Scientia Pharmaceutica

Article

Synthesis and Catalytic Activity of Novel Complexes Based on Cyano-Substituted Phthalocyanines as Promising Drug Conversion Agents

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Abstract: This paper presents the results of obtaining new cobalt and zinc complexes based on dicyanophenoxy-substituted carboxypthalocyanine. The original method of synthesis and isolation of the compound is shown; its spectroscopic and photophysical characteristics are studied. Studies show the absence of aggregation processes in organic media for solutions of complexes in working concentration ranges. This shows the possibility of the practical application of structures as catalysts. The high catalytic activity of cobalt complexes with dicyanophenoxy-substituted carboxyphthalocyanine ligand in the conversion reaction of sodium diethyldithiocarbamate to disulfiram, which is an active component of drugs for the treatment of alcohol dependence, is determined.

Keywords: metal complexes; cyano-substituted phthalocyanine; spectroscopy; catalysis

Citation: Erzunov, D.; Tonkova, S.; Sarvin, I.; Vashurin, A. Synthesis and Catalytic Activity of Novel Complexes Based on Cyano-Substituted Phthalocyanines as Promising Drug Conversion Agents. *Sci. Pharm.* **2024**, *92*, 47. https://doi.org/10.3390/scipharm92030047

Academic Editor: Valentina Onnis

Received: 1 June 2024
Revised: 7 August 2024
Accepted: 12 August 2024
Published: 28 August 2024

1. Introduction

Currently, high intensification of the production of medicines for various purposes is taking place. In this regard, processes that make it possible to obtain precursors for medicine with a high degree of selectivity, under mild conditions and with good yields are of particular importance. One of the most popular drugs for the treatment of alcohol dependence is Antabuse® (the active component is disulfiram) [1]. It is characterized by high efficiency of inhibition of the enzyme acetaldehyde dehydrogenase, thus stopping the process of decomposition of ethyl alcohol at the stage of acetaldehyde that is toxic to the human body. Also, there is a positive effect of disulfiram on the human body associated with the coronavirus infection COVID-19 reported in the literature [2]. Nevertheless, approaches to the production of disulfiram using highly specific catalysts have not been studied in depth enough.

Earlier, we showed that the use of phthalocyanine complexes with d-metals with complex substituents on the periphery shows a good prospect for the catalytic production of disulfiram under mild conditions [3–5]. Phthalocyanines, as owners of an extended π-electron system, are well-studied and serve as components of many applications [6–13]. Due to their unique molecular structure, this class of compounds has outstanding chemical and thermal stability compared to other organometallic compounds [14–16]. Development of the structure of the phthalocyanine macrocycle by introducing substituents into peripheral and non-peripheral positions makes it possible to fine-tune their physical and chemical properties [17–19]. Thus, properties of complexes can be changed by introducing substituents of a different nature into the macrocycle [20–23]. By means of the solubility of the obtained metallophthalocyanines, their physical, chemical and coordination properties can be regulated [24–30].

Disulfiram is known as one of the most important compounds obtained catalytically in the presence of phthalocyanine complexes (Figure 1) [5,6]. The molecule has found great usability as a component of drugs for the treatment of alcohol addiction. Nevertheless, standard pathways for obtaining disulfiram require special conditions that limit the possibility of its industrial usage. Although disulfiram remained the most common pharmaceutical treatment of alcohol abuse until the end of the 20th century, today, it is often replaced or accompanied with newer drugs, primarily a combination of naltrexone and acamprosate, which directly attempt to address physiological processes in the brain associated with alcohol abuse. However, the development of cheap synthetic pathways together with mild reaction conditions may make a great improvement in the possibility of disulfiram industrial usage.

Previously, we have shown that the introduction of cyanophenoxyl fragments into the phthalocyanine structure makes it possible to achieve a high rate of catalytic conversion of N,N-diethyldithiacarbamate to disulfiram (Figure 1), while maintaining mild reaction conditions [31–33]. The presence of terminal cyano groups in the structure of the molecule opens up the possibility of fine-tuning the properties of the resulting material. Nevertheless, the main problem in this case was the strong hydrophobicity of the resulting compounds [34–36], which greatly complicated the process of a homogeneous catalytic reaction. Thus, this study presents the results of qualitative modification of structures by introducing groups into their composition that enable the solubility of molecules in aqueous media. The introduction of carboxyl groups into the macrocycle leads to solubility of the resulting compounds in aqueous media [37–39]. Such a chemical modification makes it possible to use phthalocyanines as catalysts for the oxidation of sulfur-containing compounds.

