

## Investigation of Catalytic Processes of Thio–Compounds Conversion to Disulfides Using Novel Butyl/Butoxy–Phthalocyaninates of d–Metals

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Dedicated to the memory of Prof. Andrey F. Mironov

*By the nucleophilic substitution of nitro group in 4-nitrophthalonitrile, novel 4-(4-butylphenoxy) and 4-(4-butoxyphenoxy)phthalonitriles were obtained, which were used to synthesize phthalocyanines and complexes with copper, cobalt and zinc. The structures of the compounds obtained were confirmed by FT-IR and NMR (one and two dimensional) spectroscopy, MALDI-TOF mass spectrometry and elemental analysis. The spectroscopic and catalytic properties as well as resistance to heating of the obtained compounds were studied. The compounds investigated showed high thermal resistance in comparison with the known complexes, which determines their profitability. The complexes were found to exhibit high catalytic activity in desulfurization reaction, which, along with high stability, indicates the prospects of their use as catalysts for Thiuram E obtaining.*

**Keywords:** Phthalocyanines, metal complexes, spectroscopy, catalysis, thiuram E.

## Исследование каталитических процессов превращения тиосоединений в дисульфиды с использованием новых бутил/бутоксифталоцианинатов d–металлов

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Путем нуклеофильного замещения нитрогруппы в 4-нитрофталонитриле были получены новые 4-(4-бутилфенокси) и 4-(4-бутоксифенокси)фталонитрилы, на основе которых получены фталоцианины и комплексы с медью, кобальтом и цинком. Структура полученных соединений подтверждена методами ИК- и ЯМР (одно- и двумерной) спектроскопии, MALDI-TOF масс-спектрометрии и элементного анализа. Изучены спектральные и каталитические свойства, а также устойчивость полученных соединений к нагреванию. Исследованные соединения показали высокую термическую стойкость по сравнению с известными комплексами. Показано, что комплексы проявляют высокую каталитическую активность в реакции десульфуризации, что, наряду с высокой стабильностью, указывает на перспективность их использования в качестве катализаторов для получения Тиурама Е.

**Ключевые слова:** Фталоцианины, металлокомплексы, спектроскопия, катализ, тиурам Е.

## Introduction

Phthalocyanine is a planar aromatic macrocyclic system in which four diiminoisoindoline units are conjugated into a common 18- $\pi$  electronic system.<sup>[1,2]</sup> Non-substituted on the periphery phthalocyanines or not containing a metal in the coordination center is not of particular interest due to the high aromaticity<sup>[3,4]</sup> and low reactivity of its structure.<sup>[5,6]</sup> In addition, phthalocyanine is insoluble in water and most organic solvents, and has limited solubility under stringent conditions in concentrated sulfuric acid.<sup>[7,8]</sup> The introduction of the *d*- or *f*-metal into the centre of the phthalocyanine molecule and functional fragments at its periphery leads to a radical change in its physical and chemical properties. Substituted metal phthalocyanines have been used as materials<sup>[9]</sup> for many applications such as chemical sensors,<sup>[10–12]</sup> solar cells,<sup>[13–16]</sup> thin films,<sup>[17–19]</sup> liquid crystals,<sup>[20–22]</sup> optical data storage devices, electrochromic display devices,<sup>[23–25]</sup> photosensitizers for dye sensitized solar cells<sup>[13]</sup> and oxidation or reduction catalysts and photocatalysts,<sup>[26]</sup> photodynamic therapy.<sup>[27,28]</sup> In addition, varying the nature of the peripheral environment makes it possible to control the solubility of these compounds,<sup>[29,30]</sup> for example, the introduction of sulfonic, carboxylic or crown ether groups gives amphiphilicity to these compounds. Substitution by alkyl fragments makes it possible to obtain organosoluble metal phthalocyaninates with mesomorphic properties.<sup>[31]</sup>

Some voluminous oxyaryl fragments give the phthalocyanine compounds, in addition to the dyeing properties, also antimicrobial properties,<sup>[8]</sup> which makes it possible to obtain so-called “smart” textile materials and use them in everyday human life for the manufacture of medical materials<sup>[32,33]</sup> and clothes. Also, the presence of reactive groups on the periphery of the phthalocyanine macrocycle allows it to be covalently attached to solid-phase carriers and to obtain materials, for example, having catalytic properties in the oxidation of phenol and its derivatives or mercaptan.<sup>[26]</sup>

In addition, recently the possibility of using phthalocyanine complexes as catalysts for the purification of oil fractions from mercaptan derivatives,<sup>[34–36]</sup> which strongly pollute the environment, has been considered. In this direction, substituted metal complexes with flexible long substituents on the periphery have proven themselves well.<sup>[35,36]</sup> Unfortunately, this problem is at the stage of research and a clear structure of the complex, operating stably under various conditions, has not been determined.

The oxidation of thio-compounds (RSH) solves the environmental problems of desulfurization of oil products, as well as the problems of organic synthesis of practically important disulfides, for example, disulfirams.<sup>[37]</sup> Disulfirams exhibit valuable properties in terms of synthetic or biological processes.<sup>[38]</sup> They are used as fungicides, the components of drugs necessary for the treatment of alcoholism and human immunodeficiency.<sup>[39]</sup> Disulfiram inhibits the production of acetaldehyde dehydrogenase in the liver, preventing the destruction of ethyl alcohol into carbon dioxide and water, which occurs at the stage of acetaldehyde.

It should be noted tetramethylthiuram disulfide, which has found application as a vulcanization accelerator of rubber compounds based on natural and synthetic diene type rubbers<sup>[40]</sup> and anti-drugs.<sup>[41]</sup> The synthesis of tetramethylthiuram is easily carried out by liquid-phase oxidation of *N,N*-diethylcarbamodithiolate (DTC) or its sodium salt in an alkaline medium in the presence of a catalyst,<sup>[42]</sup> however, there are technological difficulties associated with controlling the oxidation process.<sup>[43,44]</sup> The usage of classical inorganic catalysts in this process leads to the formation of a mixture of oxidation products.

