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Synthesis and Properties of Tetra-4-{[(1,1'-biphenyl)-4-yl]oxy}phthalocyanines and Their Sulfonic Acid Derivatives

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Abstract—The template condensation of 4-{[(1,1'-biphenyl)-4-yl]oxy}phthalonitrile with cobalt, copper, and magnesium acetate resulted in the synthesis of metal phthalocyanines. Sulfochlorination of the latter followed by hydrolysis gave the corresponding sulfonic acid derivatives. The spectral characteristics and chemical properties of the synthesized compounds were studied.

Keywords: metal phthalocyanines, template synthesis, sulfonic acids, thermooxidative degradation

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Unsubstituted phthalocyanines (Pc) are insoluble in the most part of organic solvents, except for some polar aprotic ones (at elevated temperatures) and concentrated sulfuric acid, which strongly limits their application. Chemical modification of Pc [1, 2] through functional substitution in the benzene rings can enhance their solubility in different media and thus facilitate isolation and purification and extend the application range of the synthesized products. Functionally substituted phthalocyanines have found application as pH-sensitive dyes, photosensitizers for photodynamic therapy of cancer, catalysts, and other fields of science and technics [3–8].

The interest in phthalocyanines containing biphenyl fragments is associated with their possible use in the synthesis of biologically active compounds, including drugs [9, 10]. Moreover, it is known that molecules containing a biphenyl fragment are soluble in volatile organic solvents [11] and also can be subjected to electrophilic substitution, for example, sulfonation, to prepare was water-soluble compounds in mild conditions. Thus, the synthesis and properties of phthalocyanines with biphenyl fragments are urgent issues.

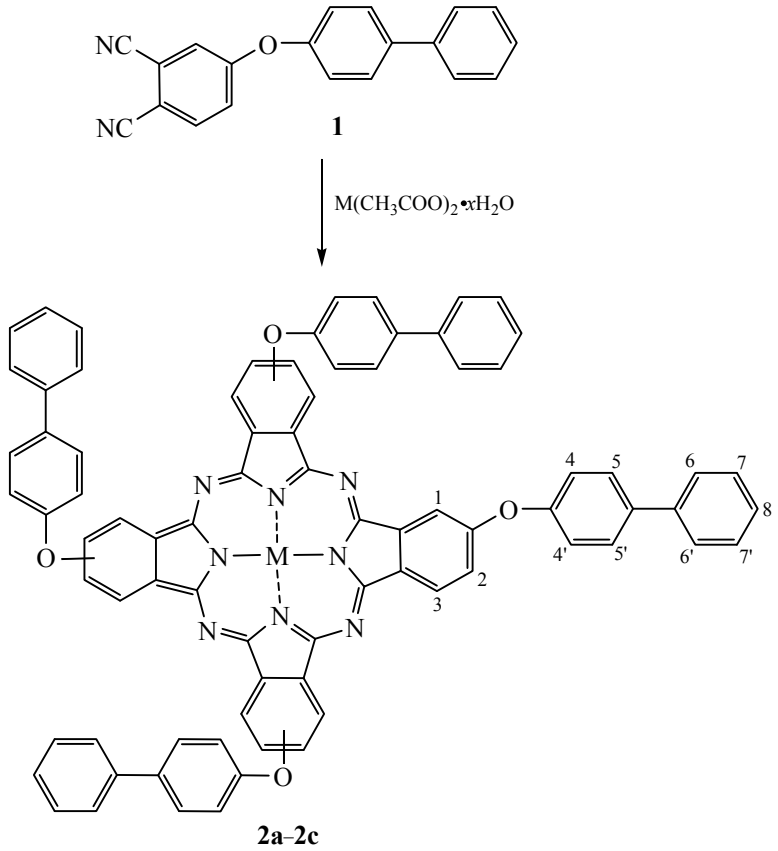
In the present paper we present the results of the synthesis and study of the properties of tetra-4-{[(1,1'-biphenyl)-4-yl]oxy}phthalocyanines and sulfonic acid. The most efficient synthetic approach to phthalocyanines is the nitrile synthesis [1]. The starting 4-{[(1,1'-biphenyl)-4-yl]oxy}phthalonitrile **1** was prepared by the nucleophilic substitution of the nitrogen group in 4-nitrophthalonitrile by a 4-oxybiphenyl group following the procedure in [12].

Further on we reacted the synthesized **1** with cobalt, copper, and magnesium acetates at 185–190°C in the presence of urea to synthesize the corresponding tetra-4-{[(1,1'-biphenyl)-4-yl]oxy}phthalocyanine **2a**–**2c** (Scheme 1).

As known, tetrasubstituted phthalocyanines form as a mixture of four positional isomers: randomers with D_{2h}, C_{4h}, C_{2v}, and C_s symmetries [2, 13]. These isomers are difficult or sometimes impossible to separate. Therefore, we did not try to separate the resulting isomer mixture.

Magnesium tetra-4-{[(1,1'-biphenyl)-4-yl]oxy}phthalocyanine **2c** was demetalated by boiling in conc. HCl to isolate the ligand tetra-4-{[(1,1'-biphenyl)-4-yl]oxy}-phthalocyanine **3** (Scheme 2). Phthalocyanines **2** and **3**

Scheme 1.