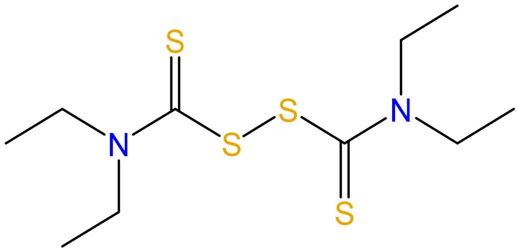


Figure 1. Structural formula of disulfiram.

Thus, in this work, phthalocyanine complexes with zinc and cobalt containing carboxylic and dicyanophenoxy groups on the periphery were synthesized. The compounds were characterized and their spectroscopic, photophysical and catalytic properties were studied.

2. Materials and Methods

The compounds 4-nitrophthalonitrile, gallic acid (3,4,5-trihydroxybenzoic acid), zinc(II) acetate ($Zn(CH_3COO)_2$), cobalt(II) acetate ($Co(CH_3COO)_2$), copper sulfate ($CuSO_4$), urea, potassium carbonate (K_2CO_3), dimethylformamide (DMF), dimethyl sulfoxide (DMSO), tetrahydrofuran (THF), chloroform ($CHCl_3$), pyridine (Py), hydrochloric acid (HCl) and sodium N, N-diethyldithiocarbamate (DTC) used in the present work were purchased from Merck© (Merck Life Science LLC, Moscow, Russia).

IR spectra were recorded using an IRAffinity-1S spectrometer (Shimadzu, Kyoto, Japan) in the frequency range 400–4000 cm^{-1} directly from compound powders without any additional sample preparation. The resolution and scan numbers utilized for IR investigations were equal to 0.5 cm^{-1} and 70, respectively.

^{1}H NMR spectra were recorded using a Bruker AVANCE 500 spectrometer (Bruker, Bremen, Germany. Tetramethylsilane was used as the internal standard) with a frequency of 500 MHz. DMSO-d_6 was used as a solvent.

Mass spectra were recorded using a time-of-flight mass spectrometer “Shimadzu Axima Confidence” (MALDI-TOF MS) (Shimadzu, London, UK). Samples with a concentration of approximately 10^{-3} M were prepared in tetrahydrofuran, and CHCA (alpha-cyano-4-hydroxycinnamic acid) was used as a matrix.

Electronic absorption spectra were captured on a UNICO2800 spectrophotometer (UNICO, Chicago, IL, USA) using quartz cuvettes with an optical path length of 1 cm. A number of organic solvents were used in the experiment, such as chloroform, tetrahydrofuran, dimethylformamide, dimethyl sulfoxide and pyridine.

2.1. Catalytic Properties

The experiment was conducted using the example of a standard reaction of aerobic catalytic oxidation of N,N-diethyldithiocarbamate (DTC) [5]. The mechanism of catalytic conversion of sulfur-containing substrates to disulfides in the presence of cobalt phthalocyanine complexes was clearly described and proved in the literature [40] and carefully checked in a number of our previous works [4,6,37]. The amounts of catalyst used in the present work were equal to 2×10^{-4} g.

The reaction was carried out in a 650 mL cell equipped with a magnetic stirrer and an air compressor at a temperature of 298.15 K with an error limit of 0.05 K.

An aqueous solution of DTC with a molar concentration of 10^{-3} M was placed in a cell; after achieving a constant temperature in the cell, a zero sample of 2 mL was taken, after which a catalyst was added, and air supply through the compressor was turned on at a speed of 2 L/min, which was taken as the moment of the reaction. Samples with a volume of 2 mL were taken every 3 min, for up to ten samples inclusive, to determine the current concentration of DTC in the reaction mixture.

