 1).

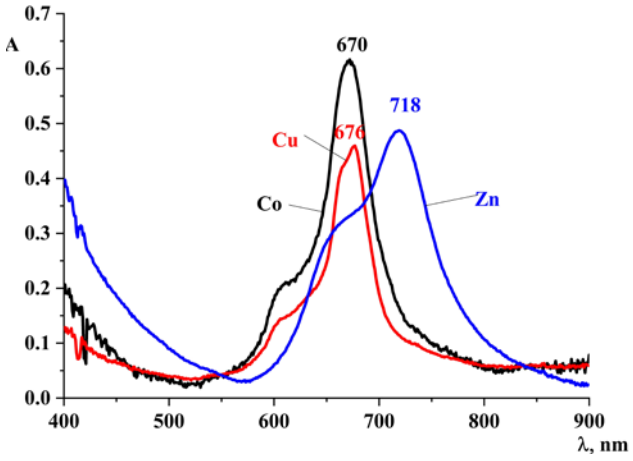


Figure 6. Electronic absorption spectra of tetra(3,6-disulfo-2,4,5-trichlorophenoxy)phthalocyanines (**7**) in water.

It can be observed due to steric difficulties associated with bulky substituents and, as a consequence, a decrease in the degree of protonation nitrogen meso-atoms of the macroring (Figure 7).

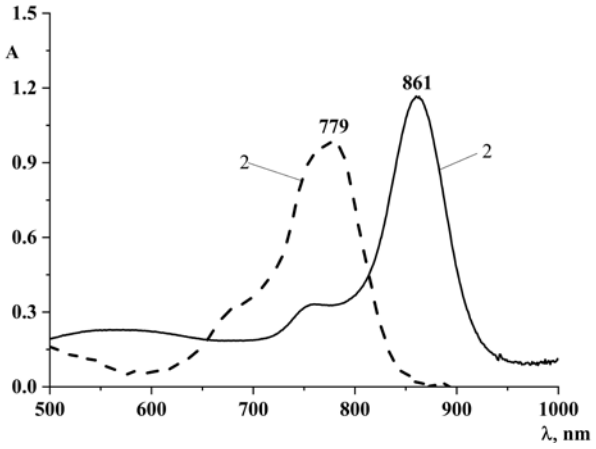


Figure 7. UV-VIS spectra **4b** (1) and **6b** (2) complexes in concentrated sulfuric acid

The nature of the metal also influences the position of the Q-band in concentrated sulfuric acid. It was noted that, as in DMF, a bathochromic displacement is observed in the following order: Co < Cu < Zn (Table 1).

As it is well known,[23-24] cobalt complexes of phthalocyanines are widely used as catalysts for oxidation of mercaptans and hydrogen sulfide in petrochemical processes. These catalysts allow the oxidation process to be carried out under mild conditions, which prevents further oxidation of the disulfide and leads to a significant increase in the quality of the product.

In this regard, the catalytic activity of tetra(2,4,5-trichloro-3,6-disulfophenoxy)phthalocyaninatocobalt(II) (**7a**) was studied in the oxidation of sodium N,N-diethyldithiocarbamate to Thiuram E (Scheme 4). Thiuram E is a crucial component for obtaining drugs for the treatment of chronic alcoholism.[25-26] It was shown that tetra(2,4,5-trichloro-3,6-disulfophenoxy)cobalt(II) (**7a**) is an active catalyst, the oxidation rate constant of sodium diethyldithiocarbamate at a catalyst $6 \cdot 10^{-5}$ mol L^{-1} and substrate 0.00203 mol·L^{-1} concentration at pH = 7.6 was found to be $41.97 \cdot 10^{-3}$ L·mol^{-1}·s^{-1}.

CONCLUSIONS

Complexes of substituted phthalocyanines with cobalt, zinc, and copper-containing 4-chlorophenoxy and 2,3,5-trichlorophenoxy-substituents, as well as their completely sulfonated analogs were prepared. The structure of the synthesized compounds was confirmed by IR and NMR spectroscopy and mass spectrometric methods.

UV-VIS spectra of the synthesized complexes were studied in various solvents, the positions of the absorption maxima depending on the nature of the solvent were determined. The conditions for the existence of complexes in aggregated and monomeric forms were also determined.

A study on the catalytic properties of the tetra(2,4,5-trichloro-3,6-disulfophenoxy)cobalt(II) was carried out in the oxidation of sodium diethyldiethiocarbamate into Thiuram E.

