

The Influence of the Nature of the Spacer Fragment of the Peripheral Substituent on the Catalytic Behavior of Carboxyphenyl Substituted Phthalocyanine Complexes

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Dedicated to Academician of RAS Professor Aslan Yu. Tsivadze on the occasion of his Anniversary

Present work reveals the study of catalytic properties of copper and cobalt complexes with phthalocyanine ligands with o-carboxyphenoxy/carboxyphenylsulfanyl/carboxyphenylamino- substituents in the peripheral positions of the macroring. For compounds, the aggregative behavior in aqueous and aqueous-alkaline media was studied. On the example of the reaction of catalytic oxidation of sodium N,N-diethylthiocarbamate, the rate constants of the formation of the corresponding disulfide were determined. The influence of the nature of the spacer fragment of the peripheral substituent on the activity of the complexes as catalysts for liquid-phase oxidation was revealed.

Keywords: Phthalocyanines, complexes, aggregation, catalysis, dithiocarbamate.

Влияние природы спейсерного фрагмента периферического заместителя на каталитическое поведение карбоксифенил-замещенных фталоцианиновых комплексов

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В работе представлено изучение каталитических свойств комплексов меди и кобальта с фталоцианиновыми лигандами с о-карбоксофенокси-/карбоксофенилсульфанил-/карбоксофениламино- заместителями в периферических положениях макрокольца. Для соединений исследовано агрегативное поведение в водных и водно-щелочных средах. На примере реакции каталитического окисления N,N-диэтилдитиокарбамата натрия определены константы скорости процесса образования соответствующего дисульфида. Выявлено влияние природы спейсерного фрагмента периферического заместителя на проявляемую комплексами активность как катализаторов жидкофазного окисления.

Ключевые слова: Фталоцианины, комплексы, агрегация, катализ, дитиокарбамат.

Introduction

Metallophthalocyanines have not only a structural analogy with porphyrins, but also a low cost, easy production in large volumes, as well as chemical and thermal stability. Phthalocyanine complexes are widely used in various fields of materials science, including semiconductor,^[1,2]

electrochromic^[3,4] and nonlinear optical devices,^[5,6] information storage systems,^[7,8] etc. In the presence of a highly coordination-active metal ion in the structure of the molecule, the compounds of this class can be effectively used in enzymatic^[9] and catalytic processes.^[10–12] So, the most attractive and intriguing in this regard are complexes of cobalt, iron, ruthenium, etc.^[12–14] In addition, the macrocyclic

substituents that make up the molecule also make a certain contribution to the properties manifested by the complexes.

To date, a large number of phthalocyanine complexes^[15,16] with various metals and substituents^[17–19] have been obtained and studied.^[20–22] However, the vast majority of studies were conducted in organic environments. Nevertheless, by introducing specific functional groupings into the phthalocyanine molecule, it is possible to achieve good solubility of these complexes in aqueous media,^[23–26] which greatly simplifies the possibility of using materials based on these structures on an industrial scale.

Complexes of macroheterocyclic compounds are used both on an industrial scale and in laboratory practice as catalysts for various processes. One of the most important types of reactions catalyzed by phthalocyanine complexes is the oxidation of sulfur-containing organic compounds.^[27–30] This reaction finds wide practical application in the processes of desulfurization of oil fractions and natural gas, acceleration of vulcanization of rubbers, in the preparation of specific drugs.^[31]

Carboxy-substituted phthalocyanines have shown themselves to be effective catalysts for the liquid-phase oxidation of sulfur-containing organic compounds.^[32,33] Along with high values of catalytic activity and good turnover, the use of these compounds is quite simple and effective in practice, and also fully meets the concept of green chemistry.

The literature describes in sufficient detail the mechanism of the catalytic action in the presence of macroheterocyclic molecules, including the phthalocyanine class compounds. Thus, it is known that this process depends on many factors, the main of which are the concentration of phthalocyanine and the converted molecule, the acidity of the medium, the presence or absence of oxygen and the rate of its supply, etc. However, due to the specific behavior of the carboxyl group in solution, it is necessary to conduct a comprehensive study of the influence of both the medium and the peripheral environment in combination on the catalytic behavior of the molecule. Thus, in complexly substituted structures, it is of interest to study the nature of the introduced heteroatoms or atomic groups in the first place both in terms of the spectral properties exhibited by the complexes and the catalytic activity of the compounds.