The usage of metal complexes with organic macroheterocyclic ligands, for example, phthalocyanines, as catalysts increases the selectivity of this process and allows the use of atmospheric oxygen as an oxidizing agent. This helps to avoid harsh reaction conditions and, therefore, increases the purity of the final product. The use of air oxygen in the processes of their production improves the quality of the target product.<sup>[45,46]</sup>

There is data in the literature on tetrasubstituted copper phthalocyanine containing 4-carboxybiphenyloxy groups on the periphery,<sup>[10]</sup> which, in a composition with a perylene derivative, exhibits high photocatalytic activity. The presence of bulk aryloxy substituents in the phthalocyanine molecule, for example, methylbiphenyloxy groups, provides them with good solubility in organic solvents, which facilitates the process of isolation and purification of the target products, and also expands the possible areas of application of these compounds.

Due to the low reactivity of phthalocyanine, the direct introduction of the necessary functional substituents on its periphery is very difficult. The most promising method is template cyclotetramerization of substituted phthalonitriles around a metal cation.<sup>[47]</sup> This method allows the most selective production of metal phthalocyaninates with a high yield of the target product.<sup>[48]</sup> Modification of the nitriles used for phthalocyaninates synthesis and analysis of their

stability under the conditions of template condensation in connection with obtaining a stable peripheral environment is very important for the production of metallophthalocyanines with liquid crystalline and catalytic properties.

In this work, we propose an approach to synthesize 4-(4-butylphenoxy)- (**2**) and 4-(4-butyloxy)phenoxyphthalonitriles (**3**), as well as free phthalocyanines and metal complexes based on them with cobalt, copper, and zinc as potential catalysts for oil demercaptanization. For the obtained compounds, the conditions of thermal degradation were determined and the catalytic activity was checked, which determined their potential for use as sensors and catalysts.

## Experimental

All reagents and starting materials were purchased from commercial sources and used as received. When necessary, solvents were purified following standard literature procedures.<sup>[37]</sup> Some reactions were carried out under an inert atmosphere, as specified in experimental procedures.

Electronic absorption spectra were recorded in organic solvents (DMF and chloroform) and concentrated sulfuric acid on a Shimadzu UV-2700 radiation spectrophotometer at a temperature of 298.15 K in the wavelength range 325–900 nm. For temperature control, a Peltier cell was used. FT-IR spectra were recorded on IRAffinity-1S Shimadzu in the region of 400–4000  $\text{cm}^{-1}$  in thin films (chloroform) and in tablets with potassium bromide. Elemental analysis was performed on an elemental analyzer CHNS-OFlashEA, 1112 series.  $^1\text{H}$  NMR and  $^{13}\text{C}$  NMR spectra for phthalonitriles were recorded on the Bruker Avance III 500 spectrometer. The operating frequency on  $^1\text{H}$  cores was 500.17 MHz, on  $^{13}\text{C}$  cores – 125.77 MHz. The error in determining the chemical shift did not exceed 0.01 ppm. The chemical shifts  $^1\text{H}$ ,  $^{13}\text{C}$  were determined relative to the internal TMS standard. NMR spectra were recorded in deuterated chloroform ( $\text{CDCl}_3$ ) at  $T = 294$  K. Mass spectra (MALDI-TOF) were obtained on a Shimadzu Biotech Axima Confidence mass spectrometer in the mode of registration of positive ions. 2,5-Dihydroxybenzoic acid was used as a matrix. Melting points were determined using a small Boetius type heating table with an RNMK 05 observation device. Thermooxidative degradation studies of synthesized phthalonitriles were carried out on a STA449 F3 Jupiter Netzsch synchronous thermal analysis apparatus in an argon atmosphere and argon – oxygen mixture, heating rate – 5 deg/min, crucible material – platinum. Before conducting elemental and thermogravimetric analysis, samples of the studied compounds were subjected to sample preparation at 110 °C for 2 h.

### Nitrile Synthesis

*General technique.* To a mixture of 10 mmol (1.73 g) of 4-nitrophthalonitrile and 10 mmol of the phenol derivative in 30 mL of dimethylformamide a solution of 10 mmol (1.56 g) of  $\text{K}_2\text{CO}_3$  in 10 mL of water was added. The reaction mass was stirred at 90–95 °C for 1.5 h and cooled. After cooling, the precipitate was filtered off, washed with 2-propanol (50 mL), water ( $3 \times 50$  mL) and dried at 30 °C. An alternative synthetic routes are described in other works.<sup>[49–52]</sup>

*4-(4-Butylphenoxy)phthalonitrile (2).* Yield: 1.56 g (77 %).  $T_{\text{melt.}} = 69\text{--}72$  °C. Found, %: C 78.05, H 5.98, N 10.10.  $\text{C}_{18}\text{H}_{16}\text{N}_2\text{O}$ . Calculated, %: C 78.24; H 5.84; N 10.14.  $^1\text{H}$  NMR ( $\text{CDCl}_3$ )  $\delta$  ppm: 7.72 d (1H;  $\text{H}^{12}$ ,  $^3J=8.7$  Hz), 7.28 d (2H;  $\text{H}^{4,5}$ ,  $^3J=8.47$  Hz), 7.27 s (1H;  $\text{H}_9$ ), 7.29 dd (1H;  $\text{H}^{10}$ ,  $^3J=8.47$  Hz,  $^4J=2.52$  Hz), 7.0 d (2H;  $\text{H}^{2,3}$ ,  $^3J=8.7$  Hz), 2.67 t (2H;  $\text{H}^{18}$ ,  $^3J=7.78$  Hz), 1.65 q (2H;  $\text{H}^{19}$ ,  $^3J=7.67$  Hz), 1.41 hx (2H;  $\text{H}^{20}$ ,  $^3J=7.49$  Hz), 0.97 t. (3H;  $\text{H}^{21}$ ,  $^3J=7.25$  Hz). FT-IR

$\nu$   $\text{cm}^{-1}$ : 2946, 2856 ( $\text{C}_{\text{Alk}}\text{-H}$ ), 2231 (CN), 1591 ( $\text{C}_{\text{Ar}}\text{-C}_{\text{Ar}}$ ), 1502, 1487 ( $\text{C}_{\text{Alk}}\text{-H}$ ), 1253 (C-O-C).