M = Co (**a**) $x = 4$, Cu (**b**) $x = 1$, Mg (**c**) $x = 4$.

are bluish green powders soluble in organic solvents (DMF, acetone, ethanol, and chloroform). Their compositions and structures were confirmed by elemental analysis, ^{1}H NMR, IR, and electronic absorption (UV-Vis) spectroscopy and MALDI–TOF mass spectrometry.

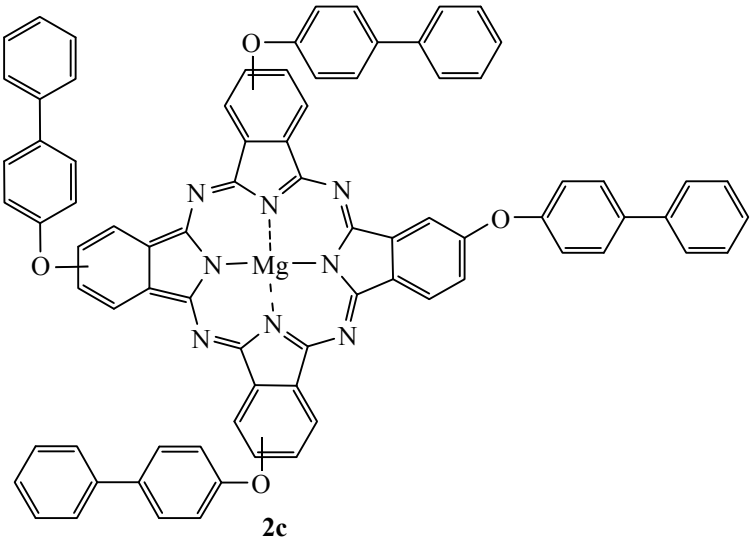
The IR spectra of the synthesized phthalocyanines **2** and **3** show absorption bands characteristic of phthalocyanine family compounds [14] and also the band of the aryloxy group (1230–1240 cm^{-1}), characteristic of the starting phthalonitrile **1** [15]. Furthermore, the IR spectrum of tetra-4-{[(1,1'-biphenyl)-4-yl]oxy}phthalocyanine **3** displays the band at 1006 cm^{-1}, which is characteristic of metal-free phthalocyanines [14].

In the ^{1}H NMR spectrum of compound **2b**, all proton signals are observed in a weak field, which is characteristic of aromatic protons. The downfield doublet at 7.85 ppm (J_{HH} = 8.0 Hz) belongs to the macrocycle H^3 protons, and the multiplet at 7.67–7.61 ppm belongs to twelve protons (H^5, $H^{5'}$, and H^1). The triplet at 7.49 ppm (J_{HH} = 7.5 Hz) is associated with twelve protons (H^6, $H^{6'}$, and H^2) and the multiplet at 7.42–7.37 ppm, to the H^7, $H^{7'}$, and H^8 protons of the substituent phenyl rings. The most upfield are the doublets of the H^4 and $H^{4'}$ protons at 7.19 ppm (J_{HH} = 7.6 Hz).

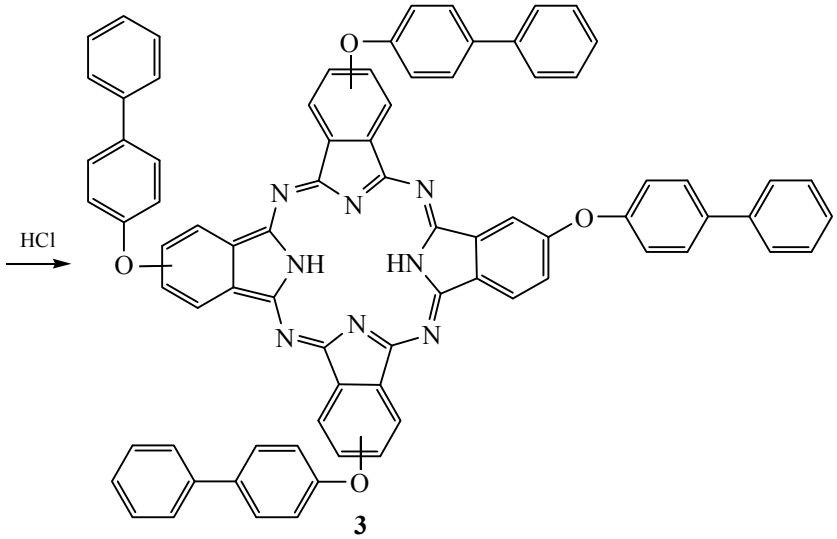
The UV-Vis spectra of all the synthesized compounds show absorption at 667–684 nm (Q bands) due to the π–π* transition in the main conjugation contour of the phthalocyanine macrocycle (Table 1). It should be noted that we observed a bathochromic shifting of the absorption bands in the series Co < Cu ≈ Mg (Table 1). Changing the solvent from chloroform to DMF leads to a hypsochromic shifting of the Q band in all the phthalocyanine spectra (Table 1).

The spectra of tetra-4-{[(1,1'-biphenyl)-4-yl]oxy}-phthalocyanine **3** in chloroform and DMF display a doublet in the longwave region (Table 1), which is characteristic of metal-free compounds and explained by the D_{2h} symmetry of the molecule [16]. In going from chloroform to DMF, like with metal complexes, hypsochromic shifts of absorption bands takes place (Table 1).

Scheme 2.



