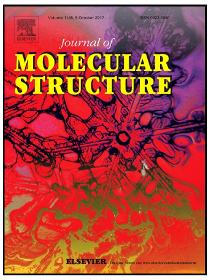

Novel Co(II) phthalocyanines of extended periphery and their water-soluble derivatives. Synthesis, spectral properties and catalytic activity

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Novel Co(II) phthalocyanines of extended periphery and their water-soluble derivatives. Synthesis, spectral properties and catalytic activity

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Key words cobalt phthalocyaninate, synthesis, substituent's, solution, aggregation, catalyst

Novel complexes of cobalt and copper with substituted phthalocyanines were synthesized and characterized. Their water-soluble derivatives were obtained by sulfonation under mild conditions and structurally proved. Aggregation equilibrium in water mediums was shown and influence of geometrical and electron parameters of macroheterocycle peripheral substituents on these processes was established. Catalytic activity upon liquid-phase oxidation of N,N-diethylcarbamodithiolate to thiuram E was studied. Kinetic parameters of substrate oxidation in presence of cobalt phthalocyanines were considered.

1. Introduction

Metal phthalocyanines exhibit prospective chemical and photophysical properties as individual compounds and parts of composites or hybrid materials [1-3], high catalytic activity upon redox processes [4-6]. Oxidation of mercaptans [7-9] and olefins [10-11] are of special attention. One more prospective direction of metal phthalocyanines application is sensorics [12-13]. Development of phthalocyanine macrocycle structure via introduction of substituents into peripheral and non-peripheral positions allows reaching of fine tuning their physical and chemical properties.

The important property of phthalocyanine compounds is their solubility determining many fields of their application. Not substituted phthalocyanines have almost no solubility in common organic solvents. Introduction of substituents into peripheral and non-peripheral positions of phthalocyanine macrocycle forms additional solvation centers and impart the solubility [14-16]. Obtainment of phthalocyanines soluble in water mediums is important from the point of green chemistry processes and technology. Introduction of sulfo- or carbon acid fragments into annulated benzene rings of phthalocyanine macrocycle provides phthalocyanines soluble in water mediums obtainment. Here the question of regulation and sometimes suppression of metallophthalocyanines self-aggregation appears. Combination of various functional groups as parts of phthalocyanine macrocycle is a key to physical and chemical of phthalocyanine compounds [15].

Synthesis of cobalt and copper complexes of bifunctionally- and symmetrically substituted phthalocyanines and their analogues is presented in the work. Catalytic activity upon liquid-phase oxidation of sodium N,N-diethylcarbamodithiolate under mild conditions is studied for water-soluble cobalt complexes in order to find out interrelationship between terminal fragment structure of phthalocyanines and their catalytic activity.

2. Experimental

2.1. Reagents

Solvents used in the work N,N-dimethylformamide (DMF), 2-propanol, acetone, chloroform were purified and stored in accordance to recommendations [17]. Inorganic salts applied for synthesis were previously recrystallized by methods recommended in [18]. Deuterated solvents, 4-(1-methyl-1-phenylethyl)phenole and 4-bromine-5-nitrophthalonitrile were purchased from Aldrich. Sodium N,N-diethylcarbamodithioate (DTC) (99%, ChemMed Synthesis, Russia) was used without additional purification.

2.2. Equipment

Elemental analysis has been carried out by means of chromatographic analyzer Flash HCNS-OEA 1112 (Germany). The flow rates of helium and oxygen were 140 mL/min and 250 mL/min, respectively; the temperature of the reactor was 1173 K, oxygen was supplied into the reactor for 250 mL/min with 12 sec time delay.

FT-IR spectra were recorded using IR-Fourier spectrophotometer Avatar 360 (USA) in 400- 4000 cm^{-1} frequency range.

NMR spectra of the solutions were recorded by means of NMR spectrometer Bruker AVANCE-500 (Germany) at operating frequency 500 MHz (^{1}H) and 100 MHz (^{13}C). Measurements were performed under the Fourier transformation conditions in 5 mm cells at various temperatures. Chemical shifts were measured with reference to the internal standard – tetramethylsilane. The accuracy of measurements was ± 0.005 ppm.

Electron absorption spectra (UV-vis) were registered by means of Unico 2800 (USA) spectrophotometer in a spectral range of 200 – 1000 nm. Quarts optical cell were used for the measurements. UV-vis spectra were recorded at 298.15 ± 0.03 K.

Mass spectra were measured on an Axima MALDI-TOF mass-spectrometer (Shimadzu, Japan).

2.3. Synthesis

2.3.1. 4-[4-(1-methyl-1-phenylethyl)phenoxy]-5-nitrophthalonitrile (**2**):

2.52 g (1 mmol) of 4-bromine-5-nitrophthalonitrile (**1**) and 2.12 g (1 mmol) of 4-(1-methyl-1-phenylethyl)phenol were dissolved in 30 mL of DMF. Solution of 1.19 g (1 mmol) of K_2CO_3 in 5 mL of water was added to the mixture, next it was stirred under 25 ºC for 30 minutes. Precipitate obtained was filtered off by means of paper filter, washed with 2-propanol, then with water till absence of 2-propanol and dried on air under 70-80 ºC. Yield is 3.15 g (91%). Elemental analysis (%): calcd. for $C_{23}H_{17}N_3O_3$ C 72.05; H 4.47; N 10.96 found C 71.95; H 5.00; N 10.74. MALDI-TOF *m/z*: calcd. 383.41 found 383.22 $[M]^+$. IR (KBr) (ν, cm^{-1}): 2922 and 2850 ($-CH_3$); 2237 (-CN); 1527 (as. $-NO_2$); 1341 (s. $-NO_2$); 1210 (Ar-O-Ar). ^1H NMR (500 MHz, $CDCl_3$) (δ, ppm) 8.33 (s, H1, 1H); 7.87 (d, H2, 1H); 7.05 (m, H3,4, 4H); 7.12 (m, H5-7, 5H); 1.76 (s, CH_3, 6H).

2.3.2. 4,5-di[4-(1-methyl-1-phenylethyl)phenoxy]phthalonitrile (**3**).

2.52 g (1 mmol) of 4-bromine-5-nitrophthalonitrile (**1**) and 4.24 g (2 mmol) of 4-(1-methyl-1-phenylethyl)phenol were dissolved in 70 mL of DMF. Solution of 2.76 g (2 mmol) of K_2CO_3 in 10 mL of water was added to the mixture, next it was stirred under 80-90 ºC for 8 hours. Yield is 2.40 g (44 %) *m.p.* = 123-125 °C. Elemental analysis (%): calcd. for $C_{38}H_{32}N_2O_2$ C 83.19; H 5.88; N 4.96 found C 82.95; H 6.02; N 5.11. MALDI-TOF *m/z*: calcd. 548.68 found 549.19 $[M+H]^+$ (34.95%); 588.13 $[M+K]^+$ (83.23%). IR (KBr) (ν, cm^{-1}): 2967, 2929 and 2869 (CH_3); 2231 (CN); 1589 (γ C-C); 1318 and 1162 (δ C_{Ar}-H); 1211 (Ar-O-Ar). ^1H

NMR (500 MHz, $CDCl_3$), (δ, ppm): 7.33 (s, H1, 2H); 7.01-7.03 (m, H2, 4H); 6.96-6.98 (m, H3, 4H); 7.09-7.17 (m, H4-6, 10H); 2.19 (s, CH_3, 12H).

