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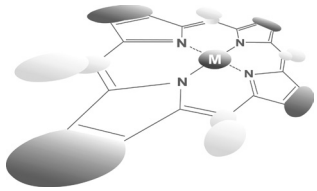

Symmetrical and difunctional substituted cobalt phthalocyanines with benzoic acids fragments: Synthesis and catalytic activity

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ABSTRACT: Difunctional and symmetric phthalonitriles were synthesized by nucleophilic substitution of brome and nitro-group in 4-bromo-5-nitro-phthalonitrile for residues 4-amino-, 4-hydroxyl- and 4-sulfanyl benzoic acid. Symmetrical and difunctional substituted cobalt phthalocyanines were obtained by template synthesis based on mentioned phthalonitriles. Their spectral properties and catalytic activity in aerobic oxidation of sodium *N*,*N*-carbomoditiolate were investigated.

KEYWORDS: 4-bromo-5-nitro-phthalonitrile, benzoic acids, synthesis, cobalt phthalocyanines, catalysis, oxidation.

INTRODUCTION

Carbon acids of metal complexes tetrapyrrolic macroheterocyclic compounds have solubility in water and buffer media. This fact combined with ability to coordinatively interact with biomolecules is used in novel methods of PDT, for example sonodynamic therapy [1] where joint action of sensitizer and supersonic waves is used. Non-covalent interaction between biopolymers and phthalocyanines containing hydrophobic and hydrophilic groups is promising for creation of novel sensitizers for PDT [2, 3]. Besides, catalytic activity in redox processes of mercaptans and olefins of these compounds is also promising [4–7].

Catalysts obtained by immobilization of metallophthalocyanines on solid-phase carriers, carbon nanotubes, organic polymers are also perspective [8–10]. Carbon residues of phthalocyanine molecule may be used as anchoring groups for linking with biological molecules containing fragments of primary amines [11], immobilization on polymer surface, for example silica [12] or nanotubes [13] that may be used to create novel materials for purposes mentioned above. Thus, investigations of phthalocyanine macrocycle structure expansion are actively continuing at the moment [14, 15].

The possibility to synthesize non-symmetrical difunctional phthalocyanines with specific location of substituents on the periphery allows to control their physical and chemical properties and consequently significantly expand the applications range.

There is data about carboxyl-substituted metallophthalocyanines, in which the carboxyl-group is linked directly with isoindole fragment and *via* phenoxy-, phenylamino- or phenylsulfanyl groups in literature [16–19]. However, they are primarily concerned the tetrasubstituted and octasubstituted phthalocyanines containing symmetrical substituents.

Meanwhile, the study of influence of the substituent located in *ortho*-position towards benzoic acid fragment electronic and structural effects on physical and chemical properties of these phthalocyanine derivatives is beneficial.

◊ SPP full member in good standing

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Introduction of the substituent may lead to cardinal changes in the catalytic activity of the compounds.

Current work is devoted to the synthesis and study of catalytic properties of symmetric and difunctionally substituted derivatives of cobalt phthalocyanine containing four to eight fragments of carbon acids included in peripheral substituents.

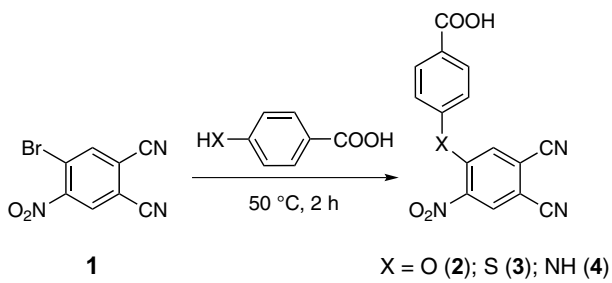
RESULTS AND DISCUSSION

Synthesis of asymmetrical nitriles

Nucleophilic substitution of bromine atom in 4-bromo-5-nitrophthalonitrile (**1**) on benzoic acid fragment was used to synthesize compounds (**2–4**) (Scheme 1).

The synthesis was carried out in DMF in presence of anhydrous potassium carbonate under the temperature of 25–35 °C for 2 h. Reaction for 4-((4,5-dicyano-2-nitrophenyl)amino)benzoic acid (**4**) was performed in presence of triethylamine. Extraction of compounds **2** and **3** was carried out by acidification of reaction mixture with 5% solution of hydrochloric acid. The formed precipitate was filtered and washed with the solution of water and HCl (0.7%). During the synthesis the precipitate of dinitrile **4** was formed and then filtered off. Additional precipitation of the dinitrile **4** from the reaction mixture was done by transfer of the filtrate to bidistilled water, wherein the nitrile precipitate was formed and then filtered. Next the desired product was washed with acidificated water. The yields of **2–4** compounds were 34–63%. Composition and structure of nitriles (**2–4**) were confirmed by elemental analysis, ^{1}H and ^{13}C NMR and IR spectroscopies, mass-spectrometry.

IR spectra of all phthalonitriles have the band of cyano-groups valent vibrations in range of 2227–2237 cm^{-1} [20]. IR spectra of all synthesized compounds have vibration bands of –OH and –C=O bonds of benzoic acids carboxyl fragments in range of 3413–3418 cm^{-1} and 1708–1725 cm^{-1} respectively. There are bands of symmetrical 1346–1383 cm^{-1} and asymmetrical 1523–1558 cm^{-1} vibrations of nitro-groups N=O bonds for compounds (**2–4**). There is band of valent vibrations of the Ar–S–Ar bond on 1117 cm^{-1} in IR spectrum of phthalonitrile **3**. For the phthalonitrile **4** containing *para*-aminobenzoic acid fragment the bands of valent 3195 cm^{-1} and deformation 1613 cm^{-1} vibrations of secondary amino N–H bond are observed. Valent vibration of Ar–O–Ar bond in range of 1245–1254 cm^{-1} is registered in IR spectrum of compound **2** that is in agreement with known data [20].



Scheme 1. General scheme of bifunctional nitriles synthesis

^{13}C NMR spectra of all studied compounds have signals of carbon atoms on 167–168 ppm, which, in accordance with theoretically calculated spectra (Table 1) and known literature [21], have to be attributed to the carbon atoms of the carboxyl groups. Besides, there are signals of cyano carbon atoms on 109–115 ppm and on 107–115 and 120–126 ppm is cyano-substituted carbon atoms.