2c

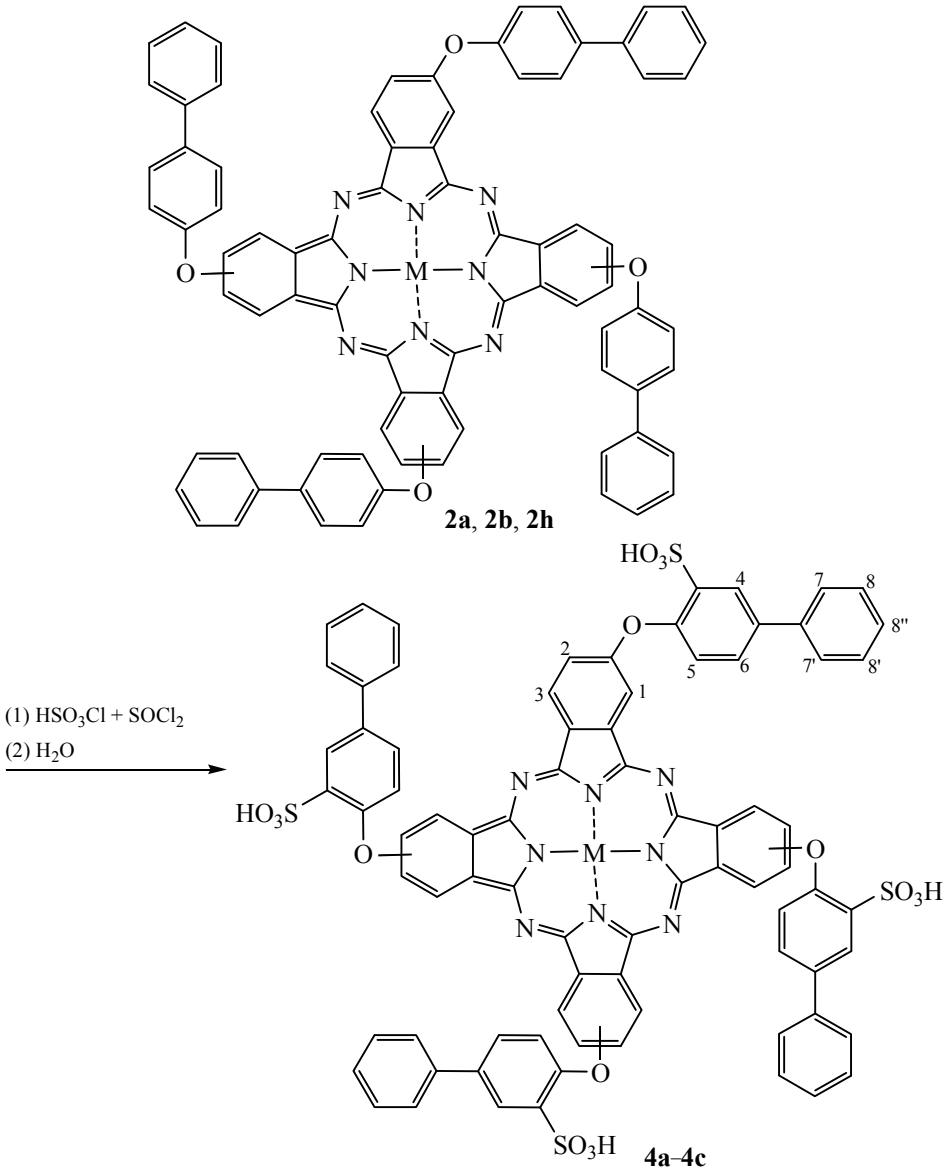


3

Table 1. Electronic absorption spectroscopy data for phthalocyanines **2**–**4**

Comp. no.	M	λ_{max} (D/D_{max})			
		chloroform	DMF	water	H_2SO_4
2a	Co	612, 672 (0.38, 1.00)	605, 667 (0.31, 1.00)	–	855
2b	Cu	616, 682 (0.34, 1.00)	611, 678 (0.33, 1.00)	–	867
2c	Mg	616, 684 (0.23, 1.00)	613, 679 (0.24, 1.00)	–	857
3	2H	614, 639, 669, 703 (0.27, 0.35, 0.92, 1.00)	612, 641, 672, 699 (0.29, 0.36, 1.00, 0.78)	–	863, 925 (0.95, 1.00)
4a	Co	–	675	679	810
4b	Cu	–	683	632	822
4c	2H	–	614, 676 (0.31, 1.00)	659	813

Scheme 3.



2a, **2b**, **2h**

4a–**4c**

M = Co (**a**), Cu (**b**), HH (**c**, **h**).

As known, the sulfonation reaction is reversible [17]. Desulfonation occurs in dilute acid under slight heating. The facility of this reaction is explained by the low energy of the C–SO_3H bond. Therefore, aromatic sulfonic acids show tendency for isomerization due to the fact that the water released during sulfonation decreases the acid concentration in the reaction system [17].

Unlike sulfonation, sulfochlorination with chlorosulfonic acid is an irreversible process [18]. However, that water released in the reaction of arenes with chlorosulfonic acid adversely affects yield of the target sulfonyl chloride due to their sensitivity to hydrolysis. This problem can be solved by adding thionyl chloride, which is a fairly strong dehydrating agent. Therewith, sulfonyl chlorides, unlike sulfonic acids, are soluble in low-boiling organic solvents (acetone). The target products are readily separated from inorganic compounds by extraction, and the latter are readily removed by filtration [19].