Thus, this paper presents a study of the aggregation properties and catalytic behavior of cobalt and copper phthalocyanines with *o*-carboxyphenyl substituents connected to the macrocycle by means of spacer atoms O, N, S. The study of catalytic activity was carried out by the example of the reaction of aerobic oxidation of sodium *N,N*-diethyldithiocarbamate in an aqueous-alkaline medium in the presence of phthalocyanine complexes as homogeneous catalysts for the disulfirization process.

Experimental

Reagents and solvents. Water was bidistilled immediately before the experiments. Sodium hydroxide (NaOH) (98%), pyridine (99%), copper(II) sulfate tetrahydrate (98%), sodium *N,N*-diethyldithiocarbamate trihydrate (DTC) (98%) were purchased from Khimmed and used without further purification. Metal complexes were obtained and characterized in our previous works.^[34]

Ultraviolet-visible spectroscopic measurements were carried out on a UNICO-2800 spectrophotometer in the wavelength range

from 190 to 1100 nm. The spectra were recorded using quartz cuvettes with an optical path length of 1 cm.

The catalytic activity was determined using the liquid-phase aerobic oxidation of sodium *N,N*-diethyldithiocarbamate (DTC) in the presence of a phthalocyanine complex as an example. Advantages of this reaction are low toxicity of initial materials, possibility to observe the concentration of initial and desired materials and identification of reaction products using electron absorption (UV-Vis spectra) and IR spectroscopy methods. Experiments to study the kinetics of DTC oxidation were carried out in thermostatic cell at 293.15 K in which DTC of 650 mL was loaded.

The air needed for oxidation was fed via micro compressor with constant rate of 2 L·min⁻¹. Under these parameters the reaction takes place in kinetic region.^[35] After reaching a constant temperature of reaction mixture, it was mixed 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 at a wavelength of 440 nm.

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.

$$dc/dt = -k_{\text{obs}}c, \quad (1)$$

where c – DTC concentration, t – time, 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:

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

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

Degree of transformation was calculated according to equation:

$$\chi_{\text{RSSR}} = (c_0 - c_t)/c_0, \quad (3)$$

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

Disulfide formation was monitored by FT-IR, ¹H NMR, and ¹³C NMR spectra. ¹H NMR of DTC before oxidation (500 MHz, D₂O) δ ppm: 4.34 (*q*, $J = 15$ Hz, 4H, CH₂); 1.39 (*t*, $J = 5$ Hz, 6H, CH₃). ¹³C NMR of DTC before oxidation (100 MHz) δ ppm: 11.65; 49.08; 205.02. IR of DTC before oxidation (KBr) ν cm⁻¹: 2979 (-CH₃ ν_{as}); 2847 (-CH₂- ν_{as}); 1476 (-CH₂- δ); 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, CDCl₃) δ ppm: 3.71–3.77 (*m*, 8H, CH₂); 1.29–1.23 (*m*, 12H, CH₃). ¹³C NMR of TMTD obtained by DTC oxidation (100 MHz) δ ppm: 10.49; 25.72; 52.04; 51.26; 190.05. IR of TMTD obtained by DTC oxidation (KBr) ν cm⁻¹: 2974 (-CH₃ ν_{as}); 2861 (-CH₂- ν_{as}); 1505 (-CH₂- δ); 1380 (-C-N *st*); 1273 (-C=S *st*); 1143, 995 (S-S).

Results and Discussion

Spectroscopic and aggregation behavior

Phthalocyanine complexes are known to exist in solution in both monomeric and aggregated forms. This fact is strongly reflected in their properties, including catalytic ones. One of the simplest and at the same time effective methods for revealing the aggregation behaviour of metal phthalocyanines is electron absorption spectroscopy in the visible region. Thus, at the first stage of the work, the spectroscopic characteristics of *o*-carboxyphenyl-substituted cobalt and copper phthalocyanines, which include a spac-

er atom of oxygen, sulfur or nitrogen in their structure, were determined (Figure 1).

Changes in the electronic absorption spectra of complexes **1b** (a) and **2b** (b) in an aqueous alkaline medium are shown in Figure 2. It is known from the literature that the comparability of the intensities of the Q-band components indicates the presence of any processes or equilibria in the solution, often aggregation.^[36] The same spectroscopic changes were observed for complexes with oxy- and amino-bridge atoms of the peripheral substituent.