The influence of the bridge-group nature on position of carbon atom signal located in *ortho*-position towards the benzoic acid fragment is detected. Thus, the signals of nitro-substituted carbon atoms are situated on 120 ppm for the compounds **2** with hydroxyl-benzoic acid fragment, on 131 ppm for the compound **4** with amino-benzoic acid fragment and on 134 ppm in the NMR spectrum of the compound **3** with sulfanylphenyl-benzoic acid fragment.

The nature of bridge-group also has an effect on the position of C_9 carbon atom signal (Table 1). Thus, the C_9 atom has a shift from 145 to 159 ppm under the transformation from the phthalonitrile containing residue of *para*-sulfanylbenzoic acid (**3**) to the compound (**2**) having 4-carboxyphenoxy-group. *para*-Carboxyphenylaminosubstituted phthalonitrile has an intermediate position (150 ppm).

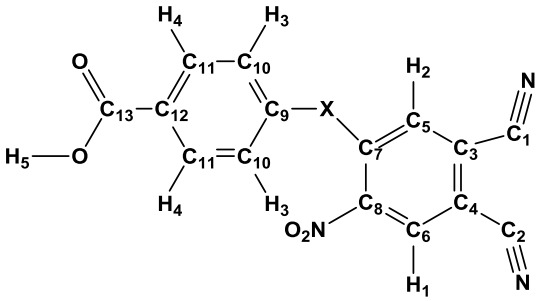
^{1}H NMR spectra of the compounds (**2–4**) have signals of the protons of phthalonitrile fragment benzyl rings and residue of corresponding benzoic acid in the range of weak field (Table 1). There is no proton signal of carboxyl-group in ^{1}H NMR spectrum for the compounds (**3, 4**) due to exchange of the proton on deuterium atom of the solvent.

Synthesis of symmetric nitriles

The 4-bromo-5-nitrophthalonitrile (**1**) was used as initial compound to obtain 4,4′-((4,5-dicyano-1,2-phenylene) bis(oxy))dibenzoic acid (**5**), 4,4′-((4,5-dicyano-1,2-phenylene)bis(sulfanediyl))dibenzoic acid (**6**) and 4,4′-((4,5-dicyano-1,2-phenylene)bis(azanediyl))dibenzoic acid (**7**). Reaction was performed by nucleophilic substitution of the brome atom and nitro-group according to the Scheme 2. Synthesis was carried out in aqueous DMF 3:5 in presence of anhydrous potassium carbonate. Reaction was done under 100 °C during 24 h for simultaneous substitution of brome atom and nitro-group contained in **1** on benzoic acid fragment. Triethylamine was used in case of the compound **7** containing *para*-aminobenzoic acid fragment as substituent.

Extraction of the compounds **5** and **6** was performed by pouring of the reaction mixture into 5% aqueous solution of hydrochloric acid. The formed precipitate was filtered off and washed with distilled water. The yields of the compounds **5** and **6** were 72 and 88% respectively.

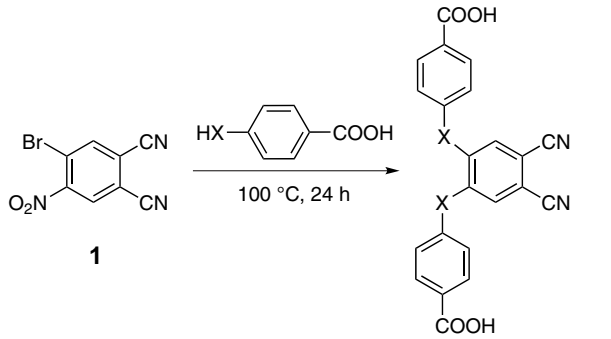
Table 1. Chemical shift in ^{13}C и ^{1}H NMR spectra of bifunctional-substituted phthalonitriles, DMSO (d_6), standart TMS



Number	δ, ppm					
	X = O (**2**)		X = S (**3**)		X = NH (**4**)	
	Calcd.	Exp.	Calcd.	Exp.	Calcd.	Exp.
C_1	112	115	114	115	115	115
C_2	110	109	110	113	110	111
C_3	121	120	121	126	120	120
C_4	109	109	113	115	107	107
C_5	128	131	129	131	112	111
C_6	143	144	129	131	150	150
C_7	160	160	147	146	137	138
C_8	123	120	133	134	130	131
C_9	157	159	145	145	150	150
C_{10}	118	116	129	131	124	120
C_{11}	131	131	131	129	124	120
C_{12}	124	128	131	128	122	120
C_{13}	168	168	169	167	168	168
H_1	8.85	8.83	9.10	9.00	9.13	8.85
H_2	7.78	7.61	7.70	7.74	8.05	8.07
H_3	7.87	7.85	7.83	7.95	7.34	7.61
H_4	8.08	8.07	8.15	8.07	7.77	7.85
H_5	11.72	9.10	11.72	—	10.20	—
–NH	—	—	—	—	10.20	8.83

In case of phthalonitrile **7** the reaction mixture was poured in water, the desired product was extracted by chloroform and then the organic layer was exposed to liquid column chromatography on silicagel using chloroform as eluent. The phthalonitrile **7** was dried *in vacuum* under 70 °C after removing of the solvent. The yield of the desired product was 40%.

It should be noted that the compounds **5** and **6** may be obtained by the introduction of the second fragment of the corresponding derivative of the benzoic acid in the molecules **2** and **3** respectively instead of nitro-groups. Such synthesizes were done and characterized by lower yields of the final product. Herewith, implementation of the synthesis in two steps needs isolation of the intermediate that increases duration of the synthesis and leads to additional losses during purification. Synthesis of the compound **7** from 4-((4,5-dicyano-2-nitrophenyl) amono)benzoic acid (**4**) was failed.