*2.3.3. tetra-4-[4-(1-methyl-1-phenylethyl)phenoxy]tetra-5-nitrophthalocianinates of cobalt and copper (**1a, 1b**).*

Thoroughly grounded mixture of 0.38 g (0.1 mmol) of 4-[4-(1-methyl-1-phenylethyl)phenoxy]-5-nitrophthalonitirle (**2**), 0.05 g (0.8 mmol) of urea and 0.57 g (0.2 mmol) of $CoCl_2 \times 6H_2O$ was heated under 200 ºC for 2 hours. Reaction mixture after process is finished was washed with diluted hydrochloric acid to remove urea destruction products, then with water till absence of reaction on chloride-anions with silver nitrate, next it was dried on air under 70-80 ºC, dissolved in chloroform and exposed column chromatography on aluminum oxide eluting with chloroform. Obtained solid of dark-green color insoluble in water is well soluble in chloroform and DMF. Copper complexes were obtained by similar method using copper chloride.

1a: Yield is 0.33 g. (92 %). Elemental analysis (%): calcd. for $C_{92}H_{68}CoN_{12}O_{12}$ C 69.39; H 4.30; N 10.55 found C 69.21; H 4.11; N 10.42. MALDI -TOF *m/z*: calcd. 1591.44 found 1591.89 $[M]^+$. IR (KBr) (ν, cm^{-1}): 2953, 2935 and 2850 (CH_3); 1538 (as NO_2); 1352 (s NO_2); 1242 (Ar-O-Ar).

1b: Yield is 0.35 g. (87 %). Elemental analysis (%): calcd. for $C_{92}H_{68}CuN_{12}O_{12}$ C 69.19; H 4.29; N 10.52 found C 69.00; H 4.56; N 10.20. MALDI-TOF *m/z*: calcd. 1597.17 found 1597.82 $[M]^+$. IR (KBr) (ν, cm^{-1}): 2964, 2923 and 2850 (CH_3); 1538 (as NO_2); 1346 (s NO_2); 1209 (Ar-O-Ar).^{1}H NMR (500 MHz, $CDCl_3$), (δ, ppm): 8.33 (s, H1, 4H); 7.43 (m, H2, 4H); 7.17 (m, H5, 6, 7, 24H); 7.05 (m, H3, 4, 16H); 1.75 (s, CH_3, 24H).

octa-4,5-[4-(1-methyl-1-phenylethyl)phenoxy]phthalocyaninate of cobalt and copper (**2a**, **2b**).

Thoroughly grounded mixture of 55 mg (0.1 mmol) of the compound (**5**), 50 mg (0.8 mmol) of urea and 23.8 mg (0.1 mmol) of $CoCl_2 \times 6H_2O$ was heated under

155-160 ºC for 1.5 hours. Reaction mixture after process is finished was dissolved in chloroform and exposed column chromatography on aluminum oxide eluting with chloroform. Obtained solid of dark-green color insoluble in water is well soluble in chloroform, acetone and DMF. Copper complexes were obtained by similar method using copper chloride.

2a: Yield is 42.5 mg (78%). Elemental analysis (%): calcd. for $C_{152}H_{128}CoN_8O_8$ C 81.01; H 5.72; N 4.97 found C 80.82; H 6.00; N 4.82. MALDI-TOF *m/z*: calcd. 2251.13 found 2252.63 $[M+H]^+$. IR (KBr) (*ν,* cm^{-1}): 2954, 2923 and 2862 (CH_3); 1561 (γ C-C); 1328 and 1125 (δ C_{Ar}-H); 1213 (Ar-O-Ar).

2b: Yield is 43.8 mg (80%). Elemental analysis (%): calcd. for $C_{152}H_{128}CuN_8O_8$ C 80.84; H 5.71; N 4.96 found C 80.22; H 5.95; N 4.90. MALDI-TOF *m/z*: calcd. 2255.91 found 2257.57 $[M+2H]^+$. IR (KBr) (*ν,* cm^{-1}): 2966, 2929 and 2872 (CH_3); 1602 (γ C-C); 1272 and 1137 (δ C_{Ar-H}); 1207 (Ar-O-Ar). ^1H NMR (500 MHz, $CDCl_3$), (*δ*, ppm): 7.33 (s, H1, 8H); 7.01-7.03 (m, H2, 16H); 6.96-6.98 (m, H3, 16H); 7.07-7.22 (m, H4-6, 40H); 2.17 (s, C-H_3, 48H).

2.3.4. tetra-4-{4-[1-methyl-1-(4-sulfophenyl)ethyl]phenoxy}tetra-5-nitrophthalocyaninate of cobalt (**1c**).

Tetra-5-[4-(1-methyl-1-phenylethyl)phenoxy]tetra-4-nitrophthalocyanine of cobalt (**1a**) (160 mg, 0.01 mmol) was combined with mixture of 2 mL (18 mmol) of chlorsulfonic acid and 2 mL (18 mmol) of thionilchloride under room temperature for 2 hours [19]. The reaction mixture was poured onto ice treated with sodium chloride after the stirring is finished. Formed precipitate was collected by means of Shotts filter, dried in exicator over sulfuric acid for 3 days. Obtained sulfochloride was extracted with acetone, the solvent was distilled off. The mixture next was boiled with water till entire dissolving. The solvent then was distilled off. Final purification was performed via column chromatography: eluent – DMF, sorbent – silica gel M 60. Obtained products are solid compounds of dark-green color soluble in water, ammonia solution water-alkali solutions, DMF. Yield is 137 mg (72%). Elemental analysis (%): calcd. for $C_{92}H_{68}CoN_{12}O_{24}S_4$ C 57.77; N 8.79;

H 3.58; S 6.70 found C 57.71; N 8.56; H 3.96; S 6.38. IR (KBr) (*v,* cm^{-1}): 2919, 2852 (CH_3); 1504 (as NO_2); 1340 (as NO_2); 1174 (S=O); 1020 (C-S).