Sulfochlorination of the synthesized phthalocyanines **2** and **3** followed by hydrolysis of the resuting sulfonyl chlorides gave the corresponding tetra-4-{[(1,1'-biphenyl)-4-yl]oxy}phthalocyanine sulfonic acids **4a**–**4c** (Scheme 3). The products are insoluble in chloroform

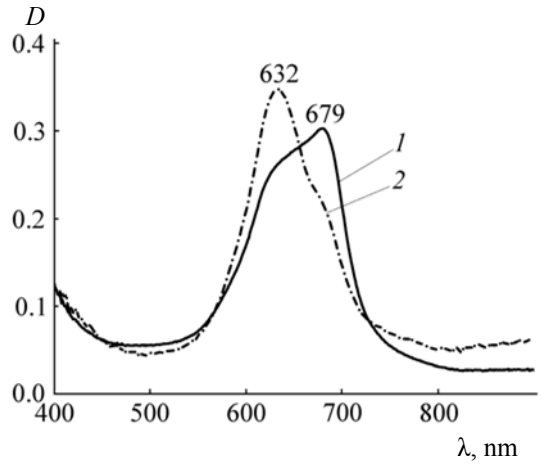


Fig. 1. Electronic absorption spectra of compounds (*1*) **4a** and (*2*) **4b** in water.

and acetone and soluble in water and aqueous alkaline solutions.

The IR spectra of sulfonic acids **4a**–**4c** are similar to the spectra of the corresponding starting phthalocyanines **2a**–**2c**, and **3**. In addition, the spectra of compounds **4a**–**4c** display stretching absorption bands of the S=O (1230–1150 and 1430–1350 cm^{-1}) and C–S bonds (1200–1050 cm^{-1}) [14, 15, 20, 21].

Comparison of the ^1H NMR spectra of compound **4b** and its parent complex **2b** revealed a downfield shifting of all signals. Analysis of signal positions allowed us to establish the sulfonation position of phthalocyanine **4b**. It was found that the H^2 proton signal in the spectrum of **4b** is shifted downfield by 0.5 ppm against the respective signal in the spectrum of complex **2b**, which is explained by the introduction of the electron-acceptor sulfo group ortho to the oxygen atom of the oxybiphenyl substituent.

Analyzing the UV-Vis spectra of the synthesized sulfonic acids **4a**–**4c** in DMF we revealed a bathochromic shifting of the absorption bands in going from cobalt to copper, like is the case with the starting complexes **2** (Table 1). Furthermore, a bathochromic shifting of bands with respect to those for nonsulfonated phthalocyanines is observed (Table 1).

In going from DMF to water, the character of spectral curves changes (Fig. 1). Band broadening and hyprochromic shifting compared to what is observed in DMF suggest associative processes. It is important to note that the cobalt complexes show the weakest tendency for association, on account of the higher coordinating power of cobalt. Cobalt phthalocyanines form extra complexes in aprotic solvents, and, therewith, the function of extra ligands can be played by solvent molecules which hinder intermolecular interactions [22].

In going from organic solvents and water to concentrated sulfuric acid, the absorption bands of all the synthesized phthalocyanines **2**–**4** undergo a large bathochromic shifting, on account of the protonation of the phthalocyanine macrocycle by *meso*-nitrogen atoms [16]. The absorption bands of sulfonated phthalocyanines **4** in sulfuric acid undergo a hypsochromic shift with respect to the respective bands of the corresponding starting complexes (Table 1).

To assess the thermal stability of the synthesized compounds, we studied their thermooxidation degradation. The main parameters of the obtained thermoanalytical curves are listed in Table 2. The thermoanalytical curves (Figs. 2 and 3) are similar to each other. At the first stage (heating to 200°C), the TG curves show a weight loss of 3–4% associated with elimination of the occluded solvent and/or water. Further heating to 350–400°C produces a strong weight loss, which is likely to be explained by changes involving the peripheral substituents and macromolecule itself (Figs. 2 and 3).

It should be noted that the synthesized phthalocyanines are thermally stable compounds, but their thermal stability is strongly dependent on the nature of the substituent. Thus, SO_3H substitution in the metal-free phthalocyanine decreases thermal stability, whereas with the cobalt complex the opposite situation is observed (Table 2, Figs. 2 and 3).

The nature of the complexing metal affects the temperature of thermal degradation processes. Metal complexes decompose at slightly lower temperatures than metal-free Pc. The least stable are substituted cobalt phthalocyanines (Table 2). A similar picture is

Table 2. Thermoanalytical data for phthalocyanines **2**–**4**

Comp. no.	M	Peak weight loss temperature, °C	Peak exothermic effect temperature, °C
2a	Co	390	411
2b	Cu	394	415
3	2H	483	562
4a	Co	391	528
4c	2H	459	515

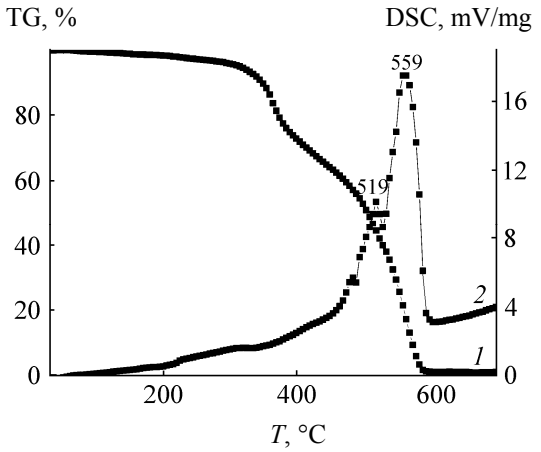


Fig. 2. Thermoanalytical curve for tetra-4-{[(1,1'-biphenyl)-4-yl]oxy}phthalocyanine **3:** (*1*) TG and (*2*) DSC.