*4-(4-Butoxyphenoxy)phthalonitrile (3).* Yield: 2.36 g (81 %).  $T_{\text{melt.}} = 65\text{--}66$  °C. Found, %: C 73.78, H 5.75, N 9.39.  $\text{C}_{18}\text{H}_{16}\text{N}_2\text{O}_2$ . Calculated, %: C 73.95; H 5.52; N 9.58.  $^1\text{H}$  NMR ( $\text{CDCl}_3$ )  $\delta$  ppm: 7.72 d (1H;  $\text{H}^{12}$ ,  $^3J=8.6$  Hz), 7.25 s (1H;  $\text{H}^9$ ), 7.23 dd (1H;  $\text{H}^{10}$ ,  $^3J=8.47$  Hz,  $^4J=2.52$  Hz), 7.0 d (2H;  $\text{H}^{4,5}$ ,  $^3J=9.18$  Hz), 6.97 d (2H;  $\text{H}^{2,3}$ ,  $^3J=9.18$  Hz), 4.0 t (2H;  $\text{H}^{18}$ ,  $^3J=6.58$  Hz), 1.82 q (2H;  $\text{H}^{19}$ ,  $^3J=7.15$  Hz), 1.55 hx (2H;  $\text{H}^{20}$ ,  $^3J=7.44$  Hz), 1.02 t (3H;  $\text{H}^{19}$ ,  $^3J=7.34$  Hz). FT-IR  $\nu$   $\text{cm}^{-1}$ : 2930, 2867 ( $\text{C}_{\text{Alk}}\text{-H}$ ), 2226 (CN), 1589 ( $\text{C}_{\text{Ar}}\text{-C}_{\text{Ar}}$ ), 1507, 1477 ( $\text{C}_{\text{Alk}}\text{-H}$ ), 1239, 1199 (C-O-C).

### Synthesis of Tetra(4-butyl/butoxy-phenoxy)phthalocyanines of Co, Zn and Cu

*General technique.* A thoroughly ground mixture of 1 mmol of the corresponding substituted phthalonitrile **2–3** and 0.3 mmol of the acetate of the corresponding metal was heated at 185–190 °C until solidification. Then the reaction mass was washed with dilute hydrochloric acid and water until the reaction to chloride anions with silver nitrate disappeared, then it was dried in air at 70–80 °C. The final purification was performed by silica gel column chromatography M 60, eluting with chloroform.

*Tetra(4-butylphenoxy)phthalocyaninatocobalt (4a).* Yield: 0.25 g (86 %). Found, C 74.12; H 5.67; N 9.57;  $\text{C}_{72}\text{H}_{64}\text{CoN}_8\text{O}_4$ . Calculated, % C 74.28; H 5.54; N 9.62.  $m/z$ : 1164.29  $[\text{M}]^+$  calculated 1164.29. FT-IR  $\nu$   $\text{cm}^{-1}$ : 2942, 2857 ( $\text{C}_{\text{Alk}}\text{-H}$ ), 1252 (C-O-C).

*Tetra(4-butylphenoxy)phthalocyaninatocopper (4b).* Yield: 0.24 g (82 %). Found, %: C 73.90; H 5.61; N 9.53.  $\text{C}_{72}\text{H}_{64}\text{CuN}_8\text{O}_4$ . Calculated, %: C 73.98; H 5.52; N 9.59.  $m/z$ : 1168.89  $[\text{M}]^+$ , calculated 1168.90. FT-IR  $\nu$   $\text{cm}^{-1}$ : 2940, 2856 ( $\text{C}_{\text{Alk}}\text{-H}$ ), 1252 (C-O-C).

*Tetra(4-butylphenoxy)phthalocyaninatozinc (4c).* Yield: 0.23 g (80 %). Found, %: C 73.85; H 5.54; N 9.55.  $\text{C}_{72}\text{H}_{64}\text{ZnN}_8\text{O}_4$ . Calculated, %: C 73.87; H 5.51; N 9.57.  $m/z$ : 1171.72  $[\text{M}+\text{H}]^+$ , calculated 1170.74. FT-IR  $\nu$   $\text{cm}^{-1}$ : 2941, 2856 ( $\text{C}_{\text{Alk}}\text{-H}$ ), 1250 (C-O-C).

*Tetra(4-butoxyphenoxy)phthalocyaninatocobalt (5a).* Yield: 0.21 g (69 %). Found, % C 70.34; H 5.30; N 9.09.  $\text{C}_{72}\text{H}_{64}\text{CoN}_8\text{O}_8$ . Calculated, % C 70.41; H 5.25; N 9.12.  $m/z$ : 1228.28  $[\text{M}]^+$ , calculated 1228.29. FT-IR  $\nu$   $\text{cm}^{-1}$ : 2867, 2930 ( $\text{C}_{\text{Alk}}\text{-H}$ ), 1240, 1196 (C-O-C).

*Tetra(4-butoxyphenoxy)phthalocyaninatocopper (5b).* Yield: 0.20 g (65 %). Found, % C 70.06; H 5.40; N 9.01.  $\text{C}_{72}\text{H}_{64}\text{CuN}_8\text{O}_8$ . Calculated, % C 70.14; H 5.23; N 9.09.  $m/z$ : 1232.90  $[\text{M}]^+$ , calculated 1232.90. FT-IR  $\nu$   $\text{cm}^{-1}$ : 2868, 2932 ( $\text{C}_{\text{Alk}}\text{-H}$ ), 1239, 1198 (C-O-C).

*Tetra(4-butoxyphenoxy)phthalocyaninatozinc (5c).* Yield: 0.21 g (68 %). Found, % C 70.02; H 5.29; N 9.06.  $\text{C}_{72}\text{H}_{64}\text{ZnN}_8\text{O}_8$ . Calculated, % C 70.04; H 5.22; N 9.08.  $m/z$ : 1233.72  $[\text{M}+\text{H}]^+$ , calculated 1234.73. FT-IR  $\nu$   $\text{cm}^{-1}$ : 2868, 2931 ( $\text{C}_{\text{Alk}}\text{-H}$ ), 1237, 1198 (C-O-C).