2.3.5. octa-4,5-{4-[1-methyl-1-(4-sulfophenyl)ethyl]phenoxy}-phthalocyanine (**2c**)

Into double-necked flask 2 mL of thionylchloride and 2 mL of chlorsulfonic acid were loaded, then 226 mg (0.01 mmol) of cobalt octa-4,5-[4-(1-methyl-1-phenylethyl)phenoxy]phthalocyaninate (**2a**) was added. The mixture was stirred under 20-25 °C for 2 hours. The reaction mixture was poured onto ice treated with sodium chloride after the stirring is finished. Formed precipitate was collected by means of Shotts filter, dried in exicator over sulfuric acid for 3 days till complete drying and absence of thionylchloride odor. Desired compound was extracted with acetone. The extract was filtered off by means of paper filter, moved to porcelain beaker and solvent was removed. Aqueous DMF (75-80%) was added to obtained solution, solvent was distilled off on water bath without boiling. The mixture after process finish was dissolved in DMF and exposed to column chromatography on silica gel M60 eluting with DMF. Yield is 273 mg (94%). Elemental analysis (%): calcd. for $C_{152}H_{128}CoN_8O_{32}S_8$ C 63.08; H 4.46; N 3.87 found C 62.72; H 4.82; N 3.56. MALDI-TOF *m/z*: calcd. 2891.57 found 2891.84 $[M]^+$. IR (KBr) (*v,* cm^{-1}): 2921 (CH_3); 1238 (Ar-O-Ar); 1122 (S=O); 1039 (C-S).

2.4. Spectral studies

Spectral researches were carried out for isomolar series of solutions. Calculation of stability constant for molecular complex of metal phthalocyanine with DMF formation was carried out based on changes of absorption density of solution in range of Q-band. Equilibrium concentration of molecular complex was calculated as:

$$c_{CoPc\cdot DMF} = c^0_{CoPc} \cdot \frac{\left(A_0 - A_c\right)}{\left(A_0 - A_\infty\right)} \qquad (1)$$

where $c_{\mathrm{CoPc \cdot DMF}}$ – equilibrium concentration of molecular complex, c^0_{CoPc} – initial concentration of macrocycle. A_0, A_c and A_∞ – initial, equilibrium and final values of solution’s optical density of Q-band respectively.

Concentration of free ligand was determined according to equation:

$$c_{DMF} = c^0_{DMF} - c^0_{CoPc} \cdot \frac{\left(A_0 - A_c\right)}{\left(A_0 - A_\infty\right)} \tag{2}$$

Taking into account equations 1 and 2 the formula for calculation of stability constant will be:

$$K_s = \frac{\left[\left(A_0 - A_c\right)/\left(A_c - A_\infty\right)\right]}{\left[c^0_{DMF} - c^0_{CoPc} \cdot \left(A_0 - A_c\right)/\left(A_0 - A_\infty\right)\right]} \tag{3}$$

The investigation was carried out with excess of ligand relative to the metallophthalocyanine. That is why equilibrium concentration of DMF is considered to be equal to its initial concentration. It simplified the process of calculating of K_s:

$$K_s = \frac{A_0 - A_c}{(A_0 - A_\infty)c^0_{\mathrm{DMF}}} \tag{4}$$

To estimate the number of units of forming sandwich associates the semi-log method of Bent-French by value of the slope of plots was applied:

$$\lg\left(\frac{A_0 - A_c}{A_c - A_\infty}\right) = f(\lg c_L) \tag{5}$$

where c_L – equilibrium concentration of axial ligand, A_0, A_c и A_∞ – initial, equilibrium and final values of solution’s optical density respectively.

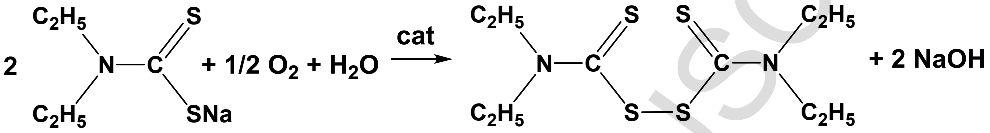
Dimerization constants were calculated based on spectral data according to known method [20]. Equation (6) was used.

$$K_{\mathrm{dim}} = \frac{\left(\varepsilon_M - \varepsilon_D\right)^2}{2\left(\varepsilon_i - \varepsilon_D\right)^2 c^i_{CoPc}} \tag{6}$$

here ε_M – CoPc monomer extinction, ε_D – CoPc dimer extinction, ε_i – extinction of investigated CoPc solution, c^i – current concentration of CoPc.

2.5. Studies of catalytic activity

The catalytic activity of metallophthalocyanines was tested with a known [21-22] reaction of sodium N,N-diethylcarbamodithioate (DTC) oxidation. It proceeds according to general scheme 1.



Scheme 1. Scheme of disulfide formation.

Advantages of this reaction are low toxicity of initial materials and possibility of monitoring of concentration of initial and desired materials and identification of reaction products using electron absorption (UV-vis spectra) and FT-IR spectroscopy methods. Experiments to study the kinetics of DTC oxidation were carried out in thermostatic cell in which the solution of DTC of 650 mL was loaded.

The air needed for oxidation was fed via micro compressor with constant rate of 2 L/min. The reaction takes place in kinetic region under these parameters [23]. After establishing a constant temperature of reaction mixture, it was stirred and sample of 2 mL was taken to determine initial concentration of DTC, then compressor was turned on. This moment was taken as the beginning of the reaction. Samples of 2 mL were taken periodically during the experiment to determine current concentration of DTC. The concentration of DTC was monitored by spectrophotometric method.

Under conditions of constant concentrations of oxygen and catalyst, constant pH of solution the rate of DTC oxidation is described by first order kinetic equation:

$$\frac{\partial c}{\partial t} = -k_{obs} c_{DTC} \tag{7}$$

where k_{obs} – observed constant of the rate, s^{-1}.

It is confirmed by straightness of graphics in coordinates ln$c$ − t and constancy of rate constants calculated according to the equation:

$$k_{obs} = \frac{\ln \frac{c_0}{c}}{t} \tag{8}$$

where c_0 – initial concentration of DTC, c – current (t) concentration of DTC.

The rate constants of (n + 1)-order were calculated using Eq. (9).

$$k_w^{298} = \frac{k_{obs}}{c_{DTC}^{i}} \tag{9}$$

The activation energy ($E^{\neq}$) for the studied temperature range was calculated by the Arrhenius equation in the integrated form:

$$E^{\neq} = 19.1\left(\frac{T_1 T_2}{T_2 - T_1}\right)\lg\frac{k_2}{k_1} \tag{10}$$

where T_1 and T_2—temperatures and k_2 and k_1 - observed rate constants at current temperatures.

Entropy change for the formation of transition state $\Delta S^{\neq}$ was calculated with eq (11):

$$\Delta S^{\neq} = 19.1\ln k_w^{298} + \frac{E^{\neq}}{298} - 253 \tag{11}$$

Degree of transformation was calculated according to eq. (12):

$$\chi = (c_0 - c_\tau)/c_0 \tag{12}$$

where c_0 – initial concentration of DTC, c_τ– current concentration of DTC.