Scheme 2. General scheme of symmetrical nitriles synthesis

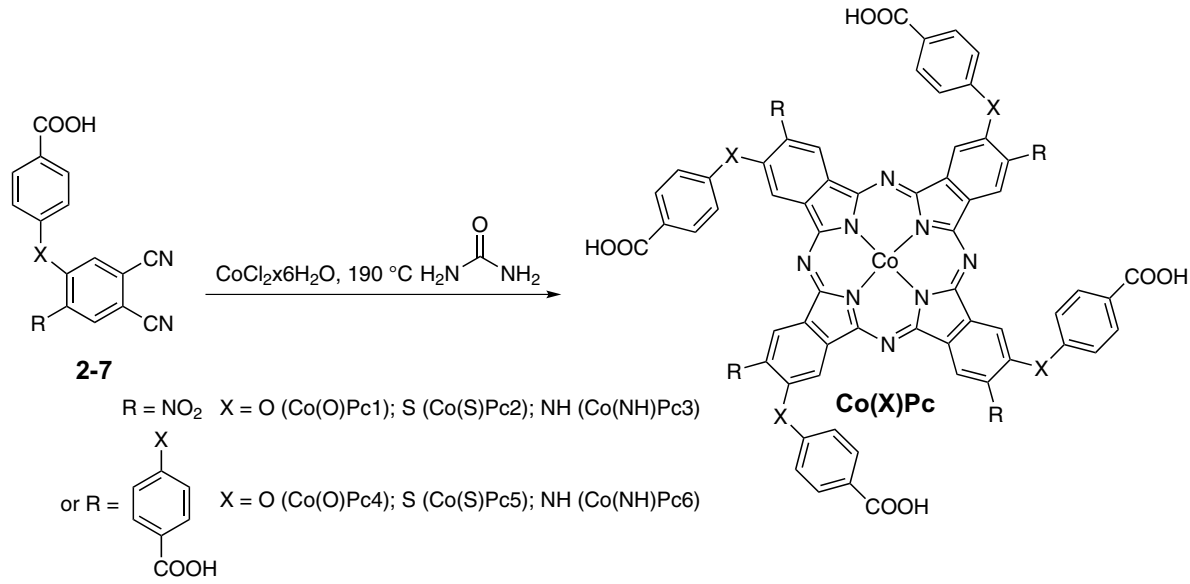
IR spectra of all phthalonitriles have the bond of valent vibrations in range of 2229–2237 cm^{-1} indicating cyano-groups. There is dependence of the position of this band from the nature of the bridge-group consisting of its shift in the field of increase in wave numbers according to the following order: **6** < **7** < **5**. For bifunctional phthalonitriles the position of the valent vibrations band of cyano-group also depends on nature of the bridge-group and represents in a different sequence: **2** < **3** < **4**.

Besides, spectra of all synthesized compounds have bands of valent vibrations of O–H and C=O bands of carboxy-groups in range of 3417–3457 cm^{-1} and 1706–1710 cm^{-1} respectively. There are no bands of N=O vibrations in IR spectra of symmetrically substituted phthalonitriles that indicates completed nucleophilic substitution of nitro-group in the compound **1**. IR spectrum of the compound **6** shows band of valent vibrations of Ar–S–Ar bond on 1104 cm^{-1}. For the compound **7** containing *para*-aminobenzoic acid fragment bands of valent 3195 cm^{-1} and deformation 1604 cm^{-1} vibrations of N–H bond of the secondary amino-group are registered. IR spectrum for the compound **5** has band of valent vibrations of Ar–O–Ar bond on 1220 cm^{-1}.

Synthesis of phthalocyanine cobalt complexes

Cobalt complexes of substituted phthalocyanines were obtained by template method under heating of corresponding phthalonitrile (**2**–**7**) with cobalt chloride in presence of urea under the temperature of 190 °C for solidification of the reaction mixture according to Scheme 3.

Reaction mixture was cooled after the finish of the process, then stirred and transferred on filter, where it was washed first with acidified water to remove the products of interaction of urea and excess of cobalt chloride, then with acetone. Next the precipitate was



Scheme 3. General scheme of phthalocyanines synthesis

dried. Desired compounds were extracted by DMF, the solvent was removed. Obtained products are powders of dark-green color, insoluble in acetone, chloroform, partially soluble in water and well-soluble in aqueous-alkaline solutions. Solubility in DMF of Co(X)Pc4-6 is higher than Co(X)Pc1-3 caused by presence of additional centers of solvation presented by four carboxyl groups.

The band of valent vibrations of cyano-groups in range of 2225–2240 cm^{-1} [20] in IR spectra of synthesized cobalt phthalocyanines is not registered. This fact indicates absence of impurity of the starting compounds in investigated samples. There are bands of valent vibrations of functional groups bonds in all spectra of the synthesized macroheterocycles, which were registered under analysis of initial phthalonitiles (**2**–**7**) IR spectra. It suggests that they are still contained in molecules of obtained cobalt phthalocyanines. The shift of the C=O bonds position under transformation from phthalonitriles to phthalocyanines towards lower wave numbers is observed.

Electronic absorption spectra of Co(X)Pc in aqueous mediums (Fig. 1) have diffuse character that is characteristic for associated macrocycle forms. Previously [22] we have studied tetraderivative analogues of investigated compounds, which have no peripheral substituent in fifth position of annulated benzene ring. It was established that the nature of hetero-bridge affects aggregation processes in water-alkali media. Thus, there was no association for tetracarboxyl derivative containing amino-bridge observed, whereas it is predominant for phthalocyanine containing thio-bridge [22].

The nature of bridge heteroatom (X) has almost no influence on the position of long-wavelength absorption bands Co(X)Pc (Table 2).

Transition from aqueous and organic solutions to concentrated sulfuric acid is accompanied by bathochromic

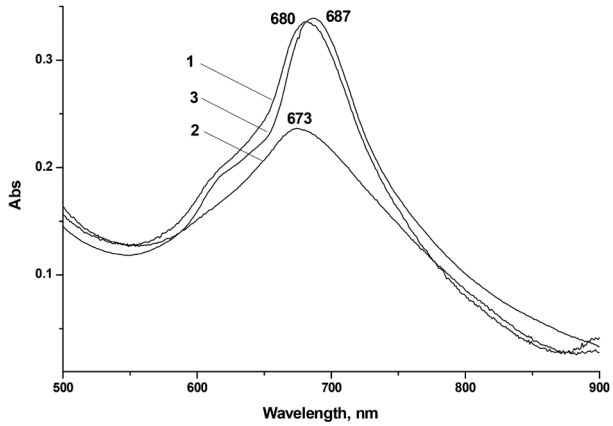


Figure 1. UV-vis spectra of Co(X)Pc (c 4.5×10^{-6} M) in DMF: (1) Co(O)Pc4, (2) Co(S)Pc5, (3) Co(NH)Pc6 at 298.15 K

shift of long-wavelength absorption bands. Comparison of UV-vis spectra of phthalocyanines combining fragments of benzoic acids and nitro-groups have showed that the value of bathochromic shift of Q-band under transition from DMF to concentrated sulfuric acid depends on the nature of bridge hetero-atom binding benzoic acid fragment and phthalocyanine molecule. The value of bathochromic shift of Q-band decreases in the following order $\Delta\lambda$ Co(S)Pc2 > Co(NH)Pc3 > Co(O)Pc1.