A volume of 4 mL of 0.5 M aqueous solution of copper sulfate was added to the samples collected in test tubes, after which the formation of a dark-brown precipitate of Cu complex (DTC) was observed. Next, 0.05 mL of 50% acetic acid and 5 mL of chloroform were poured into each tube, and the mixtures were mixed for about 1.5–2 min until complete extraction of the unreacted DTC. The resulting organic fractions were diluted with chloroform to the label and, further, their optical density was determined at a wavelength of 436 nm, corresponding to the maximum absorption of the complex. Finally, based on the known value of the molar extinction coefficient $Cu(DTC)_2$, their concentrations were calculated at the designated time intervals of the reaction.

The formation of disulfide was controlled using IR and NMR spectroscopic methods. Spectral data are given in the literature [5] and coincide with those obtained.

N,N-sodium diethyldithiocarbamate

IR (KBr): υ, 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, (-C-S). ^{1}H NMR (500 MHz, D_2O): δ, ppm.: 4.34 (m, J = 15 Hz, CH_2, 4H); 1.39 (t, J = 5 Hz, CH_3, 6H). ^{13}C NMR (100 MHz): δ, ppm.: 11.65, 27.50, 49.08, 205.02.

Tetramethylthiuram disulfide

IR (KBr): υ, cm^{-1}: 2974 ($-CH_3$ υ_{as}), 2861 ($-CH_2-$ υ_{as}), 1505 ($-CH_2-$δ), 1380 ($-C-N_{st}$), 1273 ($-C{=}S_{st}$), 1143, 995 (-S-S-). ^{1}H NMR (500 MHz, $CDCl_3$): δ, ppm.: 3.71–3.77 (m, CH_2, 8H); 1.29–1.23 (m, CH_3, 12H). ^{13}C NMR (100 MHz): δ, ppm.: 10.49, 25.72, 52.04, 51.26, 190.05.

2.2. Synthesis

3,4,5-tris(3,4-dicyanophenoxy)benzoic acid (1)

A mass of 1.00 g (5.8 mmol) 3,4,5-trihydroxybenzoic acid was dissolved in 30 mL of DMSO, and 2.44 g (17.6 mmol) dry potassium carbonate was added, after which the mixture was left at 80 °C with stirring for 1 h. Then, 3.51 g (20.0 mmol) 4-nitrophthalonitrile was added to the reaction mass and mixing of the mixture was continued for another 7 h at the same temperature. After that, the mixture was cooled and poured into 90 mL of ice-cold distilled water. The resulting precipitate was filtered and washed with 0.1 M hydrochloric acid solution and then distilled water to obtain a neutral pH value of the medium. The resulting yellow–brown powder was recrystallized from ethanol.

Yield: 2.43 g (20%). IR, ν, cm^{-1}: 3550−3500 (-OH), 3102−3040 (C_{ar}-N), 2232 ($C{\equiv}N$), 1653 (C=O), 1588−1486 ($C_{ar}{=}C_{ar}$), 1249 (Ar-O-Ar). ^{1}H NMR ($CDCl_3$), δ, ppm.: 12.72 s (1H), 7.83 dd (3H), 7.64 s (3H), 7.28 dd (3H), 7.09 s (2H). Mass spectrum, m/z: 547.46 $[M]^+$, calculated: 548.47.

General procedure for the preparation of tetrakis-4-(2,6-bis(3,4-dicyanophenoxy),4-carboxyphenoxy)zinc phthalocyanine (2) and tetrakis-4-(2,6-bis(3,4-dicyanophenoxy),4-carboxyphenoxy)cobalt phthalocyanine (3)

The compounds 3,4,5-tris(3,4-dicyanophenoxy)benzoic acid (1) (0.05 g, 0.91 mmol) and anhydrous zinc/cobalt acetate (0.95 mmol) were placed in a ceramic crucible and then heated at 190 °C for 30 min in the absence of a solvent. After solidification of the melt, the mixture was cooled to room temperature, filtered with a Schott filter and washed with chloroform. The solvent was distilled, and the filtrate was purified using column chromatography (silica gel M60, chloroform–THF gradient (from 0 to 5 vol.%)) and size exclusion chromatography (3% THF in chloroform). The complexes were obtained in the form of a dark-green powder, soluble in THF, DMF, DMSO and pyridine.