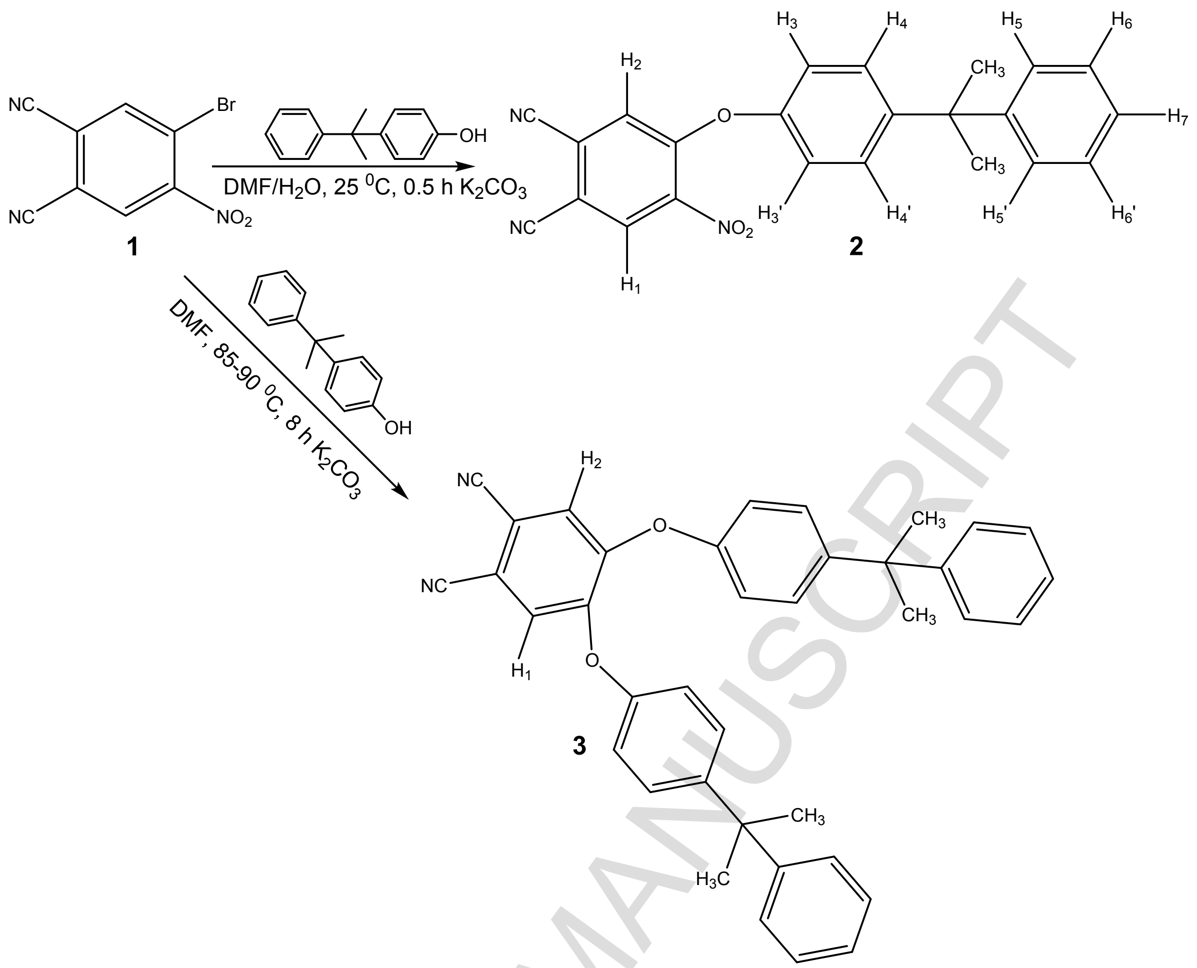
Disulfide formation was monitored with FT-IR spectra, and ^{1}H NMR, and ^{13}C NMR. ^{1}H NMR of DTC oxidation (500 MHz, D_2O), (δ, ppm): 4.32 (m, J = 15 Hz, 4H, CH_2); 1.39 (t, J = 5 Hz, 6H, CH_3).^{13}C NMR of DTC oxidation (100 MHz): 11.65; 27.50; 49.11; 205.02. IR of DTC oxidation IR (KBr), (ν, cm^{-1}) 2979 (as

CH_3); 2847 (as CH_2); 1476 (δ CH_2); 1378 (st C-N); 1269 (st C=S); 1075 (d C-S). During oxidation of DTC the formation of diethylcarbamothioylsulfanyl-N,N-diethylcarbamodithioate (Thiuram E) is observed. ^{1}H NMR of Thiuram E obtained by DTC oxidation (500 MHz, $CDCl_3$), (*δ*, ppm): 3.71-3.77 (m, 8H, CH_2); 1.29-1.23 (m, 12H, CH_3). ^{13}C NMR of Thiuram E obtained by DTC oxidation (100 MHz): 10.49; 25.72; 52.04; 51.26; 190.05. IR of Thiuram E obtained by DTC oxidation IR (KBr): (*v*, cm^{-1}): 2975 (as CH_3); 2861 (as CH_2); 1505 (δ CH_2); 1380 (st C-N); 1273 (st C=S); 1143 and 995 (-S-S-).

3. Results and Discussion

3.1. Nitriles synthesis

Synthesis of 4-[4-(1-methyl-1-phenylethyl)phenoxy]-5-nitrophthalonitrile (**2**) was performed according to scheme 2 using 4-bromine-5-nitrophthalonitrile (**1**) as initial compound. Reaction was carried out in aqueous DMF solution under temperature of 30 °C in presence of deprotonating agent (K_2CO_3).



Scheme 2. Synthesis of nitriles.

Composition and structure of phthalonitrile **2** were indetified using ^{1}H NMR, IR spectroscopy, MALDI-TOF mass-spectrometry and elemental analysis data. IR spectrum of the phthalonitrile has C≡N valent vibrations band on 2234 cm^{-1}, methyl groups of 4-(1-methyl-1-phenylethyl)phenoxygroup on 2950 and 2880 cm^{-1}, NO_2-group symmetrical (1365-1375 cm^{-1}) and asymmetrical (1555-1565 cm^{-1}) vibrations [24]. ^{1}H NMR spectrum of phthalonitrile **2** exhibits signals in strong field region assumed to protons of 4-(1-methyl-1-phenylethyl)phenyl substituent methyl groups on 1.76 ppm. There are signals in weak field region related to protons of phthalonitrile benzene ring and oxyaril substituent. H_1 proton signal places on 8.33 ppm.