An apparent aggregation of Co(NH)Pc3 leads to the conclusion about redistribution of electronic effects of substituents towards conjugated macrocycle π-system in case of octa-substituted phthalocyanines in contradistinction to tetra-derivatives. Intensification of dimerization of macrocycles containing nitro-groups as peripheral substituents is caused by electron acceptor properties of nitro-group introduced in *ortho*-position

Table 2. Position of long-wavelength absorption bands (λ_{max}, nm) in UV-vis spectra of Co(X)Pc solutions at 298.15 K

Macrocycle	Solvent		
	DMF	NH_4OH (5%)	H_2SO_4
Co(O)Pc1	675	651, 701	772
Co(S)Pc2	608, 680	705	813
Co(NH)Pc3	609, 676	700	807
Co(O)Pc4	680	671	813
Co(S)Pc5	673	660; 700	993
Co(NH)Pc6	687	651; 701	829

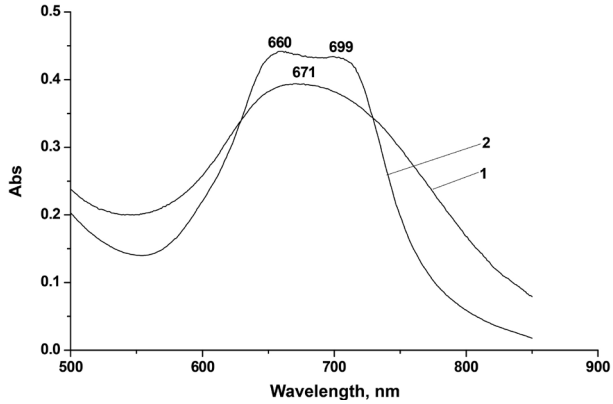


Figure 2. UV-vis spectra of Co(X)Pc (c 5.5×10^6 M) in NH_4OH 5% aqueous solution: (1) Co(O)Pc4, (2) Co(S)Pc5 at 298.15 K

relatively to the second substituent namely, the constriction of the electron density from the macrocyclic system and amplification of π–σ contraction and π–π repulsion processes. Obviously, this effect is not observed without strong electron acceptor group in macrocycle.

Based on these considerations we can conclude that these effects have to be aligned in phthalocyanines containing symmetrical peripheral substituents.

The law of Lambert–Bouguer–Beer is not observed in UV-vis spectra (Fig. 1) of Co(X)Pc4-6 solutions that also indicates aggregation of these compounds in solutions. The nature of bridge-heteroatom in that case significantly affects the position of absorption long-wavelength of the compounds (Table 2). Thus it was found that on condition of equal concentrations of the macrocycles in DMF solution the Q-band undergoes a bathochromic shift in the following order: Co(S)Pc5 > Co(O)Pc4 > Co(NH)Pc6. Aggregation degree of Co(O)Pc4 is higher compared to other studied compounds that is in agreement with our previous results [22] for their tetra-derivative analogues.

UV-vis spectra of ammonia water solution (5%) for Co(S)Pc5 (Fig. 2) has splitting of Q-band and two maximums registered, which have to be attributed to H-aggregates (660 nm) and monomer forms of phthalocyanine (700 nm). The monomer-associate equilibrium for Co(NH)Pc6 is shifted towards molecular forms of macrocycle evidenced by not broadened Q-band at 700 nm.

The position of maximums of Q-band for investigated macrocycles in sulfuric acid is bathochromic shifted. It is found that replacement of CoP(S)c2 nitro-groups by one more fragment of mercaptobenzoic acid under transformation to Co(S)Pc5 causes bathochromic shift for 180 nm. The shift is not so big in case of compounds having hydroxyl- and aminobenzoic acids fragments and it is 40 and 22 nm, respectively.

Catalytic activity in oxidation of *N,N*-carbomodithiolate

In our previous works [22, 23] it was established that tetra-derivative analogues of investigated compounds (Fig. 3) containing no substituents in *ortho*-position

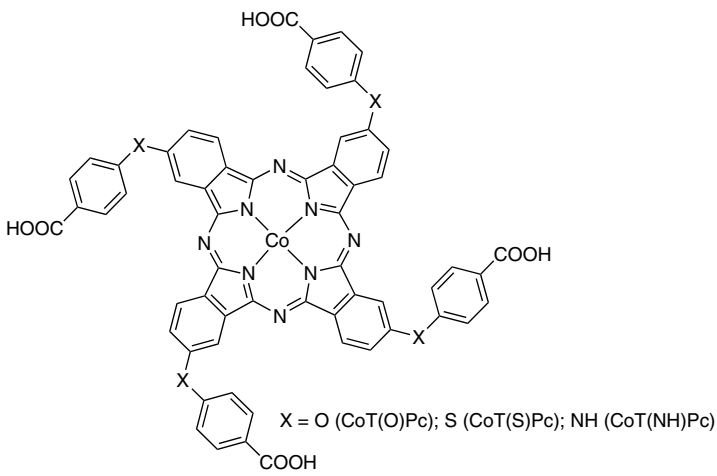


Figure 3. Cobalt complexes with tetrasubstituted phthalocyanines

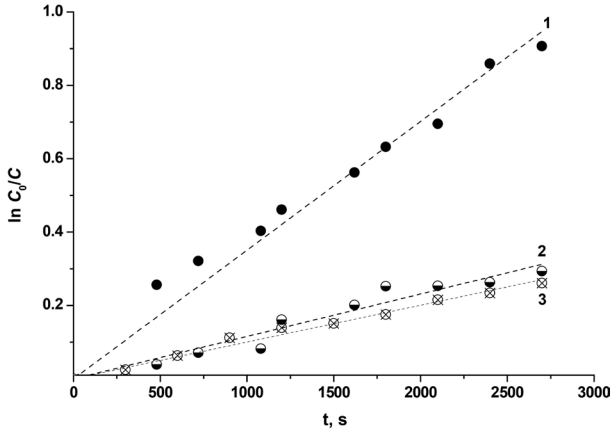


Figure 4. Kinetic dependences of DTC oxidation (c 2.6 × 10^{-3} M) in presence of homogeneous phthalocyanine catalysts (c 5.6 × 10^{-5} M) (1) Co(NH)Pc6, (2) Co(O)Pc4, (3) Co(S)Pc5 in water-alkali solution (pH 11) at 298.15 K. The dotted line: the result of the formal processing of the kinetic equation

towards benzoic acid fragments are catalytically active in oxidation of sulfur compounds.