Zinc tetrakis-4-(2,6-bis(3,4-dicyanophenoxy),4-carboxyphenoxy) phthalocyanine (2)

Yield: 0.0029 g (31%). IR, ν, cm^{-1}: 2954−2851 (C_{ar}-N), 2157 (C≡N), 1717 (-OH), 1653 (C=O), 1539−1457 (C_{ar}-C_{ar}), 1261 (Ar-O-Ar). ^1H NMR (500 MHz, DMSO-d_6), ppm.: δ 8.58 (s, 1H), 7.79 (s, 1H), 7.42–7.40 (dd, 1H), 7.39 (d, J = 7.7 Hz, 1H), 7.22 (d, J = 10.3 Hz, 2H), 7.14 (s, 2H), 7.09 (d, J = 8.9 Hz, 2H), 6.88 (s, J = 8.0 Hz, 2H).

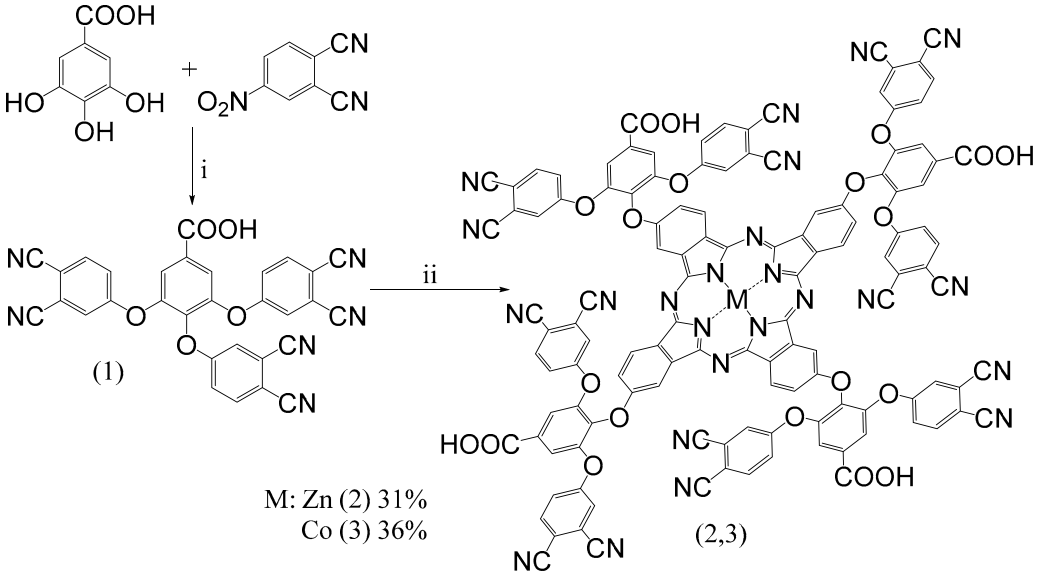
Cobalt tetrakis-4-(2,6-bis(3,4-dicyanophenoxy),4-carboxyphenoxy) phthalocyanine (3)

Yield: 0.0031 g (36%). IR, ν, cm^{-1}: 3029−2851 (C_{ar}-N), 2354 (C≡N), 1717 (-OH), 1599 (C=O), 1524−1450 (C_{ar}-C_{ar}), 1273 (Ar-O-Ar). ^1H NMR (500 MHz, DMSO-d_6), ppm.: δ 8.86–8.43 (m_{broad}, 2H), 8.02–7.79 (m_{broad}, 4H), 7.65–6.98 (m_{broad}, 6H).

3. Results

3.1. Synthesis of 3,4,5-Tris(3,4-dicyanophenoxy)benzoic Acid

The compound 3,4,5-tris(3,4-dicyanophenoxy)benzoic acid was synthesized by nucleophilic substitution of the nitro group in 4-nitrophthalonitrile for gallic acid (Scheme 1, i). Gallic acid was dissolved in DMSO and potassium carbonate was added; the mixture was left at 80 °C with stirring for 1 h. After that, 4-nitrophthalonitrile was added to the reaction mass and mixing of the mixture was continued for another 7 h at the same temperature. To isolate the compound, the mixture was poured into chilled distilled water. The resulting precipitate was filtered and washed with 0.1 M hydrochloric acid solution and then distilled water to obtain a neutral pH value of the medium. The resulting yellow–brown powder was recrystallized from ethanol. The yield was 20%.