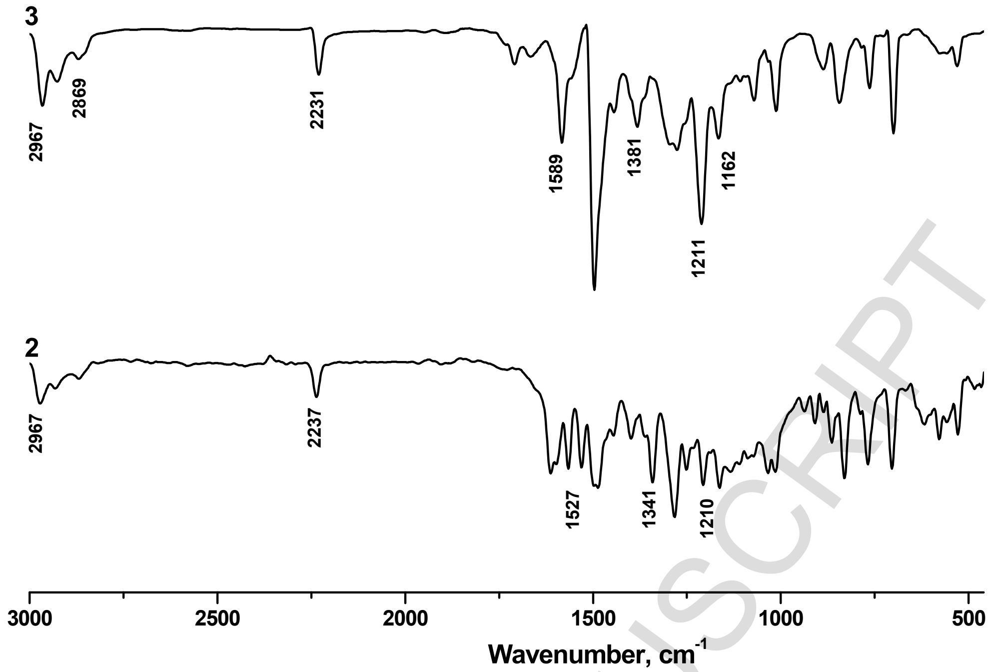


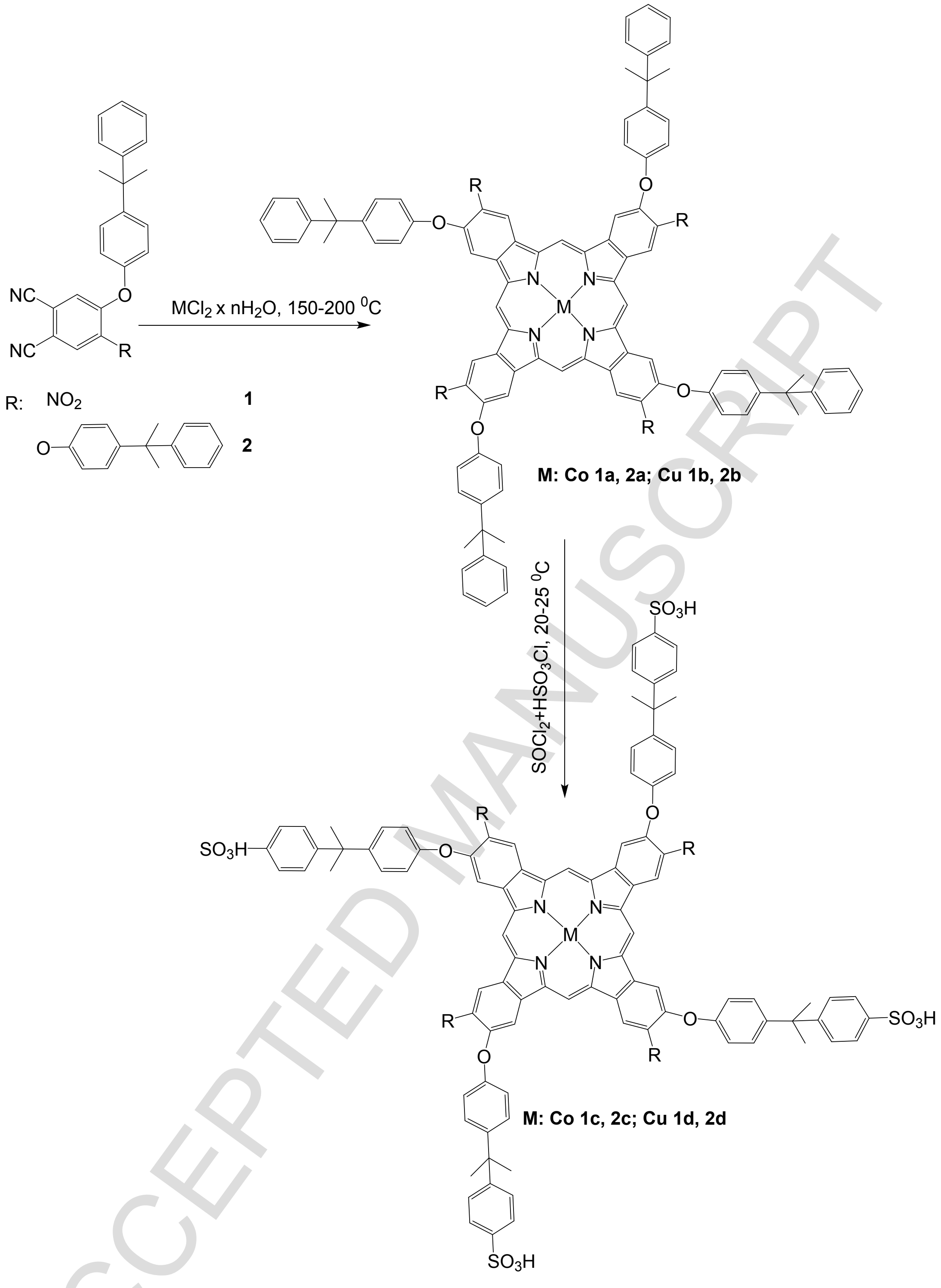
Figure 1. IR spectra of nitriles **2** and **3**.

Symmetrically-substitued phthalonitrile **3** was obtained starting from nitrile **1** under harsher conditions. In opposite to compound **2** obtained under common conditions the **3** requires holding of reaction mixture under 80-90 ºC for 8 hours. As a resulting substance viscous red-brownish liquid containing desired compound is formed. Phthalonitrile **3** was extracted from reaction mixture by means of separation funnel and placed to conical flask of 100 mL volume, then 10 mL of isopropyl alcohol and water mixture (1:1) was added and mixture held for 72 hours. Initially uncolored water-alcohol layer gained intense red-brown color and desired phthalonitrile precipitated. Obtained precipitate was filtered off, washed with 2-propanol till colorless filtrates, then with water to remove 2-propanol and dried in vacuum under 50 ºC.

IR-spectrum of **3** indicated vibrations of nitrile-group on 2233 cm^{-1} and Ar-O-Ar 1217 cm^{-1}. NO_2 – groups vibrations were not registered. There were no separated signals for H_1 and H_2 protons (7.33 ppm) within ^1H NMR spectra that indicates equivalent environment.

3.2. Metallophthalocyanines synthesis

Metal complexes of phthalocyanines were obtained by template synthesis method (Scheme 3) via melting of nitrile **2** or **3** with corresponding metal chloride. Synthesis of symmetrically-substituted cobalt and copper phthalocyaninates (**2a**, **2b**) proceeds under temperatures for 40° lower comparing to synthesis of bifunctional derivatives **1a** and **1b**, melting of which was under 200 °C.



Scheme 3. Synthesis of metallophthalocyanines.