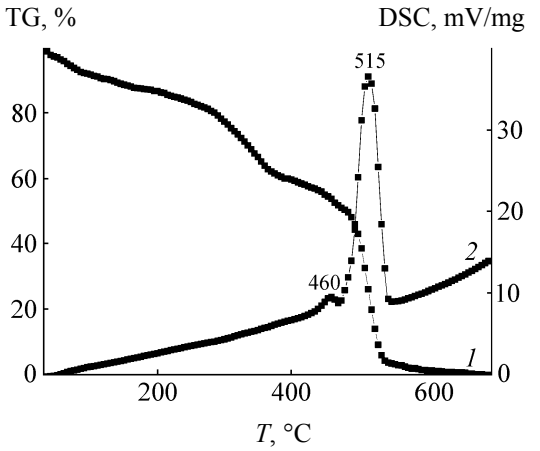


Fig. 3. Thermoanalytical curve for tetra-4-{[(1,1'-biphenyl)-4-yl]oxy}phthalocyanine **4c:** (*1*) TG and (*2*) DSC.

typical of phthalocyanine compounds [1], whereas cobalt can catalyze thermal oxidation [23].

We also studied the catalytic activity of cobalt phthalocyanine sulfonic acid derivative **4a** in the oxidation of sodium *N,N*-diethylcarbamodithioate into Thiuram E under mild conditions (Scheme 4). The interest in this specific reaction is explained by that its final product Thiuram E is the key component of drugs against chronic alcoholism [24, 25].

Phthalocyanine catalysts allow the oxidation process to be performed in mild conditions, thereby preventing further oxidation of disulfide and favoring a higher quality of the product which can be easily isolated from the reaction mixture and used in further synthesis without additional purification. Moreover, all kinetic parameters of this reaction are readily traced by spectrophotometry, which is convenient for evaluation of the catalytic activity of metal phthalocyaninates [26] in oxidative processes involving thiolate ions.

The use of metal phthalocyanine catalysts in this reaction allowed selective reaction and prevented further oxidation of the target product. The free ligand showed no catalytic effect, whereas macrocycle **4a** worked as a catalyst (Table 3).

Comparison of the catalytic properties of the presently synthesized compounds and our previous results [27, 28] reveals an effect of the nature of the terminal fragments in the phthalocyanine macrocycle. Activity is enhanced with enhancing electronic and steric effects of the peripheral substituents on the macrocycle. The kinetic parameters of the oxidation of sodium *N,N*-diethylcarbamodithiolate in the presence of cobalt phthalocyanine **4a** (Table 3) suggest that the reaction involves formation of a substrate–catalyst–oxidizer ternary complex [29]. It should be therewith noted that the product conversion in the case of cobalt phthalocyanine complexes with structurally similar substituents has an inverted pattern, which points to an essential role of factors that affect the stability of the resulting complexes and is associated with ordering of the system in the course of the catalytic process.

Thus, we synthesized tetra-4-{[(1,1'-biphenyl)-4-yl]-oxy}phthalocyanine, its metal complexes, and sulfonic acid derivatives of the latter. It was found that the introduction of sulfo groups in the Pc molecule leads to a bathochromic shifting of the absorption bands. Sulfo substitution in metal-free phthalocyanine decreases the thermal stability, whereas with cobalt complexes the opposite situation is observed. The sulfo-substituted cobalt tetra-4-{[(1,1'-biphenyl)-4-yl]-oxy}phthalocyanine catalyzes the oxidation of sodium *N,N*-diethylcarbamodithiolate into Thiuram E under mild conditions.

Scheme 4.

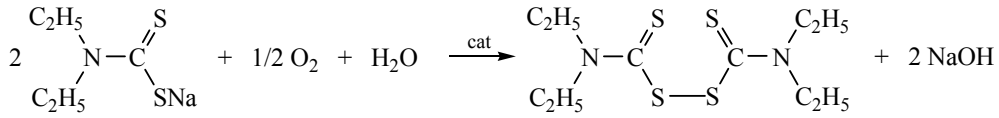
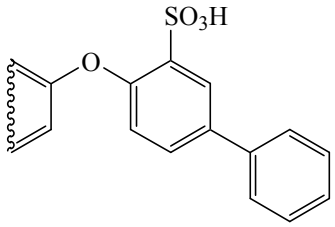
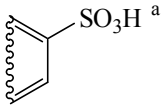
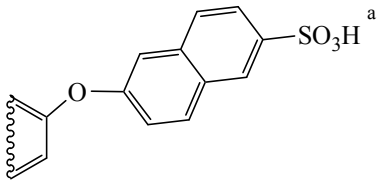
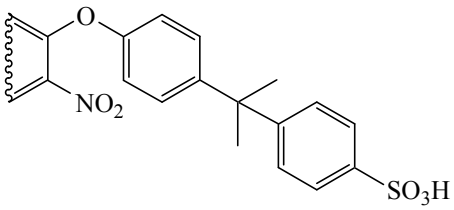
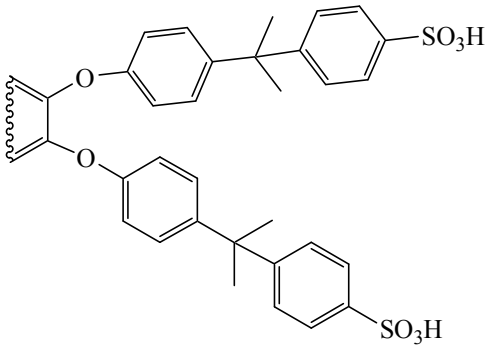