ACKNOWLEDGEMENT

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REFERENCES

[1]Vashurin, A. S., Non-covalent associates of metal phthalocyanines: the role of axial ligand and catalytic activity, *Russ. Chem. Bull*., **2016**, *65*, 2220. https://doi.org/10.1007/s11172-016-1572-z.

[2]Birnbaum, T., Hahn, T., Martin, C., Kortus, J., Fronk, M., Lungwitz, F., Zahn, D. R. T., Optical and magneto-optical properties of metal phthalocyanine and metal porphyrin thin films, *J. Phys. Condens. Matter* **2014**, *26*, 104201. https://doi.org/10.1088/0953-8984/26/10/104201.

[3]Vashurin, A., Maizlish, V., Tikhomirova, T., Nemtseva, M., Znoyko, S., Aleksandriiskii, V., Novel non-symmetrical bifunctionally-substituted phthalonitriles and corresponding *d*-metal phthalocyaninates, *J. Mol. Struc.*, **2018**, *1160*, 440-446. https://doi.org/10.1016/j.molstruc.2018.02.040.

[4]Zhang, R., Xu, B., Wang, J., Zhao, J., Binuclear transition metal phthalocyanines with superior performance as electrocatalysts for lithium/thionyl chloride battery, *J. Mater. Res.*, **2014**, *29*, 793–800. https://doi.org/10.1557/jmr.2014.48.

[5]Filippova, A., Vashurin, A., Znoyko, S., Kuzmin, I., Razumov, M., Chernova, A., Shaposhnikov, G., Koifman, O., Novel Co(II) phthalocyanines of extended periphery and their water-soluble derivatives. Synthesis, spectral properties and catalytic activity, *J. Mol. Struc.*, **2017**, *1149*, 17-26. https://doi.org/10.1016/j.molstruc.2017.07.086.

[6]Vashurin A., Kuzmin, I., Mayzlish, V., Razumov, M., Golubchikov, M., Golubchikov, O., Koifman, O., Kinetics and mechanism of the oxidation of dithiocarbamic acids in the presence of Co(II) phthalocyaninetetacarboxylic acid, *J. Serb. Chem. Soc.*, **2016**, *81(9)*, 1025-1036. https://doi.org/10.2298/JSC160105048V.

[7]Kirbac, E., Atmaca, G. Y., Erdogmus, A., Novel highly soluble fluoro, chloro, bromo-phenoxy-phenoxy substituted zinc phthalocyanines; synthesis, characterization and photophysicochemical properties, *J. Organomet. Chem.*, **2014**, *752*, 115-122. https://doi.org/10.1016/j.jorganchem.2013.12.005.

[8]Yılmaz, Y., Mack, J., Şener, M. K., Sonmez, M., Nyokong, T., Synthesis, photophysicochemical properties and TD-DFT calculations of tetrakis(2-benzoyl-4-chlorophenoxy) phthalocyanines, *J. Porph. Phthal.*, **2014**, *18*, 326-335. https://doi.org/10.1142/S1088424614500047.

[9]Xu, H. T., Xie, W. W., Guo, Y. C., Ci, Y., Chen, L. J., Peng, B. X., The Synthesis of Tetra - α - Phenoxyphthalocyanines and Research of their Physical and Chemical Properties, *J. Chin. Chem. Soc.*, **2007**, *54*, 211-217. https://doi.org/10.1002/jccs.200700031.

[10]Burat, A. K., Bayir, Z. A., Koca, A., Synthesis and Electrochemical and In Situ Spectroelectrochemical Characterization of Chloroindium(III) and Chloromanganese(III) Phthalocyanines Bearing 4 - ((4′ - Trifluoromethyl)phenoxy)phenoxy Substituents, *Electroanalysis*, **2012**, *24(2)*, p. 338–348. https://doi.org/10.1002/elan.201100388.

[11]Basova, T. V., Hassan, A., Krasnov, P. O., Gurol, I., Ahsen, V., Trimethylamine sorption into thin layers of fluoroalkyloxy and alkyloxy substituted phthalocyanines: Optical detection and DFT calculations, *Sensors and Actuators B: Chemical*, **2015**, *216*, 204-211. https://doi.org/10.1016/j.snb.2015.04.032.

[12]Basova, T. V., Mikhaleva, N. S., Hassan, A. K., Kiselev, V. G., Thin films of fluorinated 3d-metal phthalocyanines as chemical sensors of ammonia: an optical spectroscopy study, *Sensors and Actuators B: Chemical*, **2016**, *227*, 634-642. https://doi.org/10.1016/j.snb.2015.12.079.