The mechanism of the process was suggested and approved. The limiting step is formation of $RS^{\cdot}$ radicals according to the scheme $RS^{\bullet} \cdot Co^{II}Pc \cdot O^{-}_2 + H_2O \rightarrow RS^{\bullet} + H_2O \cdot Co^{III}Pc \cdot O^{2-}_2$. It was established that increase of electron acceptor ability of spacer bridge in the substituent on periphery of phthalocyanine leads to increase in catalytic activity [22, 23].

As it is seen from the data of Fig. 4 the kinetic curves of sodium *N,N*-carbomodithiolate (DTC) oxidation in presence of symmetrical octa-substituted phthalocyanines are described by formal kinetic equation of first order in substrate. Obtained kinetic data allowed us to calculate activation parameters for this process (Table 3). It should be noted that the reaction rate increases up to 80 times compared to non-catalytic oxidation [24].

Analysis of obtained results and literature data [25–27] suggests that for Co(X)Pc4-6 the mechanism including triple complex formation with followed elimination of $RS^{\cdot}$ radical from it is realized. The mechanism is presented by Equations 1–5.

$$RS^{-} + (Co^{II}Pc)_2 \overset{K_1}{\rightleftharpoons} RS^{\bullet} \cdot Co^{I}Pc + Co^{II}Pc \quad (1)$$

$$RS^{\bullet} \cdot Co^{I}Pc + O_2 \overset{K_2}{\rightleftharpoons} RS^{\bullet} \cdot Co^{II}Pc \cdot O^{-}_2 \quad (2)$$

$$RS^{\bullet} \cdot Co^{II}Pc \cdot O^{-}_2 + H_2O \xrightarrow{k_3,\ \text{slowly}} RS^{\bullet} + H_2O \cdot Co^{III}Pc \cdot O^{2-}_2 \quad (3)$$

$$2H_2O \cdot Co^{III}Pc \cdot O^{2-}_2 \xrightarrow{k_4} 2Co^{II}Pc + H_2O_2 + 2OH^{-} \quad (4)$$

$$2RS^{\bullet} \xrightarrow{\text{Instantaneous}} RSSR \quad (5)$$

Based on this mechanism the influence of the peripheral substituent nature on catalytic activity of the macrocycle is definitely depends on heteroatom effects affecting metal cation of phthalocyanine molecule, which in turn determines the stability of triple complex and aggregation degree of macrocycles in solution.

Kinetic equation obtained using Michaelis-Menten formal kinetic describes these systems well and it is linearized in Lineweaver–Burke coordinates giving Equation 6.

$$r = \frac{k_3 K_1 K_2 c^{\circ}_{(CoPc)_2} c^{\circ}_{O_2}}{1 + K_1 c_{RS^-}} \cdot c_{RS^-} \quad (6)$$

It should be noted that introduction of four additional benzoic acid fragments leads to intensification of specific solvation of the macrocycle on periphery. Besides, ionization of the macromolecule is strengthened. It leads to decrease of process rate because of competing interaction of the substrate and solvent with active centers of the catalyst. DTC oxidation rate constant decreases in the folloing order of catalysts Co(NH)Pc6 > Co(S)Pc5 ≥ Co(O)Pc4. The order is different from tetra-substituted one CoT(S)Pc > CoT(NH)Pc > CoT(O)Pc that is probably caused by difference in macrocycle association degree. Thus, CoT(NH)Pc in solution is monomeric and all its reaction centers are permanently occupied by solvent [22]. Whereas, there is possibility to compete for active center in associate Co(NH)Pc6.

The catalyst forms intermediate in solutions of high ionization degree of the macrocycle and high containing of OH^{-}. The intermediate has oxidized thiocarbamic acid

Table 3. Kinetic dependences of DTC oxidation (c 2.6 × 10^{-3} M) in presence of Co(X)Pc phthalocyanine catalysts (c 5.6 × 10^{-5} M) in water-alkali solution (pH 11)

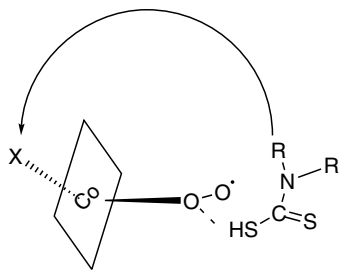
Catalyst	$k_w^{298} \times 10^2$, L.(mol.s)$^{-1}$	$E^{\neq}$, kJ.mol^{-1}	$\Delta S^{\neq}$ J.(mol.K)$^{-1}$	-lnA	χ
Co(O)Pc1	7.01	-22.09	-378	8.7	69.05
Co(S)Pc2	26.91	-12.82	-339	7.3	89.42
Co(NH)Pc3	9.57	-22.95	-375	8.5	67.43
Co(O)Pc4	3.82	10.1	-281	9.1	57.71
Co(S)Pc5	4.58	22.4	-236	9.2	68.02
Co(NH)Pc6	17.56	12.1	-245	7.7	53.86

in outer coordination sphere forming hydrogen bond with coordinated oxygen molecule. Then there is transfer of the charge from the metal to oxygen. Increase of pH leads to competing of DTC coordination processes and dimerization due to intensification of last one. This complicates the electron transfer. That is why the authors [28] suggested that electron transfer is implemented in reaction of $CoPc^{II}\cdots OH^-$ complex with other hydroxyl-ion $(CoPc^{II}\cdots OH^-)_2 + OH^- \rightarrow CoPc^{I}\cdots CoPc^{II}\cdots OH^- + O^- + H_2O$. $CoPc^{I} + O_2 \rightarrow CoPc^{II} + O_2^-$, $CoPc^{II} + O_2 \rightarrow CoPc^{III} + O_2^-$. There is permanent formation of O_2^- and $CoPc^{III}$ oxidized forms under excess of oxygen in water-alkali system that complicates the triple complex formation on condition of high content of hydroxyl ions in the solution and consequently reduces the activity of the phthalocyanine as a catalyst. It is also a characteristic of investigated by us systems.