Table 3. Kinetic parameters of the oxidation of sodium *N,N*-diethylcarbamodithioate in the presence of cobalt phthalocyaninates

Pc	$k_w \times 10^3$, L mol^{-1} s^{-1}	$E^{\neq}$, kJ/mol	$\Delta S^{\neq}$, J mol^{-1} K^{-1}	χ, %
	49	24.3	–283	74
 [a]	26	–	–	82
 [a]	32	–	–	80
	21	50.99	–86	86
	42	50.04	–88	75

[a] According to [18].

EXPERIMENTAL

Elemental analysis was performed on a Thermo FlashEA 1112 CHNSO analyzer. The UV-Vis spectra were recorded in organic solvents and water on a HITACHI U-2001 spectrophotometer at room temperature in the range 350-900 nm. The IR spectra were run on an Avatar 360 FTIR ESP instrument in the range 400−4000 cm^{-1} in KBr pellets and thin films (chloroform). The ^{1}H NMR spectra (500.17 MHz) in $CDCl_3$ and DMSO-d_6 at 294 K were measured on a Bruker AVANCE 500 spectrometer relative to TMS. The MALDI−TOF mass spectra were measured on a Shimadzu Biotech Axima Confidence in the positive ion mode, using 2,5-dihydroxybenzoic acid as a matrix. The samples were prepared mixing equal volumes of chloroform solutions of the analytes (10^{-4}–10^{-5} M) with a THF solution of the matrix (30 mg/mL). The melting points were measured on a Boetius RNMK 05 hot stage.

The thermooxidative degradation of the synthesized phthalonitriles was studied on Jupiter Netzsch STA 449 F3 synchronous thermal analysis instrument in an oxygen–argon atmosphere using a platinum crucible, heating rate 5 deg/min. Before elemental and thermogravimetric analysis the samples were thermally treated at 110°C for 2 h.

The catalytic activity of cobalt phthalocyanines in the oxidation of sodium *N,N*-diethylcarbamodithiolate was studied by the procedure in [28, 29].

Synthesis of 4-{[(1,1'-biphenyl)-4-yl]oxy}phthalonitrile (1) was performed by the procedure in [11]. Yield 82.6%, mp 165–168°C. IR spectrum, ν, cm^{-1}: 2230 (C≡N), 1246 (Ar–O–Ar). ^1H NMR spectrum ($CDCl_3$), δ, ppm: 7.77 d (1H, H^3, J_{HH} = 9.2 Hz), 7.70 d (2H, $H^{5,5'}$, J_{HH} = 8.5 Hz), 7.62–7.61 m (1H, H^1), 7.52–7.49 m (3H, $H^{6,6',2}$), 7.36 m (1H, H^8), 7.33–7.31 m (3H, $H^{7,7',8}$), 7.18 d (2H, $H^{4,4'}$, J_{HH} = 8.6 Hz). Found, %: C 80.93; H 4.21; N 9.01. $C_{20}H_{12}N_2O$. Calculated, %: C 81.07; H 4.08; N 9.45.

Synthesis of tetra-4-{[(1,1'-biphenyl)-4-yl]oxy}-phthalocyanine metal complexes. A mixture of 0.296 g (1 mmol) of 4-{[(1,1'-biphenyl)-4-yl]oxy}-phthalonitrile **1**, 0.3 mmol of cobalt, copper, or magnesium acetate, and 0.18 g (3 mmol) of urea was thoroughly triturated and heated at 180–190°C until solidified. After cooling, the material was ground and washed with HCl until transparent filtrates and then with water to neutral washings. Final purification was performed by column chromatography of M 60 silica gel, eluent chloroform.

Cobalt tetra-4-{[(1,1'-biphenyl)-4-yl]oxy}phthalocyanine (2a). Yield 0.776 g (62.4%). IR spectrum, ν, cm^{-1}: 1238 (Ar–O–Ar). Mass spectrum, *m*/*z*: 1244.48 $[M - H]^+$ (calculated for $C_{80}H_{48}CoN_8O_4$: 1244.25). Found, %: C 76.98; H; 4.06; N 8.86. $C_{80}H_{48}CoN_8O_4$. Calculated, %: C 77.23; H 3.89; N 9.01.

Copper tetra-4-{[(1,1'-biphenyl)-4-yl]oxy}phthalocyanine (2b). Yield 0.713 g (57.2%). IR spectrum, ν, cm^{-1}: 1237 (Ar–O–Ar). ^1H NMR spectrum ($CDCl_3$), δ, ppm: 7.85 d (4H, H^3, J_{HH} = 8.0 Hz), 7.68–7.61 m (12H, $H^{5,5',1}$), 7.49 t (12H, $H^{6,6',2}$, J_{HH} = 7.5 Hz), 7.45 m (12H, $H^{7,7',8}$), 7.18 d (8H, $H^{4,4'}$, J_{HH} = 7.6 Hz). Mass spectrum, *m*/*z*: 1247.56 $[M - H]^+$ (calculated $C_{80}H_{48}CuN_8O_4$: 1248.86). Found, %: C 76.21; H 4.12; N 8.13. $C_{80}H_{48}CuN_8O_4$. Calculated, %: C 76.94; H 3.87; N 8.97.