Thus, it was shown that in the studied concentration ranges (from $5 \cdot 10^{-7}$ to $2 \cdot 10^{-4}$ mol/L) in an aqueous alkaline medium, all complexes are predominantly in an aggregated state. Nevertheless, we have shown earlier^[33] that this fact is not exclusively negative in terms of its effect on the catalytic activity of the compound, but can also promote the reaction of catalytic disulfide bond formation during the oxidation of sulfur-containing organic substrates.

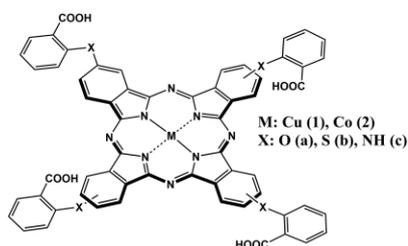


Figure 1. Structure of copper (**1a-c**) and cobalt (**2a-c**) complexes with *o*-carboxyphenyl-oxy/sulfanyl/amino-substituted phthalocyanine ligands.

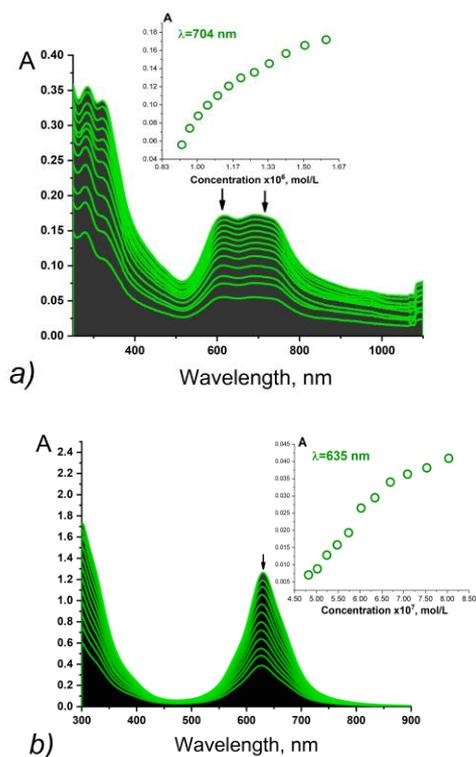


Figure 2. UV-vis changes upon the dilution of an aqueous alkaline solution ($pH=11$) of cobalt (a) and copper (b) tetrakis-4-(2-carboxyphenylsulfanyl)phthalocyanines. Insets: dilution curves.

The spectroscopic changes upon pyridine addition to water-alkaline phthalocyaninate solutions might also act as the confirmation of the presence of complexes in the aggregated state. Being a donor monodentate ligand, pyridine is incorporated into the aggregate structure, destroying it, and thereby sterically prevents aggregation. At the same time, in the electronic absorption spectra, a strong thinning of the Q-band and a decrease in the intensity of the left component (vibrational satellite) are observed (Figure 3). At the same time, the bathochromic shift of complexes main absorption band was detected (Figure 3). The values of these shifts were found to be equal to 48 nm in case of cobalt tetrakis-4-(2-carboxyphenoxy)phthalocyaninate and 61 nm for copper complex (the data on all compounds shifts are presented in Table 1).

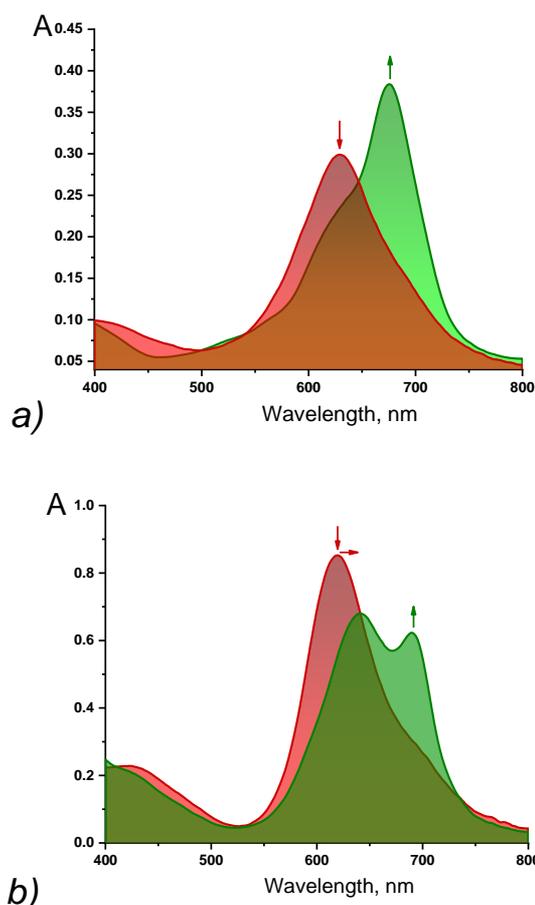


Figure 3. UV-vis changes upon the addition of pyridine ($C_{Py}=1.5 \cdot 10^{-3}$ mol/L) to cobalt (a) and copper (b) tetrakis-4-(2-carboxyphenoxy)phthalocyanines aqueous-alkaline solutions ($pH=11$, $C=1 \cdot 10^{-5}$ mol/L).