### Synthesis of Tetra(4-butyl/butoxy-phenoxy)phthalocyanines

*General technique.* A thoroughly ground mixture of 1 mmol of the corresponding substituted phthalonitrile **2–3** and 0.3 mmol of magnesium acetate was heated at 185–190 °C until it solidified. After cooling, the reaction mass was triturated in a mortar and boiled in diluted hydrochloric acid for 20 minutes. The precipitate was filtered off and washed with water until the reaction to chloride anions with silver nitrate disappeared, then it was dried in air at 70–80 °C. The final purification was carried out by column chromatography on silica gel M 60, eluting with chloroform.

*Tetra(4-butylphenoxy)phthalocyanine (6).* Yield: 0.19 g (70 %). Found, %: C 78.06; H 6.06; N 10.10.  $\text{C}_{72}\text{H}_{66}\text{N}_8\text{O}_4$ . Calculated, %: C 78.09; H 6.01; N 10.12.  $m/z$ : 1107.36  $[\text{M}]^+$ , calculated 1107.37. FT-IR  $\nu$   $\text{cm}^{-1}$ : 2942, 2857 ( $\text{C}_{\text{Alk}}\text{-H}$ ), 1252 (C-O-C), 1006 ( $\text{H}_2\text{Pc}$ ).



*Tetra(4-butoxyphenoxy)phthalocyanine (7)*. Yield: 0.19 g (65 %). Found, % C 73.80; H 5.70; N 9.55.  $C_{72}H_{66}N_8O_8$ . Calculated, % C 73.83; H 5.68; N 9.57.  $m/z$ : 1171.37  $[M]^+$ , calculated, 1171.37. FT-IR  $\nu$   $cm^{-1}$ : 2867, 2930 ( $C_{alk}-H$ ), 1240, 1198 (C-O-C), 1105 ( $H_2Pc$ ).

### Catalytic Activity Study

Catalytic activity is assessed based on the values of the effective rate constant of aerobic oxidation of sodium *N,N*-diethyldithiocarbamate in the presence of a catalyst and at specified values of acidity and temperature of the system. The reaction is carried out in a batch reactor equipped with a thermometer, a stirrer, a reflux condenser, a sampling outlet and a barometer allowing continuous air supply to the reactor at a rate of 2 L/min, which ensures the oxidation in the kinetic region. A solution of sodium *N,N*-diethyldithiocarbamate with a concentration of 0.1 g/L is loaded into the reactor. Next, a zero sample is taken (2 mL, a sample before the catalyst was introduced), then the catalyst is placed in the reactor and the air supply is turned on, after which 2 mL samples are taken every 15 minutes (up to the 150th minute). After taking each of the samples, they are mixed with 4 mL of a 0.02 N solution of copper sulfate  $CuSO_4$ , observing the formation of a dark brown precipitate of the copper complex. The mixture is stirred and 5 mL of chloroform, 3 drops of 50 % acetic acid are added to them in turn and shaken for 2 minutes in order to extract organic compounds. Further, the organic fractions containing the copper complex of *N,N*-diethyldithiocarbamate are transferred into separate flasks, after which the extraction from the aqueous fractions is repeated to increase the accuracy of further analysis. The obtained solutions of the copper complex are brought to the mark, then 2 mL samples are taken from them, after which the absorption spectra of the obtained solutions are recorded at a wavelength of 436 nm in order to determine the optical density at the absorption maximum and further calculate the effective oxidation constants.

Considering the constancy of oxygen concentration the reaction rate is described by kinetic equation of first order:

$$\delta c / \delta \tau = -k_{obs} c, \quad (1)$$

where  $c$  – current concentration of DTC,  $\tau$  – time,  $k_{obs}$  – observed rate constant of the reaction.

It is confirmed by rectilinear character of the dependence  $\ln c = f(\tau)$  and constancy of rate constants calculated by the equation:

$$k_{obs} = (1/\tau) \ln(c_0/c) \quad (2)$$

here  $c_0$  – initial concentration of diethyldithiocarbamate,  $c$  – current DTC concentration at a time  $\tau$ .

It was found in prior experiments, that non-catalytic oxidation of DTC is very slow ( $k_{obs} = 1.7 \cdot 10^{-5} s^{-1}$ ). Disulfide formation was monitored by FT-IR,  $^1H$  and  $^{13}C$  NMR spectra.  $^1H$  NMR of DTC after oxidation (500 MHz,  $D_2O$ )  $\delta$  ppm: 4.34 (m,  $J = 15$  Hz,

4H,  $CH_2$ ); 1.39 (t,  $J = 5$  Hz, 6H,  $CH_3$ ).  $^{13}C$  NMR of DTC after oxidation (100 MHz)  $\delta$  ppm: 11.65; 27.50; 49.08; 205.02. IR of DTC after oxidation (KBr)  $\nu$   $cm^{-1}$ : 2979 ( $-CH_3 \nu_{as}$ ); 2847 ( $-CH_2- \nu_{as}$ ); 1476 ( $-CH_2- \delta$ ); 1378 ( $-C-N$  st); 1269 ( $-C=S$  st); 1075, (d,  $-C-S$ ). During oxidation of DTC the formation of tetramethylthiuram disulfide (TMTD) is observed.  $^1H$  NMR of TMTD obtained by DTC oxidation (500 MHz,  $CDCl_3$ )  $\delta$  ppm: 3.71–3.77 (m, 8H,  $CH_2$ ); 1.29–1.23 (m, 12H,  $CH_3$ ).  $^{13}C$  NMR of TMTD obtained by DTC oxidation (100 MHz)  $\delta$  ppm: 10.49; 25.72; 52.04; 51.26; 190.05. IR of TMTD obtained by DTC oxidation (KBr)  $\nu$   $cm^{-1}$ : 2974 ( $-CH_3 \nu_{as}$ ), 2861 ( $-CH_2- \nu_{as}$ ), 1505 ( $-CH_2- \delta$ ), 1380 ( $-C-N$  st), 1273 ( $-C=S$  st), 1143, 995 (S-S).