Magnesium tetra-4-{[(1,1'-biphenyl)-4-yl]oxy} phthalocyanine (2c). Yield 0.8221 g (67.99%). IR spectrum, ν, cm^{-1}: 1239 (Ar–O–Ar). Mass spectrum, *m*/*z*: 1209.49 $[M]^+$ (calculated for $C_{80}H_{48}MgN_8O_4$: 1209.61). Found, %: C 78.81; H 4.15; N 9.10. $C_{80}H_{48}MgN_8O_4$. Calculated, %: C 79.44; H 4.00; N 9.26.

Tetra-4-{[(1,1'-biphenyl)-4-yl]oxy}phthalocyanines (3). A mixture of 0.80 g (0.66 mmol) of magnesium tetra-4-{[(1,1'-biphenyl)-4-yl]oxy}phthalocyanine **2c** and 25 mL of conc. HCl was heated under reflux for 20 min. The precipitate that formed was filtered off and washed with water until neutral washings. Final purification was performed by column chromatography of M 60 silica gel, eluent chloroform. Yield 0.7121 g (91.3 %). IR spectrum, ν, cm^{-1}: 1230 (Ar–O–Ar), 1006 (H_2Pc). Mass spectrum, *m*/*z*: 1208.46 $[M + 2Na - 2H]^+$. Found, %: C 80.81; H 5.01; N 9.24. $C_{80}H_{50}N_8O_4$. Calculated, %: C 80.93; H 4.24; N 9.44.

Synthesis of tetra-4-{[(1,1'-biphenyl)-4-yl]oxy}-phthalocyanine sulfonic acids. Thionyl chloride, 2 mL (30 mmol), was poured into a mixture 0.1 mmol of the corresponding tetra-4-{[(1,1'-biphenyl)-4-yl]-oxy}phthalocyanine **2a**, **2b**, or **3** and 2 mL (30 mmol) of chlorosulfonic acid. The resulting mixture was stirred for 2 h and then poured into ice with NaCl. The precipitate was filtered off on a glass frit filter and washed with ice saturated NaCl solution until a negative Congo red test. The reaction product was dried at room temperature. Sulfonyl chloride was extracted with acetone, and the solvent was removed. The resulting blue powder was boiled with water until dissolved completely. The aqueous solution was evaporated.

Cobalt tetra-4-{[2'-sulfo-(1,1'-biphenyl)-4-yl]oxy}-phthalocyanine (3a). Yield 0.1059 g (67.7%). IR spectrum, ν, cm^{-1}: 1241 (Ar–O–Ar), 1091 (C–S), 1178 (S=O). Found, %: C 61.20; H 3.82; N 6.94; S 8.13. $C_{80}H_{48}CoN_8O_{16}S_4$. Calculated, %: C 61.42; H 3.09; N 7.16; S 8.20.

Copper tetra-4-{[2'-sulfo-(1,1'-biphenyl)-4-yl]oxy}-phthalocyanine (3b). Yield 0.1247 g (79.46%). IR spectrum, ν, cm^{-1}: 1240 (Ar–O–Ar), 1092 (C–S), 1179 (S=O). ^1H NMR spectrum (DMSO-d_6), δ, ppm: 8.31 s (4H, OH), 8.11 m (8H, $H^{5,6}$), 7.95 s (4H, H^2), 7.77 d (4H, H^1, J_{HH} = 8.3 Hz), 7.74–7.69 m (12H, $H^{4,7,7'}$), 7.63 m (4H, H^3), 7.29 d.d (12H, $H^{8,8',8''}$, $^2J_{HH}$ = 6.3, $^3J_{HH}$ = 10.1 Hz). Found, %: C 60.90; H 3.95; N 6.86; S 8.00. $C_{80}H_{48}CuN_8O_{16}S_4$. Calculated, %: C 61.24; H 3.08; N 7.14; S 8.17.

Tetra-4-{[2'-sulfo-(1,1'-biphenyl)-4-yl]oxy}-phthalocyanine (3c). Yield 0.0974 g (64.6%). IR

spectrum, ν, cm^{-1}: 1240 (Ar–O–Ar), 1092 (C–S), 1178 (S=O), 1005 (H_2Pc). Found, %: C 63.04; H 4.01; N 7.23; S 8.32. $C_{80}H_{50}N_8O_{16}S_4$. Calculated, %: C 63.74; H 3.34; N 7.43; S 8.51.