Scheme 1. General pathway for substituted phthalonitrile **1** and phthalocyanines **2**–**3** synthesis. (i): K_2CO_3, DMF, 80 °C, 8 h; (ii): Zn/$CoAc_2$, 190 °C, 30 min.

The structure of the compound was confirmed using IR and NMR spectroscopic analysis methods and MALDI-TOF mass spectrometry. The IR spectrum of the compound contained all characteristic vibrations at 3550–3500 cm^{-1} (-OH), 3102–3040 cm^{-1} (C_{ar}-H), 2232 cm^{-1} (C≡N), 1653 cm^{-1} (C=O), 1588–1486 cm^{-1} (C_{ar}=C_{ar}) and 1249 cm^{-1} (Ar-O-Ar). The IR spectra also lacked bands characteristic of symmetric (1340–1350 cm^{-1}) and asymmetric (1560–1565 cm^{-1}) vibrations of the N=O bond of the nitro group in 4-nitrophthalonitrile. A band of 1249 cm^{-1} was observed, corresponding to skeletal vibrations of the Ar-O-Ar bridge group formed as a result of the reaction. In the MALDI-TOF mass spectrum of 3,4,5-tris(3,4-dicyanophenoxy)benzoic acid, the peak of the molecular ion $[M]^+$ 547.46 was detected in the mode of positive ions when using α-hydroxycoric acid as a matrix.

3.2. Synthesis of d-Metals Phthalocyanine Complexes

Synthesis of phthalocyanates was performed by template fusion of 3,4,5-tris(3,4-dicyanophenoxy)benzoic acid with anhydrous zinc and cobalt acetates at a temperature of 190–195 °C for 30 min until the melt completely solidified (Scheme 1, ii). After cooling, the resulting mass was transferred to a Schott filter and washed with chloroform. The target compound was washed off the THF filter; the solvent was distilled and the resulting complex was purified by column chromatography on silica gel with a mixture of chloroform–THF (9:1) as an eluent.

The structures of compounds **3** and **4** were identified using IR and NMR spectroscopy methods. All characteristic bands were present in the corresponding IR spectra of metal phthalocyanines. During the transition from compound **2** to the corresponding complexes, an increase in the intensity of the band responsible for fluctuations of the C≡N group (~2232 cm^{-1}) was observed, which was due to an increase in the number of these groupings in the structure of the substituted phthalocyanine.

The highest yield was observed in a complex with cobalt as the central ion.

Based on ^{1}H NMR data, the Zn phthalocyanine (**2**) structure was confirmed clearly. The weakest field signal (8.58 ppm) corresponded to a carboxylic group proton. Phthalocyanine core protons were localized at 7.79 and 7.40 ppm as a singlet and an unresolved doublet of doublets, respectively. The rest of the signals at 7.31, 7.14, 7.09 and 6.89 relate to spacer substituent fragments. However, regarding Co phthalocyanine, due to the paramagnetic nature of the central metal ion, the spectrum was subject to changes. It was expressed in both signals shifting and broadening. Thus, we were able to register only signals ranges and integral intensities. Nevertheless, the structure of complex 3 was confirmed with a good agreement based on data on the localization of proton shifts and its integral intensities combined with the results of IR spectroscopy and TLC investigations.