Electron absorption spectra (UV-vis) of compounds **1a**, **1b**, **2a** and **2b** in various solvents are specific for metal phthalocyaninates (Figure 2). Splitting of absorption Q-band designates strong aggregation of these macrocycles due to π-stacking. UV-vis show slight solvatochromic effect (Table 1) caused by change of solvent solvation characteristics.

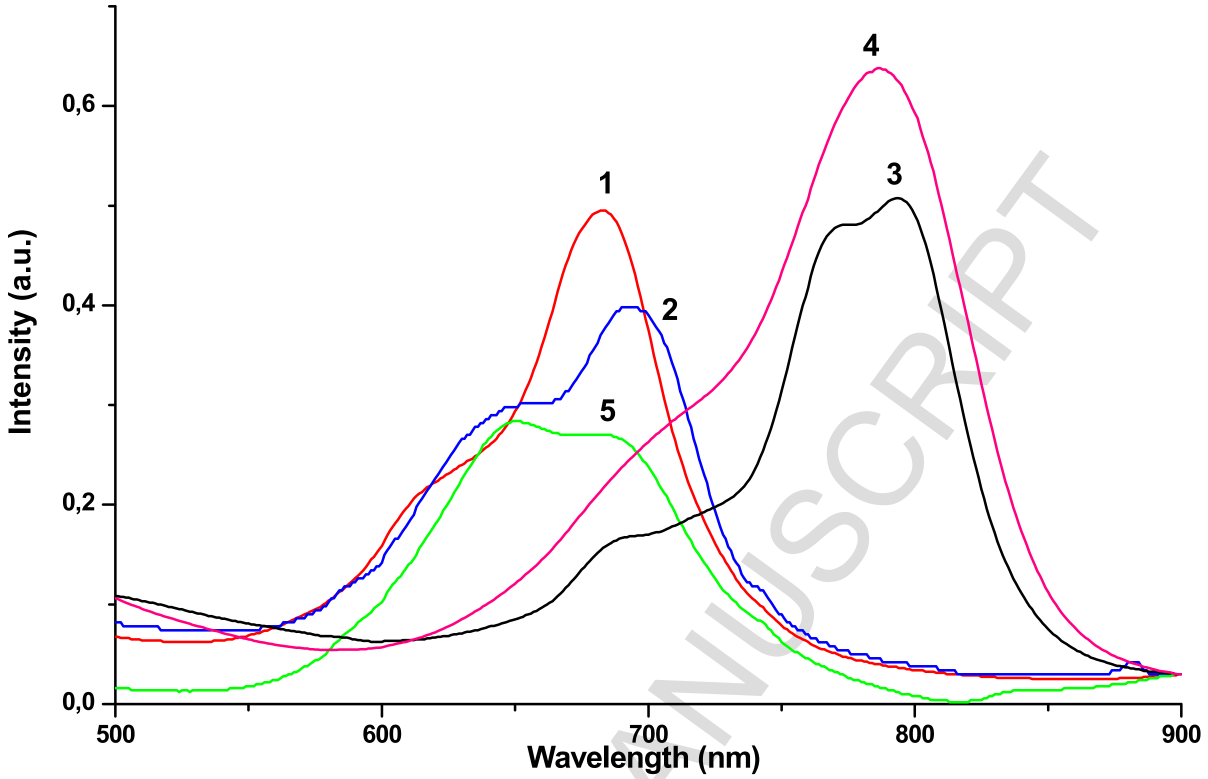


Figure 2. UV-vis spectra of nitro-substituted cobalt phthalocyaninates: 1 – **1a** in DMF, 2 **–** **1c** in DMF, 3 – **1a** in H_2SO_4, 4 – **1c** in H_2SO_4, 5 – **1c** in H_2O (pH 13).

Water-soluble derivatives were obtained via interaction of cobalt (**1a**, **2a**) and copper (**1b**, **2b**) phthalocyaninates with mixture of thionyl chloride and chlorsulfonic acid under room temperature for 2 hours till corresponding sulfochlorides obtainment (Scheme 2), which were transformed to sulfonic acids via hydrolysis. Yield of sulfonated derivatives of cobalt and copper phthalocyaninates was 78-82%.

macrocycle	solvent			
	DMF	$CHCl_3$	H_2O	H_2SO_4
1a	683	678	-	797
1b	685	696	-	804
1c	694	-	704	787
1d	696	-	690	794
2a	665	673	-	823
2b	679	684	-	838
2c	670	-	679	797

Table 1. Absorption spectral data for Q-band of metallophthalocyanines (nm) in various solvents.

Bathochromic shift of absorption Q-band is observed within solutions in organic solvents upon transformation of metal phthalocyaninate nitro-derivatives (**1a**, **1b**) to their symmetrical analogues. Observed solvatochromic effect relates to change of centers of solvent – macrocycle solvation interaction. Axial coordination of one or two solvent molecules by central metal cation is becoming predominant upon solvation of phthalocyanine macrocycle in DMF, herewith in case of chloroform this fact is caused by hydrogen bond. Significant bathochromic shift of absorption Q-band is observed within UV-vis in solutions of sulfuric acid due to protonation of *meso*-position of macrocyclic fragment and the regularity has an inverse form.

3.3. Aggregation in water mediums

Introduction of ionogenic groups to phthalocyaninates composition imparts them solubility in water mediums enhancing potential application ways as environmental-friendly catalysts and photocatalysts for mercaptanes (RSH) oxidation. Besides sulfo-group as part of metal phthalocyaninate may functionalize as anchoring group upon immobilization of the macrocycle on inorganic polymers, for example on silica [25-27].

Investigation of electron absorption spectra (Figures 2 and 3) of sulfonated metal phthalocyanines confirmed difference of aggregation for these compounds in water and DMF solutions. In this way, bifunctional derivatives of phthalocyanine macrocycles exhibit strong association that corresponds to diffuse electron absorption spectrum (Figure 2). Absorption band about 630 nm is registered in UV-vis spectrum of water and DMF solutions of **1c** and **1d** within concentration range up to 10^{-7} mol/L that corresponds to *H*-dimers according to literature data [28]. On the contrary *octa*-sulfonated macrocycles in these mediums are predominantly monomeric (Figure 3). Association processes takes place upon macrocycle concentration is over 8×10^{-5} mol/L. Some broadening of absorption Q-band for water solution of **2c** may be explained by formation of phthalocyaninate associates linked due to water structure. In this case there is no interaction between macrocycles π-systems, and solvent molecules are included into aggregate cavity. Stabilization of non-covalent associates takes place in solution for complexes **2c** and **2d** in contrary to behavior of sulfonated cobalt phthalocyanines known previously in water mediums [29]. This is possible due to interaction between extended peripheral substituents of two macrocycles significantly distanced from aromatic π-system.