[13]Vashurin, A., Pukhovskaya, S., Semeikin, A., Golubchikov, O., Catalytic Properties of Cobalt meso-Tetrakis(4-methylpyridiniumyl)-porphyrin Tetratosylate in the Oxidation of Sodium Diethyldithiocarbamate, *Macroheterocycles*, **2012**, *5*, 72. https://doi.org/10.6060/mhc2012.111251v.

[14]Nemykin, V. N., Polshyna, A. E., Borisenkova, S. A., Strelko, V. V., Preparation, characterization, and catalytic activity of synthetic carbon-supported (phthalocyaninato)cobalt-containing complexes in dodecane-1-thiol oxidation reaction, *J. Mol. Catal. A: Chem.*, **2007**, *264*, 103. https://doi.org/10.1016/j.molcata.2006.08.093.

[15]*Panorama sovremennoi khimii Rossii. Uspekhi v neftekhimicheskom sinteze polifunktsionalnikh soedinenii*, *Moscow: Chemistry*, **2005**, 328.

[16]Arslanoglu, Y., Sevim, A. M., Hamuryudan, E., Gul, A., Near-IR absorbing phthalocyanines, *Dyes Pigm.*, **2006**, *68*, 129. https://doi.org/10.1016/j.dyepig.2005.01.019.

[17]Wei, J., Li, X., Xiao, C., Lu, F., IR absorption spectroscopic characteristics of peripherally substituted thiophenyl phthalocyanine in sandwich bis(phthalocyaninato) complexes, *Vibrat. Spectr.*, **2017**, *92*, 105. https://doi.org/10.1016/j.vibspec.2017.06.002.

[18]Kuzmina, E. A., Dubinina, T. V., Zasedatelev, A. V., Baranikov, A. V., Makedonskaya S. A., Egorova, T. B., Tomilova, L. G., Hexadecachloro-substituted lanthanide(III) phthalocyaninates and their hybrid conjugates with gold nanoparticles: Synthesis and optical properties, *Polyhedron*, **2017**, *135*, 41-48. https://doi.org/10.1016/j.poly.2017.06.048.

[19]Goldshleger, N. F., Lobach, A. S., Dremova, N. N., Lapshina, M. A., Kolesnikova, A. M., Baulin, V. E., Tsivadze, A. Yu., Crown- and Sulfophthalocyanines in Low-Molecular-Weight Hydrogels: Properties, Molecular State, and Release, *Macroheterocycles*, **2017**, *10(4-5)*, 531-539. https://doi.org/10.6060/mhc170830g.

[20]Tikhomirova, T. V., Badaukaite, R.A., Kulinich, V. P., Shaposhnikov, G. P., Phthalocyanines with peripheral azo chromophores, *Russ. J. Gen. Chem.*, **2011**, *81*(*11*), 1904-1909. https://doi.org/10.1134/S1070363215100205.

[21]Kulinich, V. P., Shaposhnikov, G. P., Badaukaite, R. A., Sulfonaphthyloxysubstituted Phthalonitriles and Phthalocyanines on their Basis, *Macroheterocycles*. **2010**, *3(1)*, 23-29. 10.6060/mhc2010.1.23.

[22]Shaposhnikov, G. P., Maizlish, V. E., Kulinich, V. P., 1,3-Dihydroxynaphthalene in the Synthesis of Phosphorus-containing Macroheterocycles, *J. Gen. Chem.*, **2005**, *75(11)*, 1916-1924. https://doi.org/10.1007/s11176-006-0013-3.

[23]Tyapochkin, E. M., Kozliak, E. I., Kinetic and binding studies of the thiolate–cobalt tetrasulfophthalocyanine anaerobic reaction as a subset of the Merox process, *J. Mol. Catal. A: Chem.*, **2005**, *242*, 1-17. https://doi.org/10.1016/j.molcata.2005.07.008.

[24]Vashurin, A. S., Filippova, A. A., Znoyko, S. A., Voronina, A. A., Lefedova, O. V. Kuzmin, I. A., Maizlish, V. E., Koifman, O. I., New water-soluble sulfonated cobalt(II) phthalocyanines: Synthesis, spectral, coordination and catalytic properties, *J. Porph. Phthal.*, **2015**, *19(08)*, 983. DOI: 10.1142/S1088424615500753

[25]Gessner, P. K., Gessner, T., *Disulfiram and its Metabolite, Diethyldithiocarbamate*, Springer Netherlands, Amsterdam, **1992**, 452.

[26]Victoriano, L. I., The reactivity of metal species towards thiuram sulfides: an alternative route to the syntheses of metal dithiocarbamates, *Coord. Chem. Rev.*, **2000**, *196*, 383. https://doi.org/10.1016/S0010-8545(99)00221-0.

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