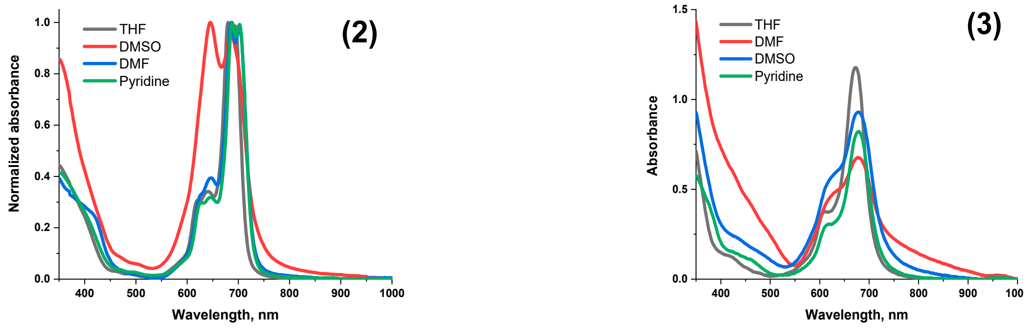
3.3. Spectroscopic Properties

Aggregation is an important phenomenon in the chemistry of phthalocyanines. Phthalocyanines in an aggregated state differ in properties from compounds in a non-aggregated form. Aggregation behavior depends on the nature of the solvent and substituents, the metal ion in the coordination center, the concentration of the solution and temperature. The most common method for determining the presence of an aggregation processes is electron absorption spectroscopy. Depending on the nature of the change in the electronic absorption spectra of solutions, *H*- and *J*-aggregates are distinguished. *H*-aggregates are characterized by hypsochromic displacement, i.e., in the short-wavelength region, the absorption bands are relative to the maximum of the monomer. There is also a significant decrease in absorption intensity and a strong broadening of the bands in the long-wavelength part of the spectrum. *J*-aggregates are distinguished by the appearance of a narrow intense absorption band, which is shifted bathochromically relative to the monomer band. At the first stage of studying the spectral properties of the obtained compounds, their characteristics in various organic solvents were studied (Table 1).

Table 1. Spectroscopic properties of phthalocyanines **2**–**3** in various solvents.

Compound	Absorption Maximum, nm (lgε)			
	THF	DMF	DMSO	Pyridine
2	680–693 (4.83)	686–702 (4.29)	685 (4.61)	688–702 (4.86)
3	673 (4.31)	675 (4.09)	671 (4.18)	680 (4.38)

Upon changing the solvent for phthalocyanine **3** solutions, the appearance of the spectrum did not change; only a bathochromic or hypsochromic shift occurred. Phthalocyanine **2** was characterized by splitting of the absorption maximum, which may be due to the presence of difficult-to-separate regioisomers in the solution (Figure 2).



(**a**) (**b**)

Figure 2. Electronic absorption spectra of phthalocyanines **2** (**a**) and **3** (**b**) in various solvents.

The aggregation behavior of the synthesized compounds was studied using electron spectroscopy in various solvents, such as tetrahydrofuran, dimethylformamide and dimethyl sulfoxide. Upon the dilution of compound **2** and **3** solutions, deviations from the linear dependence of concentration on optical density were observed, which may indicate the presence of aggregation for these compounds in specific concentration ranges (starting from 9.0×10^{-6} mol/L for **2** and 4.3×10^{-6} mol/L for **3**) (Figure 3).

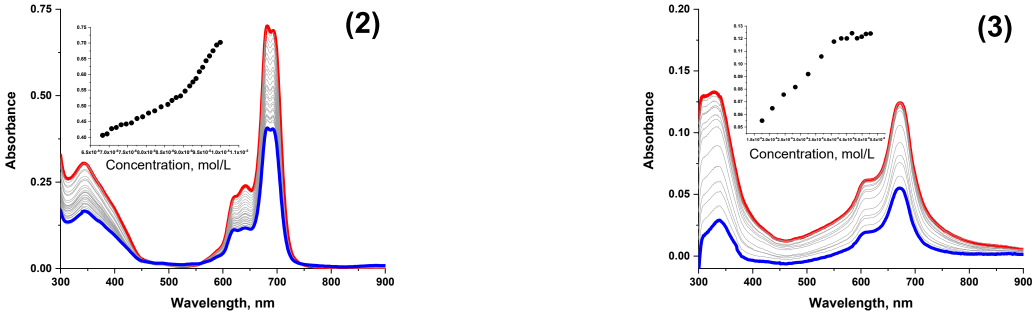


Figure 3. Changes in the electronic spectra of solutions of compounds **2** and **3** in THF during dilution in a concentration range from 5.46×10^{-5} mol/L to 1.17×10^{-5} mol/L. Red curve—initial spectrum, blue curve—finite spectrum. Insertion—Lambert–Bueger–Behr dependencies in THF.