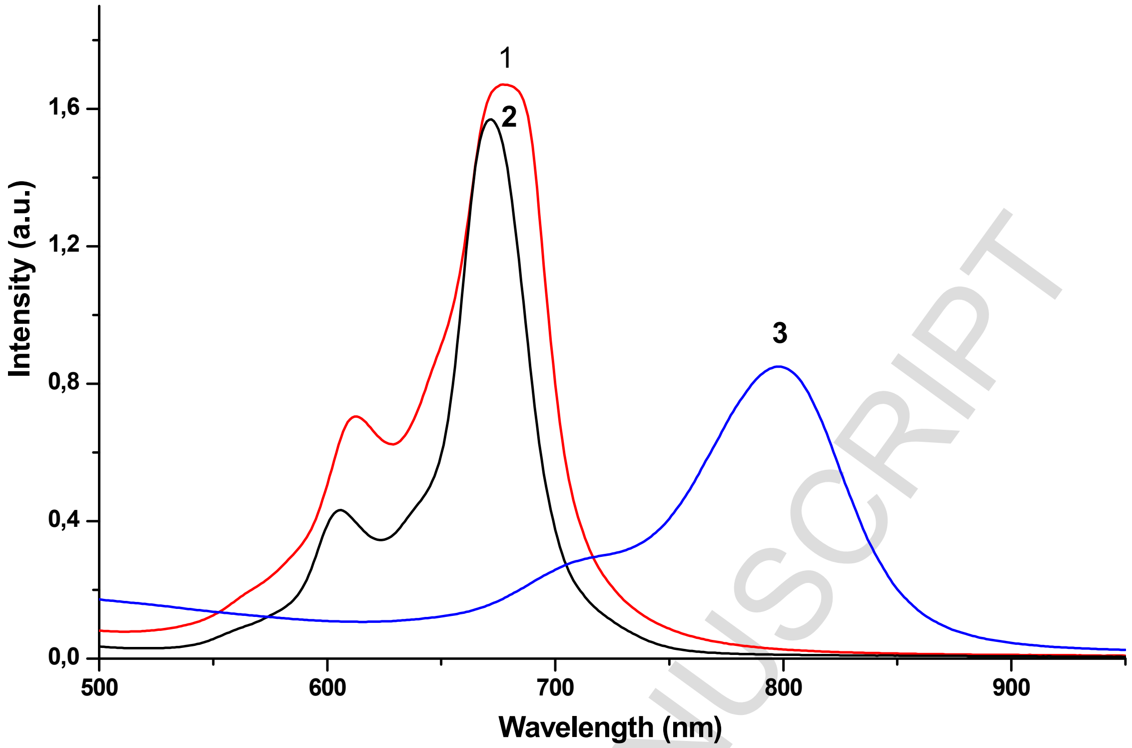


Figure 3. UV-vis spectra of cobalt phthalocyaninates solutions: 1 – **2c** in H_2O (pH 13), 2 – **2c** in DMF, 3 – **2c** in H_2SO_4.

Inversion of solvatochromic effect for sulfonated metallophthalocyanine derivatives compared to predecessors is caused by change of solvation centers on phthalocyanine macrocycle periphery and aggregation equilibriums of the system.

High degree of sulfo-groups ionization in water-alkali mediums leads to competing both solvent and ionized peripheral substituent of nearest macrocycle for central metal cation accompanied with *J*-aggregates formation.

Aggregation degree and type of the aggregates have significant influence on catalytic activity of these macrocycles upon liquid-phase processes. Data on aggregation and religanding processes helps to evaluate catalytic properties more detailed. Possibility of solvent replacement on introduced substrate in water-alkali mediums is promising for transformation of mercaptanes to disulfides by means of phthalocyaninate complexes, before all cobalt ones, as catalysts.

As it was shown previously, macrocycle **1c** is aggregated in water-alkali solution, electron absorption spectrum registers broad maximum of diffuse nature.

Investigation of UV-vis concentration dependence for water-alkali solution of **1c** indicates unavailability of association equilibrium shift toward monomeric forms due to dilution.

$$(\mathrm{CoPc})_n \rightleftarrows n\mathrm{CoPc} \qquad (13)$$

Method of mathematical decomposition of electron absorption spectrum on the components was applied to determine contribution of monomeric and associated **1c** macrocycle forms [30-31] (Figure 4). Obtained results showed the shift of association equilibrium toward monomers upon dilution of solution keeping H-associates linked by interaction of peripheral substituents. Concentration limit of aggregation beginning in water mediums for **1c** is 2×10^{-7} mol/L.

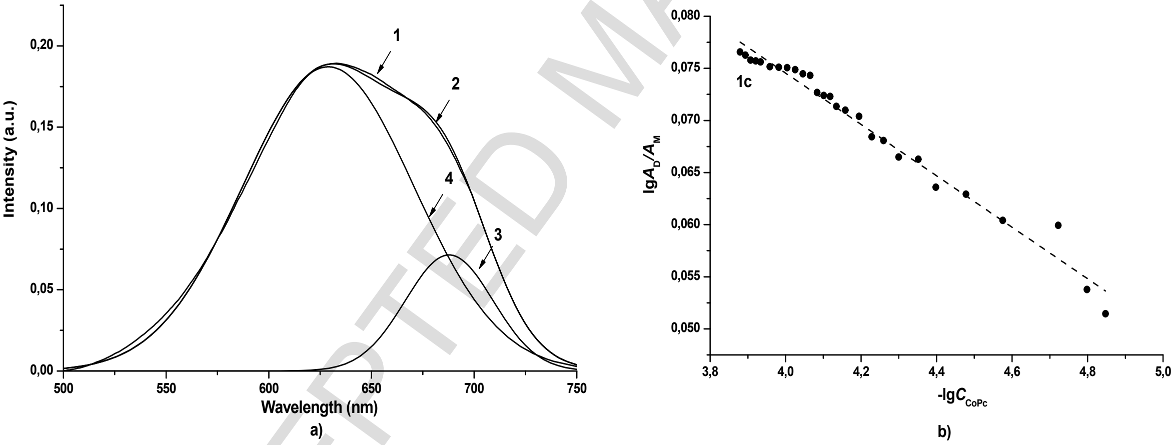


Figure 4. a) – decomposition of UV-vis spectra for **1c** 1 – experimental data, 2 – calculated curve, 3 – monomer absorption, 4 – dimer absorption; b) – concentration dependence of monomer-dimer equilibrium.

Accessibility of phthalocyanine macrocycle coordination unit upon catalytic process determines efficiency and selectivity of phthalocyanines as catalysts. We investigated the process of solvent displacement from macrocycle coordination sphere.

macrocycle	lgε (H-aggregate)	lgε (monomer)	lgK_{dim}	CoPc:DMF	K_s
1c	3.39	4.98	6.74	1:2	3.79
2c	3.94	4.53	3.97	2:5	3.37

Table 2. Aggregation parameters of cobalt phthalocyaninate sulfonic acids.

Coordination of DMF for **1c** proceeds in one stage forming stable complex (Table 2). Complex composition determined with angle tangent from equation 5 resulted in CoPc:DMF 1:2 that indicates solvent replacement from fifth and sixth coordination positions of metal phthalocyanine and exchange it on DMF.