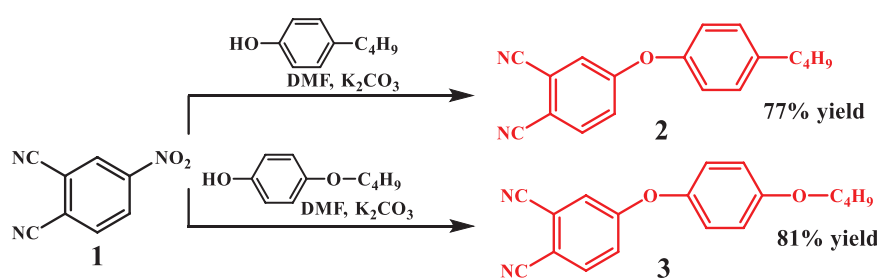
### Results and Discussion

This work presents data on the synthesis and study of 4-(4-butylphenoxy)- (**2**) and 4-(4-butoxy)phenoxyphthalonitriles (**3**) and phthalocyanines based on them.

As the starting compound for the synthesis of 4-(4-butyl/butoxyphenoxy)phthalonitriles (**2**, **3**), 4-nitrophthalonitrile (**1**) was used (Scheme 1). The electron-withdrawing cyano- groups present in the benzene core of compound (**1**) create a sufficiently effective positive charge on the carbon atom bonded to the nitro group, which causes its substitution under the action of a nucleophilic reagent. Butylphenol and butoxyphenol were used as nucleophiles. The reaction was carried out in dimethylformamide solution in the presence of potassium carbonate as an alkaline agent.

The synthesized phthalonitriles are white powders having a relatively low melting point. The obtained compounds were identified using  $^1H$  and  $^{13}C$  NMR, IR, and electron spectroscopy data.

Using the Gaussian software package (DFT method, B3LYP / 631-G + basis (d, p)), the theoretical IR spectra of the synthesized phthalonitriles were calculated, which show good agreement with the experimental data (Figure 1S, *Supporting Materials*). In the IR spectra of phthalonitriles **2**, **3**, absorption was observed in the region of 2226–2231  $cm^{-1}$ , corresponding to stretching vibrations of the nitrile group, and bands of stretching vibrations of C-H bonds of methyl and methylene groups were recorded in the region of 2856–2646  $cm^{-1}$ . The stretching vibrations of multiple C–C aromatic bonds were observed at 1589  $cm^{-1}$  (**3**) and 1591  $cm^{-1}$  (**2**), and in the region of 1477–1507  $cm^{-1}$ , deformation vibrations of the C–H bonds of methyl and methylene groups were noted. The deformation vibrations of the  $C_{Ar}-O-C_{Ar}$  bond are found at 1239  $cm^{-1}$  (**3**) and 1253  $cm^{-1}$  (**2**). Also, in the IR spectrum of 4-(4-butoxyphenoxy)phthalonitrile band appears at 1199  $cm^{-1}$ , cor-



**Scheme 1.** Synthesis of initial butyl/butoxy-substituted phthalonitriles.

responding to vibrations of the  $C_{Ar}$  bond  $-O-C_{Alk}$  (Figure 1S).

The good solubility of the synthesized phthalonitriles (**2**, **3**) in organic solvents, in particular chloroform, made it possible to study them by  $^1H$ ,  $^{13}C$  NMR spectroscopy (Figures 2S, 3S). Figure 2S presents the experimental (a) and theoretical (b)  $^1H$  NMR spectra of compound **2**. There are no impurity signals in the spectrum, which confirms the purity of the obtained compound. An analysis of chemical shifts and integrated intensities in the  $^1H$  NMR spectrum unambiguously proves the structure of this compound (see Experimental part and Figure 2aS).

Experimental (a) and theoretical (b)  $^{13}C$  NMR spectra of phthalonitrile **2** are shown in Figure 3S. In a weak field (110 – 170 ppm), there are 14 signals from carbon nuclei of the aromatic part of the molecule. The signals  $C_8$ ,  $C_1$ ,  $C_6$  are most unscreened due to the influence of the oxygen atom on the electron density distribution. The chemical shifts of nuclei 2,3 and 4,5, respectively, coincide due to magnetic equivalence. In a weak field, there are 4 signals from an aliphatic substituent. We note a fairly good correlation between the experimental (Figure 3aS) and theoretical (Figure 3bS) chemical shifts  $^{13}C$ .

In addition to theoretical spectra, two-dimensional correlation spectra COSY  $^1H$ - $^1H$  (Figure 4S), HSQC  $^{13}C$ - $^1H$  (Figure 5S), HMBC  $^{13}C$ - $^1H$  (Figure 6S) were used to assign NMR signals. COSY  $^1H$ - $^1H$  correlation spectroscopy makes it possible to evaluate the magnetic interactions between protons through the electrons of the chemical bonds that separate them. For compound **2**, Figure 4S shows the signals from the interaction of aromatic protons  $H_{12}$ - $H_{10}$ ;  $H_3$ - $H_5$ ; ( $H_2$ - $H_4$ ) and the aliphatic chain  $H_{18}$ - $H_{19}$ ;  $H_{19}$ - $H_{20}$ ;  $H_{20}$ - $H_{21}$ .

HSQC  $^1H$ - $^{13}C$  correlation spectroscopy makes it possible to evaluate magnetic interactions between carbon atoms of directly related protons, *i.e.* for C-H bonds (Figure 5S shows the corresponding signals of the carbon atoms of phthalonitrile **2**). HMBC correlation  $^1H$ - $^{13}C$  spectroscopy allows to evaluate long-distance interactions between carbon atoms by protons (usually through 2 or 3 bonds) (Figure 6S).

Figure 8S shows fragments of the spectra of nitriles **2** (1) and **3** (2), illustrating the effect of the introduction of an oxygen atom in the terminal substituent on chemical shifts. The introduction of oxygen into the aliphatic substituent leads to a shift of the signal of the protons of the 4, 5 phenyl ring into a strong field (increased magnetic shielding). At the same time, the signals of  $-CH_2-$  groups are

shifted to the weak field (de-screening) due to an increase in the electron density, with the strongest change occurring for the protons of the methyl group directly associated with oxygen.