However, UV–vis spectra for complexes with cobalt have a broadened appearance and retain it even when diluted in a large concentration range (Figure 4).

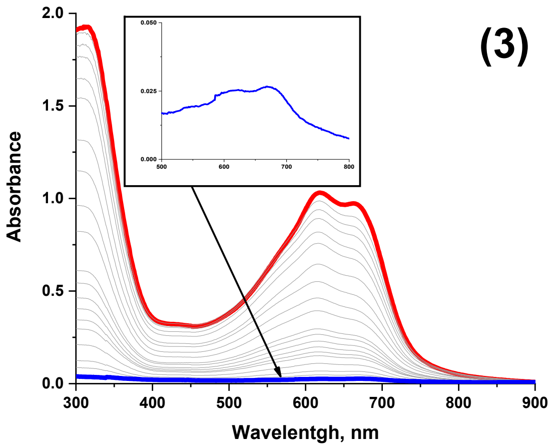
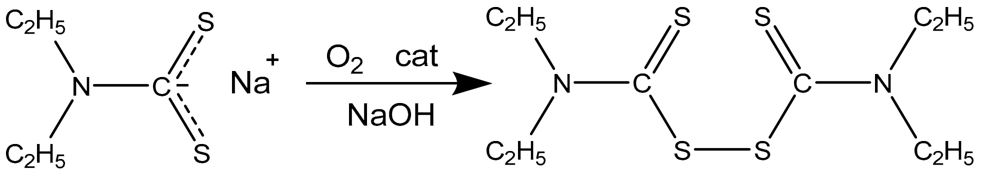


Figure 4. Change in the electronic spectra of solutions of compound **3** in DMSO upon dilution in a concentration range from 5.46 × 10^{-5} mol/L to 1.17 × 10^{-5} mol/L. Red curve—initial spectrum, blue curve—finite spectrum. The insert is an electronic absorption spectrum at a concentration of 1.17 × 10^{-5} mol/L.

3.4. Catalytic Properties

Catalytic properties were studied in the oxidation reaction of sodium diethyldithiocarbamate with atmospheric oxygen (Scheme 2). The study of catalytic activity was carried out at 20 °C at pH 7 and 11.



Scheme 2. Equation of the catalytic oxidation reaction of DTC.

DTC solution with a concentration of 10^{-3} mol/L of the required pH value was prepared for the reaction. Then, the test substance was added to the solution, weighing 1 × 10^{-3} g. The reaction was carried out by blowing oxygen through the air and stirring intensively. A 2 mL sample of the reaction mixture was taken every 10 min. Copper sulfate was used as an agent binding the unreacted DTC during the reaction. Chloroform was used to extract the oxidation product.

After separation of the reaction product, the organic fraction was studied using an electronic absorption spectrum. Kinetic curves were constructed based on the obtained data (Figure 5).

The obtained rate constants are shown in Table 2. The highest catalytic activity in the presented series is shown by compound **3** at pH 11. Cobalt complexes showed higher activity compared to zinc analogs. This is obviously due to the coordination mechanism of the reaction and the greater coordination unsaturation of the cobalt ion. The resulting catalytic activity of both cobalt complexes **2** and **3** was found to exceed the constant values of alkoxy-substituted complexes obtained earlier several times [41].

Table 2. Parameters of the catalytic conversion reaction of N,N-diethyldithiocarbamate.