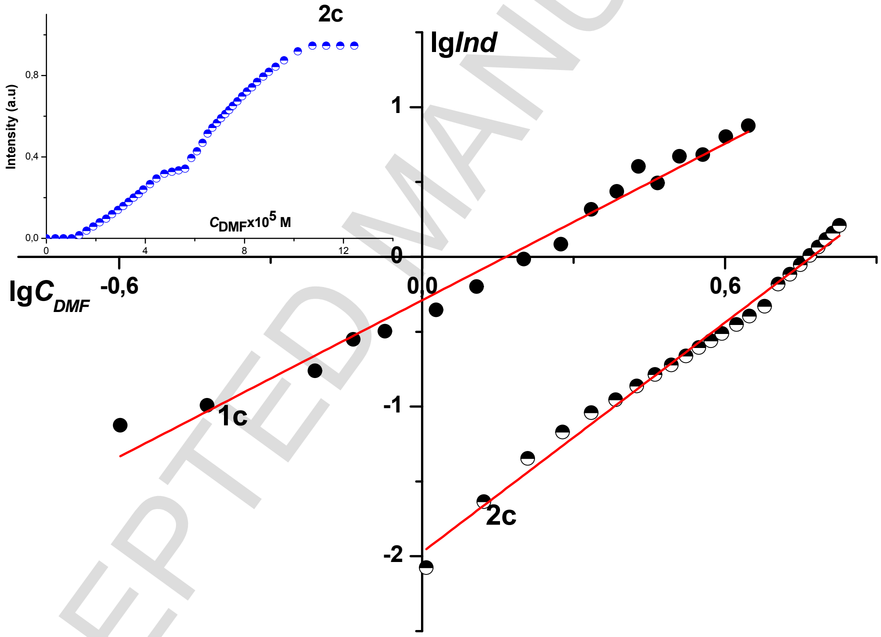
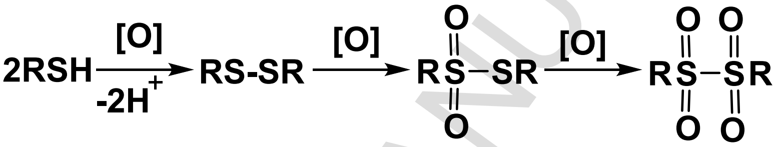


Figure 5. Dependence of indication ratio from ligand concentration within specific solvation region. DMF titration curve for **2c** (inserted).

Solvation interaction of **2c** and introduced ligand proceeds in two steps (Figure 2, inserted). The first one is formation of specific coordination complex of 2:5 composition. Interaction transforms from specific to universal upon increase of DMF concentration in water-alkali solution of **2c**. This fact suggests key role of peripheral substituents electron effects affecting conjugated macrocycle π-system and hence on coordination unit upon solvation of **1c**. In case of symmetrically-substituted macrocycle **2c** structural effects of substituents linking ligand on the periphery become predominant. Observed phenomena are crucial for further interpretation of catalytic data involving metallophthalocyanines.

3.4. Catalytic activity

Catalytic activity of **1c** and **2c** was tested within liquid-phase oxidation of sodium N,N-carbamodithiolate. Mercaptans oxidation proceeds in several steps according to scheme 4 depending on process conditions.



Scheme. 4. Scheme of mercaptans oxidation.

Our previous researches showed substituted cobalt phthalocyanine derivatives to have high selectivity with the termination of the reaction at the stage of disulfide formation [32-35]. Moreover, mild reaction conditions, namely use of air oxygen as oxidant and relatively low basicity of the medium, promote this.

Based on kinetic research [32] catalytic activity of these compounds is determined by influence of peripheral substituents, their nature and structure on macrocycle. This is caused by change of both peripheral substituents electron effects and restructuring of macrocycles in solutions.

Figure 6 presents temperature dependence of DTC oxidation rate in presence of catalysts **1c** and **2c**.

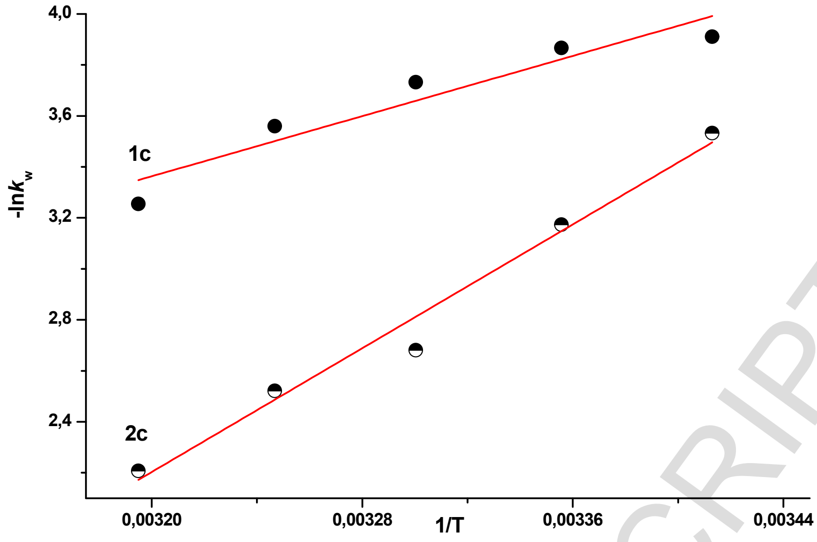


Figure 6. Temperature dependence of DTC oxidation rate.

Equal activation parameters of DTC oxidation (Table 3) catalyzed by **1c** and **2c** indicate similar state and nature of active centers during catalysis. Based on known data about mercaptans oxidation mechanism involving metallophthalocyanines [32, 36] formation of triple substrate-catalyst-oxygen intermediate complex requires increase of system order that is reflected in negative values of system activation entropy (Table 3). This means both aggregated form **1c** and macrocycle exciting in solution as monomers (**2c**) are less ordered than monomolecular complex.

phthalocyanine	$k_w \times 10^3$ L×(mol×s)$^{-1}$	E$^{\neq}$ kJ×mol^{-1}	ΔS$^{\neq}$ J ×(mol×K)$^{-1}$	χ
1c	21	2.67	-248	0.86
2c	42	2.62	-247	0.75

Table 3. Kinetic parameters of DTC oxidation.

Conclusion

Resulting from work bifunctionally- and symmetrically substituted phthalocyanines were synthesized. Catalytic activity of the water-soluble compounds was studied. Series of obtained phthalocyanines was found to exhibit interrelationships between structure of the terminal fragment and catalytic properties. Based on this, one may conclude the possibility to predict catalytic performance of the compounds based on their structure.

Obtained results provide possibility of compensation aggregation state of macrocycle upon catalysis by sterical effect of peripheral substituent allowing increase of process rate without mechanism change.

Acknowledgments

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Highlights

- Novel cobalt and copper phthalocyaninates bearing with bulky fragments on periphery are synthesized. Their water-soluble analogues are obtained.
- The compounds are fully characterized.
- The compounds are prospective as catalysts.