Absolutely unexpected results are obtained for Co(X)Pc1-3. There is inhibition of the oxidation under increase of the temperature while maintaining the formal first-order kinetic reaction on the substrate. The calculation of the activation parameters of the system showed negative energies of activation process (Table 3).These data characterizes the process as complex. Obviously, the rate constant of the process (3), which is limiting stage, is increased under increase of temperature. But the presence of strong acceptor groups (NO_2) contained in the macrocycle in *para*-position towards benzoic acid fragments leads to contraction of π-electronic density from central metal cation and decrease of partially positive charge compensation [29]. Macrocycle-solvent coordination interaction compensates this charge.

Increase of activation entropy change indicates the desolvation of activated complex (Fig. 5) and introducing of substrate or oxygen into coordination sphere, which characterizes the transfer towards association-dissociation mechanism of the process.

Obviously, there is an exchange between DTC and coordinated by phthalocyanine ligand (Fig. 5) which can be presented by solvent or molecular oxygen [30]. The exchange depends essentially on electron-donor power of second ligand, for ions — on their basicity.



where X = solvent or molecular oxygen

Figure 5. Exchange of ligands

Wherein, the concentration of associated macrocycle forms participated in reaction (1) decreases under temperature increase. Decrease of dimer concentration is faster than increase of reaction (3) rate constant that leads to decrease of the total rate of the process. The total process rate changes in order CoT(S)Pc > CoT(NH)Pc > CoT(O)Pc, which correlates to the series of tetra-substituted CoT(X)Pc.

EXPERIMENTAL

Equipment

Elemental analysis has been carried out by means of chromatographic analyzer Flash HCNS-OEA 1112 (Germany). The flowrates 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 s 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 (^1H) 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 (TMS). 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).

pH values of the solutions were controlled with pH meter S220 Seven Compact (Mettler Toledo, Switzerland). Relative error of pH determining was ±0.002.

Synthesis of bifunctional nitriles

4-bromo-5-nitrophthalonitrile (**1**) was synthesized according to the method recommended in [31]. Physical and chemical properties of the obtained compound are in good agreement with literature data. mp 140–142 °C (%). Elemental analysis found C, 38.10; N, 16.50; H, 0.68%. Anal. calcd. for ($C_8H_2BrN_3O_2$) C, 38.16; N, 16.67; H, 0.80. IR (KBr): ν, cm^{-1} 2241 (C≡N), 1560 (NO_2), 1341 (NO_2), 813 (C–Br).

General method. 2.52 g (0.01 mol) 4-bromo-5-nitrophthalonitrile (**1**) and 0.01 mol of corresponding benzoic acid were dissolved in 50 mL of DMF and placed into two-necked flask equipped with a reflux. The

solution of 1.38 g (0.01 mol) of anhydrous potassium carbonate in 7 mL of water was added to the mixture. The reaction mixture was stirred at 25 °C for 1 h. Obtained precipitate was filtered off and washed with 5% aqueous solution of hydrochloric acid until the colorless filtrate. Then it was dried on air under 70–80 °C. Extraction was performed by acidification of the reaction mixture by 5% solution of hydrochloric acid. The precipitate was filtered and washed with acidified water.

4-(4,5-Dicyano-2-nitrophenoxy)benzoic acid (2). It was synthesized from 1.38 g of *para*-hydroxybenzoic acid. The yield is 1.76 g (57%). Elemental analysis found C, 59.02; H, 2.32; N, 13.30%. Anal. calcd. for ($C_{15}H_7N_3O_5$) C, 58.26; H, 2.28; N, 13.59. IR (KBr): ν, cm^{-1} 3014 (OH), 2231 (C≡N), 1719 (C=O), 1558 (NO_2), 1380 (NO_2), 1254 (Ar–O–Ar). MS (MALDI-TOF): *m/z* 309.29 [M], calcd. [M] 309.24.

4-((4,5-Dicyano-2-nitrophenyl)thio)benzoic acid (3). It was synthesized from 1.54 g of *para*-phenylsulfanylbenzoic acid. Yield 1.12 g (34%). Elemental analysis found C, 55.25; H, 2.02; N, 13.00%. Anal. calcd. for ($C_{15}H_7N_3O_4S$) C, 55.38; H, 2.17; N, 12.92. IR (KBr): ν, cm^{-1} 3417 (OH), 2232 (C≡N), 1725 (C=O), 1550 (NO_2), 1383 (NO_2), 1117 (Ar–S–Ar). MS (MALDI-TOF): *m/z* 324.71 $[M–H]^-$, calcd. [M] 325.65.

4-((4,5-Dicyano-2-nitrophenyl)amino)benzoic acid (4). It was synthesized from 1.37 *r para*-aminobenzoic acid in presence of 2 mL of triethylamine. Yield 1.96 g (63%). Elemental analysis found C, 58.20; H, 3.00; N, 18.10%. Anal. calcd. for ($C_{15}H_7N_4O_4$) C, 58.45; H, 2.62; N, 18.18. IR (KBr): ν, cm^{-1} 3418 (OH), 3195 (NH), 2237 (C≡N), 1708 (C=O), 1613 (NH), 1523 (NO_2), 1406 (NH), 1346 (NO_2). MS (MALDI-TOF): *m/z* 332.01 $[M + Na]^+$, calcd. [M] 308.25.

Synthesis of symmetrical nitriles

General methods. *I variant.* 2.52 g (0.01 mol) of 4-bromo-5-nitrophthalonitrile (**1**) and 0.02 mol of corresponding benzoic acid were dissolved in 50 mL of DMF and placed into two-necked flask equipped with reflux. The solution of 5.52 g (0.04 mol) of anhydrous potassium carbonate in 7 mL of water was added to the mixture. The reaction mixture was stirred under 100 °C for 24 h, then poured onto acidic water and desired product was collected from the filter. The precipitate obtained was filtered of and washed with 5% aqueous solution of hydrochloric acid until colorless filtrate.