Compounds	***k*, 1/min**	
	7 pH	**11 pH**
2	13	40
3	0.0014	0.0055

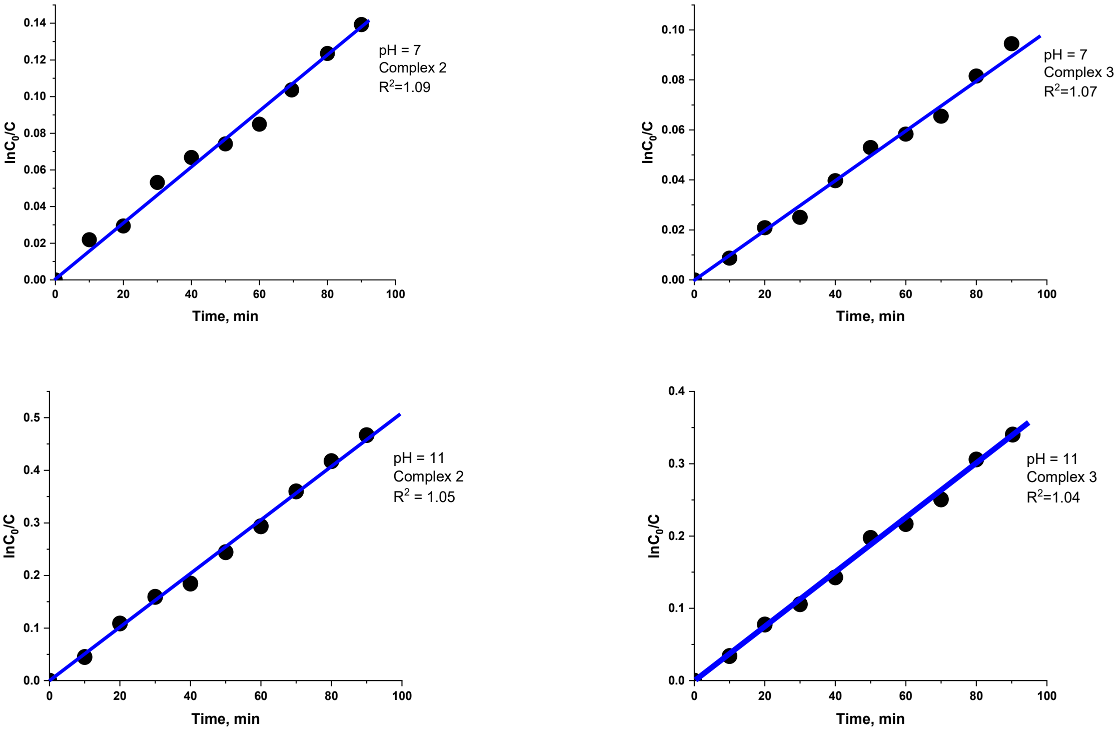


Figure 5. Kinetic curves of DTC oxidation in the presence of compounds **2** and **3** at pH 7 and 11.

4. Conclusions

New complexes of phthalocyanines of a complex structure containing cyanophenoxyl groups and carboxy groups at the same time have been obtained. The compounds were obtained and the structure was confirmed using IR spectroscopy and ^{1}H NMR analysis approaches. Due to the combination of these groups, high catalytic activity of the obtained compounds in the reaction of sodium N,N-diethyldithiocarbamate to disulfiram under mild conditions was ensured. It is shown that an increase in the basicity of the medium leads to a significant acceleration of the catalytic conversion reaction.

It is shown that when specific concentration values are reached in the liquid phase, the compounds tend to aggregate, which is explained by the high steric tension of the structures.

The obtained cobalt complexes containing dicyanophenoxyl and carboxyl groups showed high catalytic activity exceeding the performance of alkoxy-substituted structures by several orders of magnitude. This makes them promising candidates for introduction into usage as catalysts for the production of DTC.

Author Contributions: Conceptualization, D.E. and A.V.; methodology, D.E. and A.V.; software, D.E., S.T. and I.S.; validation, A.V.; formal analysis, D.E. and A.V.; investigation, D.E., S.T. and I.S.; resources, A.V.; data curation, D.E. and A.V.; writing—original draft preparation, D.E.; writing—review and editing, D.E. and A.V.; visualization, D.E., S.T. and I.S.; supervision, A.V.; project administration, A.V.; funding acquisition, A.V. All authors have read and agreed to the published version of the manuscript.

Funding: This research was funded by the Russian Science Foundation, grant number 22-73-10158.

Institutional Review Board Statement: Not applicable.

Informed Consent Statement: Not applicable.

Data Availability Statement: Dataset available on request from the authors.

Conflicts of Interest: The authors declare no conflicts of interest.

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