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Electrochemical, spectrochemical and catalytical properties of cobalt(II) phthalocyanine regioisomers studies



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A R T I C L E I N F O	A B S T R A C T
Keywords: Catalysis Cyclic voltammetry Cyclohexene Regioisomer Phthalocyanine	Two regioisomers of tetrasubstituted cobalt(II) phthalocyanine bearing L-menthol moieties in the periphery, were synthesized through remetallation reaction of metal-free phthalocyanines as substrates. Mass spectrometry and UV-Vis spectrophotometry were employed for characteristics. Cyclic voltammetry (CV) and differential pulse voltammetry (DPV) studies indicate three one-electron ring-based oxidation processes, oxidation/reduction of cobalt center (Co(II)/Co(I)) and one ring-based reduction. The comparative studies of catalytic activity of the two phthalocyanines were investigated. Cyclohexene oxidation using tert-butylhydroperoxide (TBHP) and cobalt(II) phthalocyanines results in formation of 2-cyclohexen-1-one, 2-cyclohexen-1-ol, cyclohexanol, cyclohexene epoxide. Formation of 2-cyclohexen-1-one were favored.

1. Introduction

Phthalocyanines (Pcs) are macrocycles related to porphyrins, but of purely synthetic origin. Due to their unique properties, such as intense light absorption and high chemical stability. Pcs are intensively studied as dyes [1], photosensitizers for photodynamic therapy [2,3], materials for dye-sensitized solar cells [4], electrode modifiers for analytical applications [5], or catalysts [6]. Pcs structure may be modified by substituents in the non-peripheral (α) or peripheral (β) positions and metal ions in the coordination center [7]. Variations in substituents and metal ions allows to significantly modify the Pc properties [8]. Metallophthalocyanines are considered attractive candidates for being oxidant catalysts. They are structural analogues of porphyrin metal complexes, but studied to a lesser extent. They outweigh porphyrins with their stability in oxidation conditions, availability and low price. Variously substituted phthalocyanines have been studied for their ability in the oxidation of alkanes [9,10], alkenes [11], and arenes [12,13]. Oxidation reaction require the presence of an oxygen donor like tert-butylhydroperoxide (TBHP) [14,15], hydrogen peroxide [16] or iodosylbenzene [11]. TBHP seems to be the mildest, as it does not cause decomposition of phthalocyanine ring and even promoting higher activity [17,18]. The selectivity of phthalocyanine complexes and their performance as catalysts can be tuned by changing the metal ion in the macrocyclic ring or the substituents in the periphery. The type of the ion present in the coordination center of the macrocyclic ring has a decisive influence whether the oxidation is a catalytic process or photocatalytic; the most frequently chosen complexes are those of transition metals: Fe (II), Mn(II), Co(II), where oxygen binds to the metal ion forming an oxide that interacts with the substrate and consequently leads to the oxidation [19,20].

Enzymatic systems such as cytochrome P-450 monooxygenases found in living organisms have been inspiring catalysis research. Characteristic cytochrome-catalyzed reactions are hydroxylation of alkanes, aromatics, and epoxidation of alkenes [21]. Porphyrinoids, especially porphyrins are particularly suitable to mimic the reactions carried out by the cytochrome P-450 enzymes [22–24]. The experiments revealed a relationship between the selectivity and the type of the substituents in the porphyrin molecule [25]. On this basis, it was concluded that porphyrins are involved in the process of oxygen transfer to the substrate.

The use of tetrasubstituted cobalt(II) phthalocyanines as catalysts for the oxidation of cyclohexene has been reported [26]. It was observed that both complexes oxidize cyclohexene but slightly differed in the selectivity of the products and conversion yield. These results indicate that modifications in the structure of the catalyst molecule can determine the direction of the reaction in order to obtain a specific product with the required yield, similar to cytochrome P-450.

The phthalocyanines modified with chiral moieties have the potential to show differences in biological properties and other properties

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such as interaction with chemical compounds. Therefore we decided to synthesize phthalocyanines with chiral menthol substituents in this study.