4,4′-((4,5-Dicyano-1,2-phenylene)bis(oxy)) dibenzoic acid (5). It was synthesized from 2.76 g of *para*-hydroxybenzoic acid. Yield 2.88 g (72%). Elemental analysis found C, 64.59; H, 3.12; N, 6.83%. Anal. calcd. for ($C_{22}H_{12}N_2O_6$) C, 66.00; H, 3.02; N, 7.00. ^{1}H NMR (DMSO-d_6): δ, ppm 10.58 s (COOH, 2H), 7.66 s (H^1, 2H), 6.96–7.06 d (H^2, 4H, *J* 2.01 Hz), 8.03–8.12 d (H^3, 4H, *J* 2.05 Hz). IR (KBr): ν, cm^{-1} 3457 (OH); 2237 (C≡N); 1708 (C=O); 1220 (Ar–O–Ar). MS (MALDI-TOF): *m/z* 399.30 $[M–H]^-$; calcd. [M] 400.07.

4,4′-((4,5-Dicyano-1,2-phenylene)bis(sulfanediyl)) dibenzoic acid (6). It was synthesized from 3.08 g of *para*-mercaptobenzoic acid. Yield 3.80 g (88%). Elemental analysis found C, 60.95; H, 2.93; N, 6.15; S, 14.35%. Anal. calcd. for ($C_{22}H_{12}N_2O_4S_2$) C, 61.10; H, 2.80; N, 6.48; S, 14.83. ^{1}H NMR (DMSO-d_6): δ, ppm 10.55 s (COOH, 2H), 7.88 s (H^1, 2H), 7.57–7.60 d (H^2, 4H; *J* 2.05 Hz), 7.96–8.02 d (H^3, 4H; *J* 2.04 Hz). IR (KBr): ν, cm^{-1} 3417 (OH); 2229 (C≡N); 1710 (C=O); 1104 (Ar–S–Ar). MS (MALDI-TOF): *m/z* 431.28 $[M–H]^-$; calcd. [M] 432.02.

4,4′-((4,5-Dicyano-1,2-phenylene)bis(azanediyl)) dibenzoic acid (7). It was synthesized from 2.74 g of *para*-aminobenzoic in presence of 2 mL of triethylamine. After finish of the synthesis the desired compound was extracted by pouring of the reaction mixture onto water and then adding chloroform. Next the chloroform was separated from water part on separating funnel, after this the solvent was removed. The compound was column chromatographed on silica using chloroform as eluent. Yield 1.59 g (40%). Elemental analysis found C, 65.20; H, 3.33; N, 14.10%. Anal. calcd. for ($C_{22}H_{14}N_4O_4$) C, 66.33; H, 3.54; N, 14.06. ^{1}H NMR (DMSO-d_6): δ, ppm 8.58 s (COOH, 2H), 8.51 s (NH, 2H), 8.01 s (H^1, 2H), 7.52–7.53 d (H^2, 1H; *J* 2.05 Hz), 7.62–7.63 d (H^3, 2H; *J* 2.01 Hz). IR (KBr): ν, cm^{-1} 3418 (OH), 3195 (NH), 2234 (C≡N), 1706 (C=O), 1604 (NH), 1434 (NH). MS (MALDI-TOF): *m/z* 399.34 $[M + H]^+$; calcd. [M] 398.38.

General methods. *II variant.* 0.1 mmol of nitrile (**2**–**3**) and 0.1 mmol of corresponding benzoic acid were dissolved in 5 mL of DMF and placed into two-necked flask equipped with reflux. The solution of 0.14 g (0.1 mmol) of anhydrous potassium carbonate in 0.7 mL of water was added to the mixture. It was stirred under 80–90 °C for 24 h. The precipitate obtained was filtered off and washed with aqueous solution of hydrochloric acid (5%) until colorless filtrate. Then it was dried on air under 70–80 °C.

The compound (**7**) was not obtained by this method.

4,4′-((4,5-Dicyano-1,2-phenylene)bis(oxy)) dibenzoic acid (5). It was synthesized from 0.31 g of 4-(4,5-dicyano-2-nitrophenoxy)benzoic acid **(2)** and 0.14 g of *para*-hydroxybenzoic acid. Yield 0.21 g (52%). Elemental analysis found C, 64.63; H, 3.14; N, 6.67%. Anal. calcd. for ($C_{22}H_{12}N_2O_6$) C, 65.70; H, 3.02; N, 7.00. IR (KBr): ν, cm^{-1} 3454 (OH); 2237 (C≡N); 1708 (C=O); 1220 (Ar–O–Ar).

4,4′-((4,5-Dicyano-1,2-phenylene)bis(sulfanediyl)) dibenzoic acid (6). It was synthesized from 0.33 g 4-((4,5-dicyano-2-nitrophenyl)thio)benzoic acid **(3)** and 0.15 g *para*-mercaptobenzoic acid. Yield 0.27 g (62%). Elemental analysis found C, 60.90; H, 2.90; N, 6.24; S, 14.52%. Anal. calcd. for ($C_{22}H_{12}N_2O_4S_2$) C, 61.10; H, 2.80; N, 6.48; S 14.83. IR (KBr): ν, cm^{-1} 3417 (OH); 2229 (C≡N); 1710 (C=O); 1104 (Ar–S–Ar).

Synthesis of cobalt complex of phthalocyanines

General method. Carefully stirred mixture of 0.33 mmol of corresponding substituted phthalonitrile, 54 mg (0.20 mmol) of cobalt chloride hexahydrate and 60 mg (1 mmol) of urea was held under the temperature of 190–195 °C until solidifying of the reaction mixture. Next, it was stirred, washed with acidic water and acetone, then dried on air under 70–80 °C.