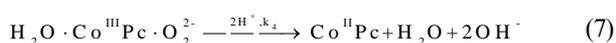
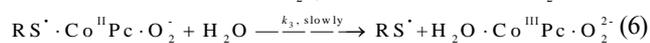
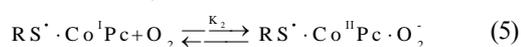
Table 1. The ratios of Q-band shift upon the pyridine addition to cobalt and copper tetrakis-4-(2-carboxyphenyl-oxy/sulfanyl/amino)-phthalocyanines aqueous-alkaline solutions.

M	Substitution type		
	S	O	NH
Co	43 nm	48 nm	45 nm
Cu	59 nm	61 nm	60 nm

Catalytic activity study

Previously,^[33,34] we have determined the catalytic parameters for *p*- and *m*-carboxyphenyl substituted phthalocyaninates with oxygen, sulfur, and nitrogen atoms as the spacer fragments. However, the activity of complexes with a *o*-oriented carboxy- group has not been studied. This fact limits the completeness of information about the effect of the nature and structure of the substituent of the phthalocyanine macrocycle on the properties exhibited by the complexes. Thus, a series of experiments on the catalytic aerobic oxidation of sodium *N,N*-diethyldithiocarbamate in the presence of cobalt and copper *o*-carboxyphenoxy-/phenylsulfanyl-/phenylamino-phthalocyaninates were carried out.

According to the literature, the mechanism of this reaction is described by the formation of a substrate-phthalocyaninate-oxygen triple complex (eq.5)^[32,33] and is presented as follows:



It should be noted that the oxidation reaction of sulfur containing organic substrates is known to proceed quite slowly in absence of catalyst ($k_{obs}=1.7 \cdot 10^{-5} s^{-1}$ for DTC oxidation).

In accordance with the mechanism, the nature of the substituent, along with the nature of the central metal ion, has one of the determining effects on the catalytic activity

of phthalocyaninates. This is explained by their strong influence both on the ability to form a triple complex and on its stability in the system during oxidation. In this regard, complexes with *o*-carboxy substitution due to the greatest spatial proximity of the functional group to the macrocycle and spacer atoms can exhibit interesting and unexpected properties.

The results of the catalytic aerobic liquid-phase oxidation of sodium *N,N*-diethyldithiocarbamate with the formation of disulfide in the presence of *o*-carboxyphenoxy-/phenylsulfanyl-/phenylamino-substituted cobalt and copper phthalocyaninates are presented in Table 2.

According to the calculated values of the constants, for *o*-carboxy-substituted phthalocyaninates, a regular change in catalytic activity is observed, which increases in the series of $O > N > S$ spacer atoms. The obtained dependences are characteristic of both cobalt and copper complexes. Moreover, this result correlates well with the data obtained earlier for *para*-substituted structures.^[33] This is associated with the redistribution of electron density in the process of formation of the substrate-phthalocyaninate-oxygen triple complex (eq. 5). The oxygen atom, which is the least donor in nature, is not able to fully compensate for the loss of electron density on the central metal ion. The sulfur spacer, in turn, is best suited in this case.

Passing from cobalt complexes to copper complexes, a decrease in the values of the effective reaction rate constants is observed. This is explained by the fact that the oxidation proceeds according to the coordination mechanism presented earlier. The cobalt ion is more coordinatively active than the copper ion.

The resulting catalytic oxidation curves for sodium *N,N*-diethyldithiocarbamate are shown in Figure 4.

Table 2. The effective rate constants and conversion degrees of DTC catalytic oxidation in the presence of cobalt and copper *o*-carboxyphenyl-substituted phthalocyaninates with O, S and N spacer atoms.