2. Materials and methods

2.1. General

Synthesis of **1** and **2** was previously reported [27]. Merck silica gel, particle size 40–63 mm was used for flash column chromatography. Merck Kieselgel 60 F254 plates were used for thin layer chromatography. Shimadzu UV-160A was used for spectrophotometric studies. Brucker UltrafleXtreme (Wielkopolska Centre for Advanced Technologies in Poznan) was used for mass spectrometry. Brucker 436-GC equipment (30 m \times 0.25 mm \times 0.25 µm BR 5-ms column, MS detector) was used for gas chromatographic measurements at Poznan Science and Technology Park.

2.2. Synthesis

2.2.1. Cobalt(II) 1,8,15,25-tetrakis-[(1R,2S,5R)-2-isopropyl-5-methylcy-clohexyloxy]phthalocyanine (3)

Round-bottom flask was charged with Pc 1 (0.080 g, 0.07 mmol), cobalt(II) acetate (0.062 g, 0.353 mmol) and DMF (9 mL), the reaction mixture was heated at 70 °C for 24 h. Next, the solvent was evaporated to dryness and the dry residue was chromatographed (DCM:methanol, 200:1, v/v) to give the dark green product 3 (0.073 g, 86% yield).

MS (ESI) m/z 1188.6336 $[M+H]^+$, $C_{72}H_{89}N_8O_4Co$ requires 1188.6339 $[M+H]^+$, UV-Vis in DCM λ_{max} , nm (loge): 313 (4.76), 629 (4.55), 699 (5.22).

2.2.2. Cobalt(II) 1,8,18,25-tetrakis-[(1R,2S,5R)-2-isopropyl-5-methylcyclohexyloxy]phthalocyanine (4)

Round-bottom flask was charged with Pc **2** (0.060 g, 0.05 mmol), cobalt(II) acetate (0.0469 g, 0.265 mmol) and DMF (9 mL), the reaction mixture was heated at 70 °C for 24 h. Next, the solvent was evaporated to dryness and the dry residue was chromatographed (DCM:methanol, 200:1, v/v) to give the dark green product **4** (0.058 g, 92% yield).

MS (ESI) m/z 1188.6352 $[M+H]^+$, $C_{72}H_{89}N_8O_4Co$ requires 1188.6339 $[M+H]^+$, UV-Vis in DCM λ_{max} , nm (loge): 313 (4.79), 630 (4.57), 701 (5.23).

2.3. Cyclic voltammetry

Electrochemical measurements were carried out with an Autolab (PGSTAT-30) an electrochemical analyzer (Eco Chemie, Netherlands). A three-electrode system was used with Ag/AgCl wire pseudo-reference electrode and platinum wire as a counter electrode. A glassy carbon electrode (GC) with a diameter of 1 mm (BASi, USA) functioned as a working electrode. Before each electrochemical measurement, the GC electrode was polished with an aqueous suspension of Al_2O_3 (Buehler, 50 nm average diameter) on a polishing cloth and then washed in an ultrasonic bath with 1:1 v/v water/acetone for 10 min to remove any impurities.

A 0.1 M TBAP dissolved in dichloromethane (TBAP/DCM) served as a supporting electrolyte. TBAP/DCM was deoxygenated through purging with pure nitrogen gas. Half-waves potentials, $E_{1/2}$, are given in this work versus the ferrocene/ferrocenium (Fc⁺/Fc) couple. After each of electrochemical experiment ferrocene was added to the electrochemical cell in order to set the potential values.

2.4. Catalytic experiments

2.4.1. Cyclohexene oxidation

The catalytic activity and selectivity of **3** and **4** have been studied for the oxidation of cyclohexene with TBHP under the same experimental conditions in DCM. The 10 mL glass vial with cap was charged with cyclohexene (1.22×10^{-3} mol), compound **3** (4.09×10^{-6} mol) or compound **4** (4.09×10^{-6} mol) and TBHP (2.04×10^{-3} mol) in DCM (10 mL) and stirred at 35 °C with 700 rpm stirring for 3 h. The formed products were monitored with GC-MS and compered with standards. Control experiment without the catalyst were done to confirm the vital role of the catalyst in the oxidation process.