Similar evolutions occur with chemical shifts of carbon nuclei (Figure 9S). Signals  $C_6$ ,  $C_{18}$  are shifted to a weak field, and  $C_1$ ,  $C_{4,5}$ ,  $C_{2,3}$ ,  $C_{19}$ ,  $C_{20}$  to a strong field due to the redistribution of electron density as a result of the introduction of an oxygen atom. In this case, the chemical shifts of carbon nuclei and protons of the phenyl ring with nitrile groups are practically unchanged.

The stability of the synthesized phthalonitriles **2**, **3** to thermal oxidative degradation was studied, as well as the effect of the oxidation ability between the terminal alkyl substituent and the phenoxy-group on this process.

It was found the melting points of these compounds practically coincide, and their thermal oxidation proceeds in the temperature range 200–320 °C. In this case, the mass loss in this temperature range in the case of 4-(4'-butylphenoxy)phthalonitrile **2** is 81.2 %, and the exo-pic corresponding to the maximum mass loss is observed at 220 °C. In the case of 4-(4'-butoxyphenoxy)phthalonitrile **3**, this exo-pic is shifted to higher temperatures up to 278 °C. Thus, it was found that the introduction of an oxy bridge between the phenoxy- group and the terminal alkyl fragment has practically no effect on the melting temperature, but increases the thermal stability of the corresponding phthalonitrile.

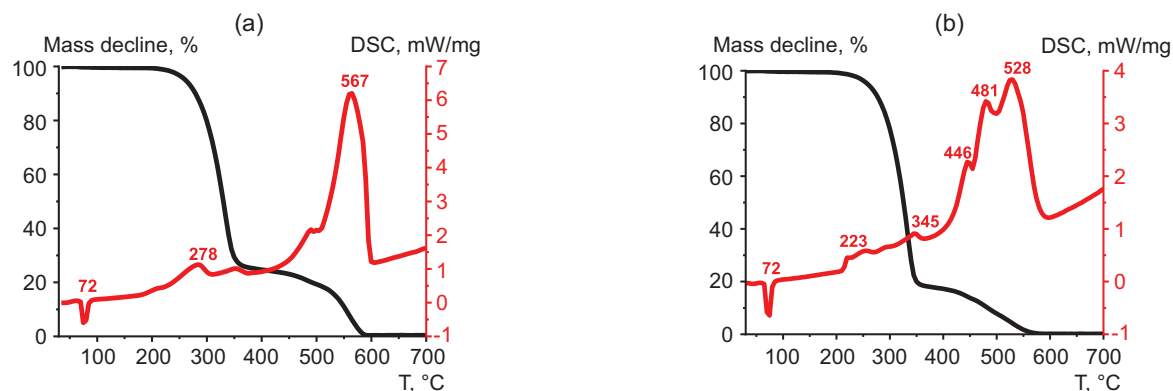
In addition, it was noted that under the synthesis conditions, the considered phthalonitriles **2**, **3** are stable and do not lose their chemical structure.

The synthesis of metal complexes **4–5** was carried out by the interaction of phthalonitriles **2–3** with cobalt, copper, and zinc acetates at 185–190 °C (Scheme 2).

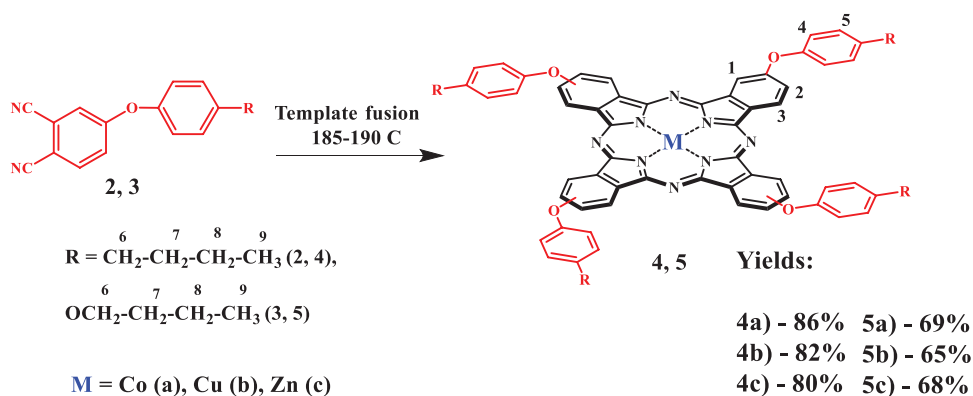
Free ligands **6–7** were obtained by fusion of substituted phthalonitriles with magnesium acetates and subsequent demetallation of magnesium complexes with hot hydrochloric acid (Scheme 3).

The synthesized compounds are colored powdery substances that dissolve in chloroform, acetone and DMF.

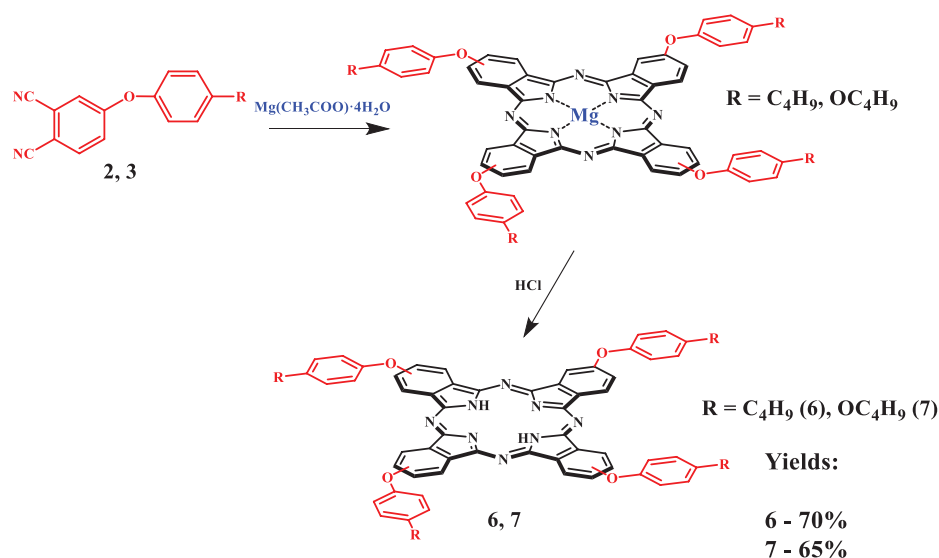
The composition and structure of the synthesized compounds were confirmed using elemental analysis, IR and electron spectroscopy, and MALDI-TOF spectrometry. Due to the presence of extended alkyl substituents, the complexes under study failed to crystallize and obtain a single



**Figure 1.** Thermograms of the nitriles synthesized: a) 4-(4'-butoxyphenoxy)phthalonitrile **3**, b) 4-(4'-butylphenoxy)phthalonitrile **2**.