Parameters		Compound					
		1a	1b	1c	2a	2b	2c
$k_{obs} \times 10^7, s^{-1}$	pH = 10	4	290	370	90	5200	2900
	pH = 11	3	220	180	70	3700	2100
$\chi_{RSSR}, \%$	pH = 10	78.55	89.35	78.90	81.46	90.12	82.70
	pH = 11	78.93	89.98	79.32	82.83	91.57	83.01

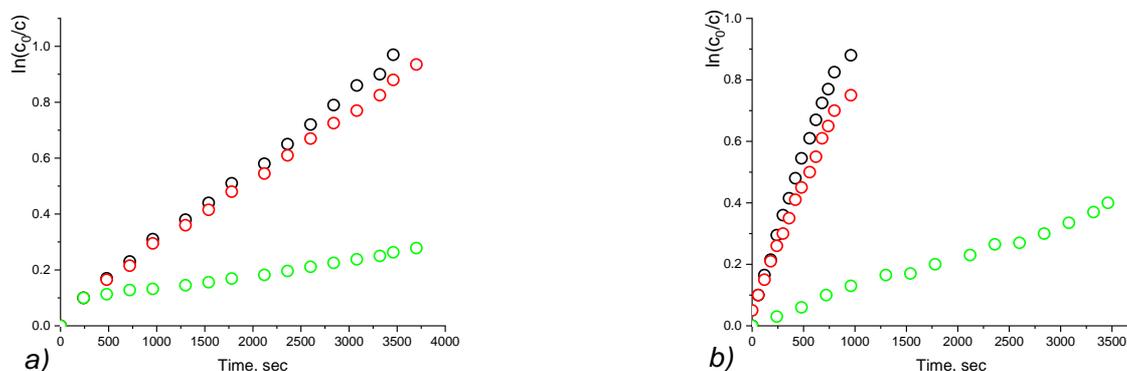


Figure 4. Kinetic curves of the catalytic oxidation of DTC in the presence of complexes: a) **1a** (green circles), **1b** (black circles) and **1c** (red circles); b) **2a** (green circles), **2b** (black circles) and **2c** (red circles).

As can be seen from the values of the constants (Table 1), with an increase in pH from 10 to 11, a decrease in the catalytic activity of the complexes is observed. Thus, an increase in the basicity of the medium adversely affects the efficiency of the complexes as catalysts. This is explained by the competitive equilibrium between RS⁻ and OH⁻ for the cavity of the central metal ion of the phthalocyanine molecule. This fact is confirmed in the literature.^[37] Besides, authors^[28] found that the phthalocyanine may be an acceptor of OH radicals. That is why there was assumption that electrons transfer may be implemented in reaction of complex CoPc^{II}...OH⁻ with other hydroxylion (CoPc^{II}...OH⁻)₂ + OH⁻ → CoPc^I...CoPc^{II}...OH⁻ + O⁻ + H₂O. CoPc^I + O₂ → CoPc^{II} + O₂⁻, CoPc^{II} + O₂ → CoPc^{III} + O₂⁻. There is permanent formation of O₂⁻ and oxidized forms of CoPc^{III} with an excess of oxygen that impedes triple complex formation under condition of increased content of hydroxyl ions in solution and decreased catalytic activity of phthalocyanine. It is also characteristic of the systems studied by us. Obviously, there is the exchange between DTC and coordinated by phthalocyanine ligand (Figure 5) which can be presented by solvent or molecular oxygen.^[29] The exchange depends essentially on electron-donor power of second ligand, for ions – on their basicity.

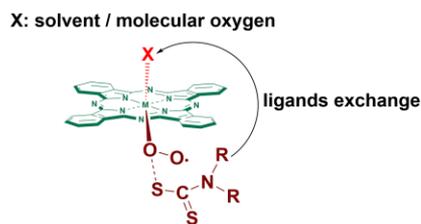


Figure 5. Exchange of ligands in triple complex.

Conclusions

The paper shows the influence of the nature of the spacer fragment of *o*-carboxyphenyl-substituted cobalt and copper phthalocyanines on their catalytic properties. It was determined that all the studied complexes in a wide concentration range exist in an aggregated state. Based on the calculated values of the effective constants of the process of catalytic aerobic oxidation of sodium N,N-diethyldithiocarbamate, it was shown that the key factor determining the influence of the spacer is the electronic effect. The efficiency of oxidation in the presence of *o*-carboxy-substituted phthalocyanines and dependence of catalytic activity on nature of spacer atoms turned out to be comparable with the values for *p*-carboxy analogues. It has been shown that with an increase in the basicity of the system, the activity of the catalysts decreases, which is associated with the competition of hydroxide anions with the substrate for the cavity of the metal ion of the macromolecule.

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