2.4.2. Esomeprazole oxidation

The 10 mL glass vial with cap was charged with S-omeprazole (1.68 \times 10⁻⁵mol), compound **3** (8.41 \times 10⁻⁷ mol) or compound **4** (8.41 \times 10⁻⁶ mol) and TBHP (1.66 \times 10⁻⁵ mol) in DCM (10 mL) and stirred at 25 °C for 24 h. Control experiment without catalyst was carried out under the same conditions. The products were isolated by preparative TLC (glass plates RP-18 F₂₅₄, 5 \times 10 cm, DCM:MeOH, 1:40 v/v) and characterized by mass spectrometer.

3. Results and discussion

3.1. Synthesis

Phthalocyanine synthesis is usually based on the cyclotetramerisation (macrocyclization) reaction of phthalic acid derivatives. On a laboratory scale phthalonitrile (1,2-dicyanobenzene) derivatives are employed, accompanied by a metal ions, serving as a template. We decided to use alternative synthetic pathway - an introduction of metal ions to the previously demetallated Pc ring core. High yields of pure product are key benefits of this method [28]. Previously synthesized demetallated compounds 1 and 2 [27] were subjected to complexation reaction with cobalt(II) acetate (Scheme 1). Separation of the regioisomers was done on the previous stage of synthetic pathway magnesium(II) Pcs bearing menthol substituents were separated [29], and demetallated. Thanks to this method, single regioisomers of metal-free Pcs were available, giving an opportunity to remetallation reactions. This approach seems to be specially useful for obtaining pure regioisomers of Pcs with paramagnetic ions, as exact assigning substitution pattern requires NMR spectroscopy. Remetallation reaction provided cobalt(II) phthalocyanine compounds 3 and 4 of symmetries C₁ and C₂, respectively. The products were chromatographically purified and obtained in yields close to 90%. Scheme 1 shows the brief schematic for the synthesis of non-peripherally L-menthol substituted cobalt phthalocyanine 3 and 4 complexes, structures of these Pcs were confirmed by mass spectrometry.

3.2. UV-Vis data

Photospectroscopic properties of compounds 3 and 4 were studied in different solvents (DCM, DMF, THF) (Table 1). The phthalocyanine solutions did not show any aggregation, as the absorbance changed linearly with the concentration (see Supplementary data). Two strong absorption bands, one with λ_{max} in the 311–313 nm range (Soret band), and Q-band with λ_{max} in the 694–701 nm range were found. The position of the Q band for two isomers are almost the same. Similar observations were obtained for previously synthesized regioisomers [27,29, 30]. Although the absorption spectra does not strongly depends on the metal ion in the macrocyclic core, the substituents in the periphery can affect Q-band position [31]. The L-menthol electron-donating character causes a significant red shift of the Q band.as compared to unsubstituted CoPc (Q-band $\lambda_{max} = 654$ nm) [32]. The other factor causing red shift of the Q-band may be non-planarity of the Pc ring, caused by the steric interaction of the bulky substituents. Previously reported magnesium(II) analogue of 3 was studied by means of X-ray crystallography [29], and Pc ring distortion was found as the isoindole units deviate from the N4 plane. We stipulate, that similar distortion may be true for 3 and 4, leading to bathochromic shift of Q-band [33,34].



Scheme 1. Synthesis of cobalt(II) phthalocyanines with menthol substituents. Reagents and conditions: (i) Co(CH3COO)2, DMF, 70 °C, 24 h.

Table 1Spectroscopic properties of the phthalocyanines.

Compound	Solvent	Soret band λ_{max} [nm], log ϵ [dm ³ mol ⁻¹ cm ⁻¹]	Vibronic band λ_{max} [nm], log ϵ [dm ³ mol ⁻¹ cm ⁻¹]	$\begin{array}{l} \text{Q-band} \\ \lambda_{max} \; [nm], \; \text{log} \; \epsilon \\ [dm^3 \; \text{mol}^{-1} \\ cm^{-1}] \end{array}$
3	DCM	313, 4.76	629, 4.55	699, 5.22
	DMF	311, 4.76	623, 4.52	697, 5.07
	THF	312, 4.60	624, 4.55	696, 5.22
4	DCM	313, 4.79	630, 4.57	701, 5.23
	DMF	311, 4.75	626, 4.52	694, 5.09
	THF	312, 4.59	625, 4.53	696, 5.19

3.3. Electrochemical studies

Pcs **3** and **4** were subjected to electrochemical studies; cyclic voltammetry (CV) and differential pulse voltammetry (DPV) were used. For both studied complexes five well-defined redox features can be seen in Fig. 1.