**Scheme 2.** Synthesis of metal phthalocyaninates with butyl/butoxy fragments.



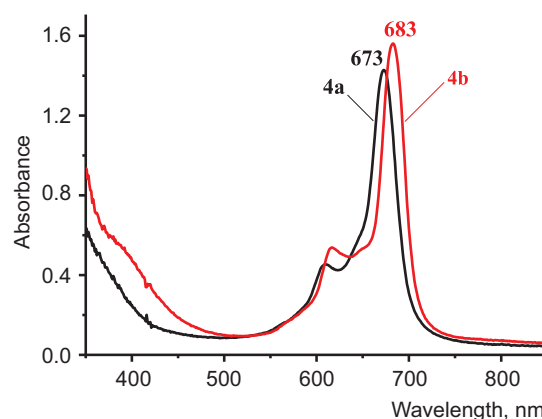
**Scheme 3.** Obtaining of metal free butyl/butoxyphthalocyanines.

crystal, thus, the study of the structure by X-ray analysis was impossible. Nevertheless, we have obtained and studied one-dimensional and two-dimensional NMR spectra to accurately confirm the structure of the complex.

The most informative mass spectrometric method for the study of synthesized phthalocyanines is the MALDI – TOF method. Signals of molecular ions corresponding to phthalocyanines were found in the mass spectra (Figures 10-17S).

The introduction of “bridge” oxygen into the substituent at the para position of the phenoxy-group practically does not affect the position of the *Q*-band in the electronic absorption spectra (Table 1). Thus, the shift of the long-wavelength absorption maximum for all the complexes obtained with such substitution does not exceed 1 nm.

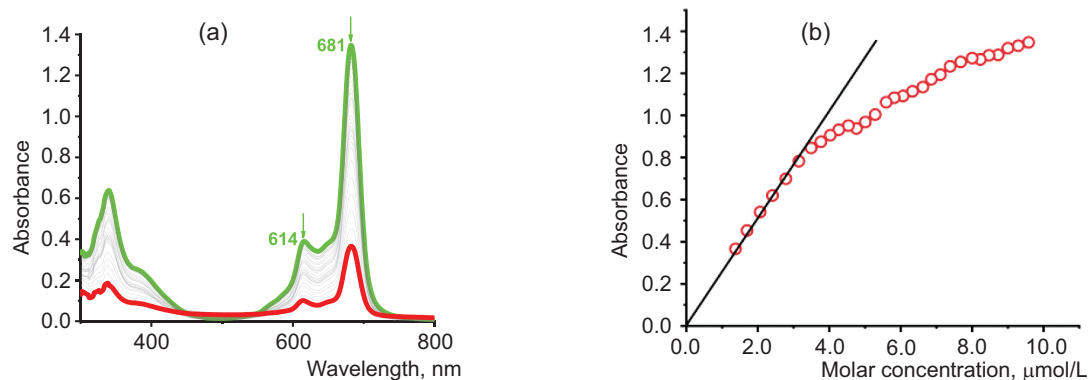
It was shown that the position of the main band in the UV-vis spectra recorded in chloroform is hypsochromically shifted by about 5–8 nm relative to the corresponding spectra recorded in DMF, acetone, and THF, the positions of which practically coincide. The UV-vis of the synthesized complexes (Figure 2) in the investigated series of organic solvents (chloroform, tetrahydrofuran,



**Figure 2.** Electronic absorption spectra of compounds 4a and 4b.

dimethylformamide, acetone) are in the associated form. Free bases, in comparison with their derivative complexes, are characterized by the presence in monomeric forms.

Copper and zinc phthalocyaninates showed limited solubility in dimethylformamide (to a concentration range



**Figure 3.** a) The spectral changes upon dilution of solution of compound **4b** in chloroform, b) the titration curve.

of about 0.1–1  $\mu\text{mol/L}$ , while cobalt complexes were also dissolved in large (up to 0.1 mmol/L) concentrations. Analyzing the nature of the spectral curves of the absorption bands for copper and zinc complexes, we can assume that they are in monomeric form, while cobalt phthalocyaninates in a solution in the form of a monomer can exist only up to concentrations of the order of 6  $\mu\text{M}$  (Figure 3). The solubility of cobalt complexes in DMF in the concentration range above 0.1  $\mu\text{M}$  is probably due to the lower propensity of these compounds for association to occur as compared to the corresponding copper and zinc phthalocyaninates, whose aggregates at this end titrations already precipitate.

In the electronic absorption spectra of the obtained phthalocyaninates, a bathochromic shift of the *Q*-band is observed upon transition from cobalt complexes to copper and zinc compounds (Table 1).

For copper complexes, thermal properties were studied due to the possibility of using them as liquid crystals.<sup>[53]</sup> Comparing the data of the thermal oxidative degradation of copper tetra(4-butyloxyphenoxy)phthalocyanine **5b** and the initial phthalonitrile **3**, it was noted that the onset of the decomposition process in phthalocyanine is shifted to the region of higher temperatures by 92  $^{\circ}\text{C}$ , while the temperature of the maximum exo-effect is shifted to lower temperatures 90  $^{\circ}\text{C}$  (Figure 4). In general, butyl-substitution showed better thermal stability for both starting phthalonitriles and phthalocyanine complexes compared to butoxy one, and the stability of the complexes investigated was found to be high.