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REFERENCES

1. Shaposhnikov, G.P., Kulinich, V.P., and Maizlish, V.E., *Modifitsirovannye ftalocianiny i ikh strukturnye analogi* (Modified Phthalocyanines and Their Structural Analogs), Moscow: KRASAND, 2012.
2. *The Porphyrin Handbook*, Kadish, K.M., Smith, K.M., and Guilard, R., New York: Academic, 2003, vol. 15.
3. Kudrik, E.V., Makarov, S.V., Ageeva, E.S., and Dereven'kov, I.A., *Macroheterocycles*, 2009, vol. 2, no. 1, p. 69.
4. Çetinkaya, M., Pişkin, M., Altun, S., Odabaş, Z., and Durmus, M., *J. Photochem. Photobiol. A*, 2017, vol. 335, p. 17. doi 10.1016/j.jphotochem.2016.11.009
5. Kuznetsova, N.A. and Kaliya, O.L., *Macroheterocycles*, 2015, vol. 8, no. 1, p. 8. doi 10.6060/mhc141243k
6. Vashurin, A.S., Filippova, A.A., Znoyko, S.A., Voronina, A.A., Lefedova, O.V. Kuzmin, I.A., Maizlish, V.E., and Koifman, O.I., *J. Porphyrins Phthalocyanines*, 2015. vol. 19, no. 8, p. 983. doi 10.1142/S10884246144501028
7. Xu, H.-N., Chen, H.-J., Zheng, B.-Y., Zheng, Y.-Q., Ke, M.-R., and Huang, J.-D., *Ultrason. Sonochem*., 2015, vol. 22, p. 125. doi 10.1016/j.ultsonch.2014.05.019
8. Kantar, C., Akal, H., Kaya, B., Islamoglu, F., Turk, M., and Sasmaz, S., *J. Org. Chem*., 2015, vol. 783, p. 28. doi 10.1016/j.jorganchem.2014.12.042
9. Tsunoda, T., Tanaka, A., Mase, T., and Sakamoto, S., *Heterocycles,* 2004, vol. 63, no. 5, p. 1113. doi 10.3987/COM-04-10025
10. Ohkanda, J., Buckner, F.S., Lockman, J.W., Yokoyama, K., Carrico, D., Eastman, R., de Luca-Fradley, K., Davies, W., Croft, S.L., Voorhis, W.C.V., Gelb, M.H., Sebti, S.M., and Hamilton, A.D., *J. Med. Chem*., 2004, vol. 47, no. 2, p. 4463. doi 10.1021/jm030236o
11. Znoiko, S.A., Maizlish, V.E., Shaposhnikov, G.P., Akopova, O.B., Bumbina, N.V., Usoltseva, N.V., and Abramov, I.G., *Russ. J. Gen. Chem*., 2014, vol. 84, no. 4, p. 708. doi 10.1134/S1070363214040185
12. US Patent 20080004391, 2007.
13. Jiang, Z., Ou, Z., Chen, N., Wang, J., Huang, J., Shao, J., and Kadish, K.M., *J. Porphyrins Phthalocyanines*, 2005, vol. 9, no. 5, p. 352. doi 10.1142/S1088424605000447
14. Arslanoğlu, Y., Sevim, A.M., Hamuryudan, E., and Gül, A., *Dyes Pigments*, 2006. vol. 68. p. 129. doi 10.1016/j.dyepig.2005.01.019
15. Wei. J., Li, X., Xiao, Ch., and Lu, F., *Vibrat. Spectrosc*., 2017, vol. 92, p. 105. doi 10.1016/j.vibspec.2017.06.002
16. Berezin, B.D. and Berezin, D.B., *Khromofornye sistemy makrotsiklov i lineinykh molekul* (Chromophoric Systems of Macrocycles and Linear Molecules), Moscow: URSS, 2013.
17. Berezin, B.D. and Berezin, D.B., *Kurs sovremennoi organicheskoi khimii* (Textbook on Modern Organic Chemistry), Moscow: Vysshaya Shkola, 1999.
18. Morrison, R.T. and Boyd, R.N., *Organic Chemistry*, Boston: Allyn and Bacon, 1973, 3rd ed.
19. Znoiko, S.A., Akopova, O.B., Bumbina, N.V., Maizlish, V.E., Shaposhnikov, G.P., and Usol'tseva, N.V., *Macroheterocycles*, 2014, vol. 7, no. 3, p. 287. doi 10.6060/mhc140930z
20. Kulinich, V.P., Shaposhnikov, G.P., and Badaukaite, R.A., *Makrogeterotsikly*, 2010, vol. 3, no. 1, p. 23.
21. Kulinich, V.P., Badaukaite, R.A., Tikhomirova, T.V., and Shaposhnikov, G.P., *Russ. J. Gen. Chem*., 2013, vol. 83, no. 4, p. 744. doi 10.1134/S1070363213040233
22. Terenin, A.R., *Fotonika molekul krasitelei i rodstvennykh soedinenii* (Photonics of Molecules of Dyes and Related), Leningrad: Nauka, 1967.
23. Vashurin, A.S., *Russ. Chem. Bull*., 2017, no. 9, p. 220. doi 10.1007/s11172-016-1572-z
24. Gessner, P.K. and Gessner, T., *Disulfiram and its Metabolite, Diethyldithiocarbamate*, Amsterdam: Springer, 1992. doi 10.1007/978-94-011-2328-0.
25. Victoriano, L.I., *Coord. Chem. Rev*., 2000, vol. 196, p. 383. doi 10.1016/S0010-8545(99)00221-0
26. Borisenkova, S.A., *Petroleum Chem*., 1991, vol. 31, no. 3, p. 391.
27. Filippova, A., Vashurin, A., Znoyko, S., Kuzmin, I., Razumov, M., Chernova, A., Shaposhnikov, G., and Koifman, O., *J. Mol. Struct*., 2017, vol. 1149, p. 17. doi 10.1016/j.molstruc.2017.07.086
28. Tyapochkin, E.M. and Kozliak, E.I., *J. Mol. Catal. A*, 2005, vol. 242, p. 1. doi 10.1016/j.molcata.2005.07.008
29. Vashurin, A.S., Pukhovskaya, S.G., Semeikin, A.S., and Golubchikov, O.A., *Makrogeterotsikly*, 2012, vol. 5, no. 1, p. 72. doi 10.6060/mhc2012.111251v