Three oxidation processes at -0.01, 0.49, and 0.69 V can be observed for **3**. These peaks can be assigned to a one-electron oxidation/reduction of phthalocyanine ring [29]. Similarly, **4** revealed three oxidation features at slightly less positive values (-0.04, 0.44, and 0.65 V). Comparing to previously studied magnesium phthalocyanines bearing menthol substituents, **4**, the **3** complexes present a shift of oxidative redox peaks toward more positive values [29]. Moreover, **4**

and **3** complexes revealed ring-based reduction couple positioned at -2.17 and -2.14, respectively.

Cobalt metal center is electrochemically active in applied potential window [35–37]. Peaks at $E_{1/2} = -0.93$ and -0.88 for 4 and 3, respectively are due to oxidation/reduction of cobalt center (Co(II)/Co(I)) [35]. In non-coordinating solvents such as DCM only one-electron transition assigned to (Co(II)/Co(I)) can be expected since cobalt-based macrocycles are rather not susceptible to undergo a Co (III)/Co(II) redox transition [36–38] in DCM.

According to CV measurements, the complexes display asymmetric and well-defined redox peaks. DPVs data of the complexes also support the reversibility of the redox processes, since these couples show symmetric oxidation and reduction signals. The electrochemical data for complexes are collected in Table 2. As seen the measured parameters such as ΔE and I_a/I_c suggest a quasi-reversible electrochemical behavior of studied complexes. The presented complexes bearing menthol substituents are relatively easy to oxidize when compared to literature data of phthalocyanines with 4-(2-(benzo[d]thiazol-2-yl)phenoxy) substituents or with ester functionalities [38,39].

3.4. Catalytic studies

3.4.1. Oxidation of cyclohexene with 3 and 4

Pcs **3** and **4** were studied as catalysts for cyclohexene oxidation. Cyclohexene and its oxidation products play an important role as synthetic intermediates in industry [40-42]. There are two possible oxidation sites in cyclohexene: C=C bond and C-H bond at the allylic



Fig. 1. (A) Cyclic voltammograms of phthalocyanines **3** and **4** recorded in 0.1 M TBAP/DCM at a scan rate of 50 mV s⁻¹, (B) differential pulse voltammograms of phthalocyanines in 0.1 M TBAP/DCM (pulse width: 50 ms, pulse height: 20 mV, scan rate: 5 mV s⁻¹).

Table 2	
Electrochemical a	parameters of 3 and 4

Complex		Red_1	Co (I)/Co (II)	Ox ₁	Ox ₂	Ox ₃
3	E _{1/2} /V	-2.14	-0.88	-0.01	0.49	0.69
	$\Delta E^{a}/mV$	75	69	83	87	88
	I_a/I_c^b	1.03	1.07	1.1	1.15	0.89
4	E _{1/2} /V	-2.17	-0.93	-0.04	0.44	0.65
	$\Delta E^a/mV$	75	70	82	84	80
	I_a/I_c^b	0.98	1.05	0.89	1.10	1.15

^a $\Delta E = E_{peak}(anodic) - E_{peak}(cathodic).$

 $^{\rm b}~I_{\rm a}$ and $I_{\rm c}$ are anodic and cathodic peak currents, respectively.

position. Oxidation at these sites can lead to formation of following products: cyclohexene epoxide, cyclohexane-1,2-diol, cvclohex-2-en-1-ol, cyclohex-2-en-1-one, cyclohexanol and cyclohexanone [43]. Formation of many possible products as well as their importance in the industrial synthesis have made many researchers choose cyclohexene as a model compound for catalytic research. In recent years, many reports have appeared for studying catalytic properties of porphyrinoids and their selectivity in relation to a given product. The choice of TBHP as an oxidant was dictated by the evidence of good selectivity of products and low destruction of the phthalocyanine macrocycle [14,18, 26]. However, the reaction color changed from dark green to brown after addition of TBHP. As observed also by other researchers this may indicate the destruction of the macrocycle [44,45]. Nevertheless, the reaction products continued to form which suggest that initially formed reaction intermediates are sufficient to carry out the oxidation reaction without the original form of the catalyst. Control experiments showed

that cyclohexene oxidation with TBHP did not occur or appears in a lesser extent in the absence of catalyst.