Cobalt tetra-4-nitro-tetra-5-(4-carboxyphenoxy) phthalocyaninate (Co(O)Pc1). It was synthesized from 101 mg of phthalonitrile **2**. Yield 62 mg (58%). Elemental analysis found C, 55.10; H, 2.54; N, 13.15%. Anal. calcd. for ($C_{60}H_{28}N_{12}O_{20}Co$) C, 55.61; H, 2.18; N, 12.97. IR (KBr): ν, cm^{-1} 3463 (OH), 1722 (C=O), 1509 (NO_2), 1384 (NO_2), 1263 (Ar–O–Ar). MS (MALDI-TOF): *m/z* 1294.90 $[M]^-$, calcd. [M] 1295.09.

Cobalt tetra-4-nitro-tetra-5-(4-carboxyphenoxyulphanyl)phthalocyaninate (Co(S)Pc2). It was synthesized from 108 mg of phthalonitrile **3**. Yield 67 mg (60%). Elemental analysis found C, 53.17; H, 2.20; N, 12.00%. Anal. calcd. for ($C_{60}H_{28}N_{12}O_{16}S_4Co$) C, 52.98; H, 2.07; N, 12.36. IR (KBr): ν, cm^{-1} 3440 (OH), 1719 (C=O), 1589 (NO_2), 1404 (NO_2) 1194 (Ar–S–Ar), 1050 (N=N), 744 (C–N). MS (MALDI-TOF): *m/z* 1382.18 [M + Na], calcd. M 1359.01.

Cobalt tetra-4-nitro-tetra-5-(4-carboxyphenylamino)phthalocyaninate (Co(NH)Pc3). It was synthesized from 101 mg of phthalonitrile **4**. Yield 51 mg (48%). Elemental analysis found C, 56.00; H, 2.38; N, 18.00%. Anal. calcd. for ($C_{60}H_{32}N_{16}O_{16}Co$) C, 55.78; H, 2.50; N, 17.35. IR (KBr): ν, cm^{-1} 3432 (OH), 3192 (NH), 1703 (C=O), 1379 (NO_2). MS (MALDI-TOF): *m/z* 1326.36 $[M + 2H_2O - H]^-$, calcd. [M] 1291.15.

Cobalt octa-4,5-(4′-carboxyphenoxy)phthalocyaninate (Co(O)Pc4). It was synthesized from 120 mg of phthalonitrile **5**. Yield 82 mg (60%). Elemental analysis found C, 63.10; H, 3.04; N, 6.55%. Anal. calcd. for ($C_{88}H_{48}N_8O_{24}Co$) C, 63.66; H, 2.91; N. 6.75. IR (KBr): ν, cm^{-1} 3443 (OH); 1712 (C=O); 1224 (Ar–O–Ar). MS (MALDI-TOF): *m/z* 1676.17 $[M + H_2O - H]^+$; calcd. [M] 1659.31.

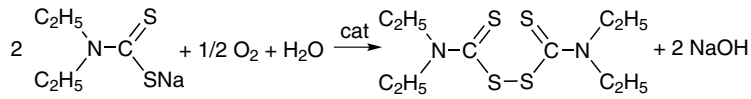
Cobalt octa-4,5-(4′-carboxyphenylsulfanyl)phthalocyaninate (Co(O)Pc5). It was synthesized from 130 mg of phthalonitrile **6**. Yield 95 mg (64%). Elemental analysis found C, 59.17; H, 2.82; N, 6.10%. Anal. calcd. for ($C_{88}H_{48}N_8O_{16}S_8Co$) C, 59.09; H, 2.70; N, 6.26. IR (KBr): ν, cm^{-1} 3447 (OH), 1711 (C=O), 1104 (Ar–S–Ar). MS (MALDI-TOF): *m/z* 1789.78 $[M + 2H]^+$; calcd. [M] 1787.03.

Cobalt octa-4,5-(4′-carboxyphenylamino)phthalocyaninate (Co(O)Pc6). It was synthesized from 120 mg of phthalonitrile **7**. Yield 50 mg (37%). Elemental analysis found C, 63.70; H, 3.55; N, 13.18%. Anal. calcd. for ($C_{88}H_{56}N_{16}O_{16}Co$)C, 63.96; H, 3.42; N, 13.56. IR (KBr): ν, cm^{-1} 3413 (OH); 3172 (NH); 1703 (C=O); 1602 (NH); 1434 (NH). MS (MALDI-TOF): *m/z* 1652.36 $[M + H]^+$; calcd. [M] 1651.34.

Studies of catalytic activity

The catalytic activity of metallophthalocyanines was tested with a known [32, 33] reaction of sodium *N*,*N*-diethylcarbamodithioate (DTC) oxidation. It proceeds according to general scheme:

Advantages of this reaction are low toxicity of initial materials and possibility of monitoring of concentration



Scheme 4. Oxidation of DTC

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 $L.min^{-1}$. 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 Equation 9.

$$k_w^{298} = \frac{k_{obs}}{c_{DTC}^{i}} \quad (9)$$

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

$$E^{\neq} = 19.1\left(\frac{T_1T_2}{T_2 - T_1}\right)\lg\frac{k_2}{k_1} \quad (10)$$

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 Equation 11:

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

Degree of transformation was calculated according to Equation 12:

$$\chi = (c_0 - c_\tau)/c_0 \quad (12)$$

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): δ, ppm 11.65, 27.50, 49.11, 205.02. IR of DTC oxidation IR (KBr): ν, cm^{-1} 2979 (–CH_3 υ_{as}), 2847 (–CH_2–υ_{as}), 1476 (–CH_2–δ), 1378 (–C–N *st*), 1269 (–C = S *st*), 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): δ, ppm 10.49, 25.72, 52.04, 51.26, 190.05. IR of Thiuram E obtained by DTC oxidation IR (KBr): ν, cm^{-1} 2975 (–CH_3 υ_{as}), 2861 (–CH_2–υ_{as}), 1505 (–CH_2–δ), 1380 (–C–N *st*), 1273 (–C=S *st*), 1143, 995 (–S–S–).

CONCLUSION

Bifunctional- and symmetrical substituted phthalonitriles and cobalt phthalocyanines based on it were synthesized in the work by nucleophilic substitution of brome in 4-bromo-5-nitrophthalonitrile on residues of benzoic acids. All synthesized macrocycles have catalytic activity in oxidation of *N*,*N*-carbomodithiolate. The nature of peripheral substituents affects rate and mechanism of the oxidation significantly. Introduction of electron acceptor groups in periphery of the phthalocyanine molecule leads to increase of catalytic activity.

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