### Heterogeneous Catalysis

High thermal stability for the detected phthalocyanines and their metal complexes determines their possible use as catalysts in fine organic synthesis. The catalytic properties were tested on a model reaction for the conversion of *N,N*-carbomodithiolate sodium to the corresponding disulfide in an aqueous alkaline medium. Oxidation of sodium *N,N*-carbomodithiolate (DTC) was studied in light-protected thermostatic cell of volume of 650 mL with DTC concentration range of 2.7–8.3 mmol/L under the temperatures of 20–40  $^{\circ}\text{C}$ . The experiments were carried out in water-alkali solutions under the *pH* values 8–10.

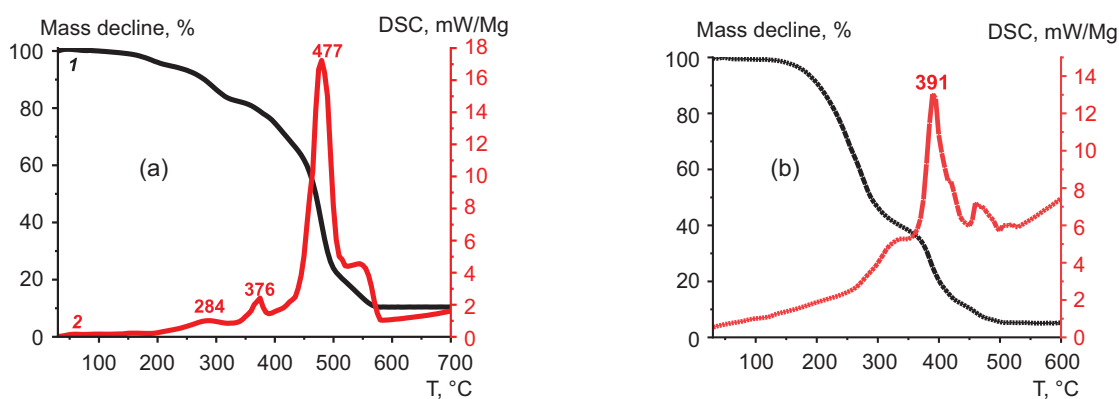
**Table 1.** Spectroscopic characteristics of metal phthalocyaninates in organic solvents.

Compounds	Q band, $\lambda_{\text{max}}$ , nm			
	Acetone	DMF	THF	$\text{CHCl}_3$
<b>4a</b>	665	666	664	673
<b>4b</b>	–	676	676	681
<b>4c</b>	674	–	676	682
<b>5a</b>	666	666	665	674
<b>5b</b>	–	676	677	683
<b>5c</b>	674	–	677	683
<b>6</b>	–	669, 699	667, 697	667, 704
<b>7</b>	–	669, 698	666, 697	666, 703

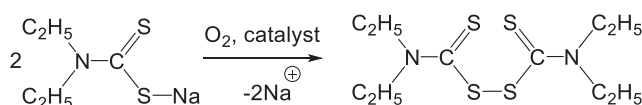
The oxidation of DTC proceeds according to the general Scheme 4.

Cobalt phthalocyaninate **4a** showed better efficiency compared to complex **5a** (Table 2).

Within 30 minutes, in the presence of **4a**, up to 50 % of the starting compound is converted to disulfide, while in the presence of **5a**, the conversion depth is at the level of 40 %. The effective rate constants in the presence of cobalt complexes are 65.4 and 47.3  $(\text{sec}\cdot\text{g})^{-1}$  for complexes **4a** and **5a**, respectively. For comparison, the DTC oxidation reaction was also performed with the addition of phthalocyanine ligands. In the presence of complexes **6** and **7**, DTC oxidation proceeds in the diffusion region, and the process parameters are close to those for non-catalytic aerobic oxidation. The degree of conversion to the target product does not exceed 4 % within 30 minutes of the reaction. These results show a greater efficiency of cobalt complexes in comparison with phthalocyanine ligands. It is noteworthy that for **6** the degree of conversion is slightly higher than for phthalocyanine **7**. A similar pattern is also observed for complexes of these ligands with cobalt. Obviously, this fact is due to the role of the peripheral environment of phthalocyanine macrocycles capable of entering into additional coordination interaction with



**Figure 4.** TG curve of copper complexes of tetra(4-butoxyphenoxy)phthalocyanine **5b** (a) and tetra(4-butylphenoxy)phthalocyanine **4b** (b).



**Scheme 4.** Reaction of aerobic oxidation of DTC in the presence of phthalocyanine catalysts.

**Table 2.** Catalytic process of DTC oxidation efficiency in the presence of phthalocyanine.

Compound	Parameters of catalytic action	
	$k_{\text{obs}}, (\text{s}\cdot\text{g})^{-1}$	$\chi, \%$
<b>4a</b>	65.42	45.56
<b>5a</b>	47.30	40.71
<b>6</b>	0.05	0.76
<b>7</b>	0.25	3.60

the substrate. So, in the peripheral fragment of ligand **7** and its complex with cobalt **5a**, there is an additional heteroatom, which in the catalytic process can act as an additional coordination center and hold one of the participants in the catalytic process, thereby creating a visible effect of reducing catalytic efficiency.

## Conclusions

Thus, as a result of the work, tetra(4-butyl/butoxyphenoxy)phthalocyanines and cobalt, zinc, and copper complexes based on them were synthesized. Through a number of research and instrumental methods, including NMR, IR spectroscopy, mass spectrometry and elemental analysis, the structures of the compounds obtained were unambiguously confirmed. The spectroscopic properties of phthalocyanines in DMF, chloroform, acetone and tetrahydrofuran were studied, the absorption maxima were determined. It is established metal complexes in these conditions are mainly in aggregated form. Finally, the parameters of thermal oxidative degradation of compounds are determined.

Introduction during the transition from alkyl substituted phthalocyanines to alkoxy-analogs, an increase in the thermal stability of the complexes was observed. The compounds showed high catalytic activity in the oxidation reaction of DTC, which, thus, may indicate the prospects for their use in the pro-processes of demercaptanization of sulfur containing compounds. Please formulate conclusions and possible development.

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