Four products were identified using gas chromatography compared with standards. These products are cyclohexene epoxide, 2-cyclohexene-1-ol, cyclohexanone and 2-cyclohexene-1-one (Table 3). It is noticeable that catalysts **3** and **4** favored the formation of 2-cyclohexen-1-one to the rest of the products. There was no significant difference in the yield of products between the two catalysts, therefore it can be concluded that the symmetry of the phthalocyanine compounds does not play a significant role in the catalytic process in this case.

3.4.2. Oxidation of esomeprazole with 3 and 4

Additional studies utilizing **3** and **4** as catalysts were conducted, employing esomeprazole as a substrate. Esomeprazole is a proton pump inhibitor drug, and a (S)-(–)-isomer of the omeprazole. TBHP was used as an oxidant; control experiments without the catalyst were run in parallel. These catalytic reaction mixtures were subjected to preparative TLC analysis. Spots, that were not present in the control experiments were isolated and the substances subjected to mass spectrometry. Obtained signals (Table 4) correspond well to esomeprazole degradation products obtained by other oxidation and degradation studies [46,47].

4. Conclusion

Remetallation reaction was an efficient way of introducing Co^{2+} ions to demetallated phthalocyanines bearing menthol moieties. The resulting cobalt(II) phthalocyanines with menthol moieties were subjected to spectrophotometric studies in DCM, DMF and THF. In comparison to unsubstituted cobalt(II) phthalocyanine [32], λ_{max} of the Q-bands are

Table 3

The product yields of cyclohexene oxidation with complex 3 and 4.

Catalyst	Time [min]	2-cyclohexen-1-one	2-cyclohexen-1-ol	Cyclohexene epoxide	Cyclohexanone
3	45	15	14	0.8	0.04
4		15	10	0.7	0.04
- (control)		3.2	0.8	0.3	-
3	180	17	11	1.0	0.05
4		16	11	0.7	0.05
- (control)		3.6	0.9	0.3	-

Table 4

Proposed formulae, observed and calculated m/z for obtained products after catalytic reaction using compounds **3** and **4**.

	-		
Proposed product formula	Observed (m/z)	Calculated (m/z)	Catalyst
$C_{10}H_{14}NO_2^+$ $C_{17}H_{20}N_3O_2^+$	180.1019 298.1546, 298.1556	180.1025 298.1556	4 3, 4
$C_{16}H_{19}N_3O_3^+$	301.1412, 301.1408	301.1426	3, 4
$C_{17}H_{18}N_3O_3^+$	312.1348	312.1348	4
$C_{19}H_{15}N_{3}O_{2}^{+}$	317.1149, 317.1157	317.1164	4 3, 4
C ₁₇ H ₂₀ N ₃ O ₂ S ⁺	330.1279	330.1276	4
$C_{17}H_{20}N_2O_3S^+$	332.1234	332.1195	3

red shifted to about 700 nm, which is caused by electron-donating properties of menthol substituents. Electrochemical studies revealed a good reversibility of ring-based redox processes. Moreover, a well-defined redox transition ascribed to Co(II)/Co(I) metal center was observed. It was presented that studied compounds reveal low catalytic activity in cyclohexene oxidation. It may be caused by rapid degradation after the addition of oxidant - TBHP.

CRediT authorship contribution statement

Joanna Szymczak: Funding acquisition, Investigation, Writing – original draft. Tomasz Rębiś: Investigation, Writing – original draft. Jadwiga Mielcarek: Writing – review & editing. Michal Kryjewski: Conceptualization, Writing – review & editing.

Declaration of Competing Interest

The authors declare that they have no known competing financial interests or personal relationships that could have appeared to influence the work reported in this paper.

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Appendix A. Supplementary material

Supplementary data associated with this article can be found in the online version at doi:10.1016/j.synthmet.2021.116971.

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