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Investigation of catalytic activity of new Co(II) phthalocyanine complexes in cyclohexene oxidation using different type of oxidants

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ABSTRACT

In this work, the new phthalonitrile derivatives **4**, **5** bearing 1,3-bis(naphthalen-1-yloxy)propan-2-ol and 1,3-bis(naphthalen-2-yloxy)propan-2-ol, cobalt phthalocyanine complexes have been synthesized. The new cobalt phthalocyanines have been prepared by cyclotetramerization of phthalonitrile derivatives **4**, **5** in the presence of the corresponding $CoCl_2$ salt in DMAE by using a microwave oven. The new compounds have been characterized by IR, ^1H NMR, ^{13}C NMR and MS spectral data. The new complexes have been tested as a catalyst for the oxidation of cyclohexene with different oxidants, such as *tert*-butylhydroperoxide (TBHP), m-chloroperoxybenzoic acid (*m*-CPBA) and hydrogen peroxide (H_2O_2), in DMF. m-CPBA is also found as the most successful oxidant in the other oxygen sources. In this sense, the substrate/catalyst ratio, the influence of temperature, oxidant/cat ratio and type of oxidant have been studied. It is observed three oxidation products. First one is 2-cyclohexene-1-ol as dominant product and the others are 2-cyclohexene-1-one and cyclohexene oxide as minor product.

1. Introduction

The industrial and environmental preoccupations meet on their common need for more efficient and cheaper catalysts. These high-tech catalysts are required for a more effective degradation of pollutants, which is one of their two main uses, or for high scale synthetic purposes. Oxidation of different type of molecules such as alkyl aromatics, alkenes and alcohols are of particular importance as it lead to small molecules used as starting products for more complex syntheses in fine chemicals production (pharmaceutics, cosmetics, polimerization monomers). As the transformed functions can lead to different products, the selectivity of the catalyst is essential to the overall catalytic system's efficiency [1].

Bioinspired heme-like catalysts were developed for synthetic purposes as their natural models are active oxidant catalysts, highly selective and performing. Porphyrin's structure common to these enzymes was therefore used by synthetic chemists aiming at developing new catalytic structures. Phthalocyanines, tetraazabenzoporphyrins analogs of porphyrins, after having been used as simple dyes and pigments, rise interests since a few decades as their multi functional structure (large delocalized aromatic system, metallation, flexibility on a substitution pattern point of view) as well as their exceptional stability in time and extreme conditions (temperature, pH, etc…). Furthermore, they are intensively used as homogenoushomogenous and heterogenous catalyst, liquid crystal, electro-and photo-chemical sensor, photoconductive materials, batteries and fuel supplies, photosensitizier in photodynamic therapy agent [2–7]. They are known to possess better catalytic properties than the prophyrins, especially thanks to their superior stability in oxidation conditions.

The higher oxidation states of the central transition metal ions are more readily accessible in the porphyrin series than in the phthalocyanine series [8]. In other words, phthalocyanine ligand tends to stabilize the lower oxidation states of metal compared to porphyrin one. This implies that high oxidation states metallophthalocyanines should be stronger oxidizing agents than their porphyrin analogs in the same oxidation state. In porphyrin series the kind of the cleavage of O—O bond is determined by the structures of porphyrin ligand and peroxide and the presence of axial ligand, which favors a heterolytic O—O bond cleavage [9]. In addition, cobalt phthalocyanine complexes are also used as oxidation catalyst for selective oxidation of olefines [10]. It is found that Co(II) phthalocyanines can transfer oxygen from various oxygen donors to alkanes, alkenes, phenols and thiols in the several studies [11–22]. Condensed aromatic compounds containing naphthalene derivatives are effective functional groups in photoemission studies [23,24]. Thus, in this paper we have aimed to synthesize a new class of cobalt phthalocyanines bearing 4-{2-(1-Naphthyloxy)-1-[(1-naphthyloxy)methyl]ethoxy}, 4-{2-(1-Naphthy

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loxy)-1-[(2-naphthyloxy)methyl]ethoxy} groups on the substituents. Additionally, the present paper also has reported on the application of phthalocyanine-based homogenous catalysts in the oxidation of cyclohexene. We have investigated the oxidation process with the purpose of developing product selectivity and increasing the range of products. Co(II) phthalocyanine complexes have been compared as best catalysts for the oxidation.

2. Experimental

All reactions were carried out under a dry nitrogen atmosphere using standard Schlenk techniques. All chemicals, solvents and reagent were of reagent grade quality and were used as purchased from commercial sources. All solvents were dried and purified as described by a reported procedure [25]. 1,3-Bis(naphthalen-1-yloxy)propan-2-ol **1** and 1,3-bis(naphthalen-2-yloxy)propan-2-ol **2** were synthesized according to the literature, respectively [26,27].

2.1. Synthesis

2.1.1. 4-{2-(1-Naphthyloxy)-1-[(1-naphthyloxy)methyl]ethoxy} phthalonitrile (4)

4-Nitrophthalonitrile **3** (0.6 g, 3.5×10^{-3} mol) was dissolved in 0.03 L dry DMF under N_2 atmosphere, and of 1,3-bis(naphthalen-1-yloxy)propan-2-ol **1** (1.2 g, 3.5×10^{-3} mol) was added to the mixture. After stirring for 30 min at 60 °C, finely ground anhydrous K_2CO_3 (1.45 g, 10.5×10^{-3} mol) was added portion wise within 2 h. The reaction mixture was stirred under N_2 at 60 °C for 4 days. At the end of this time, the reaction mixture was poured into ice-water and stirred at room temperature for 1 h to yield a crude product. The mixture was filtered and dried in vacuum over P_2O_5 for 4 h and recrystallized from ethanol to give light yellow crystalline powder. Yield: 0.6 g (35%). mp: 63–67 °C. IR (KBr pellet), ν_{max}/cm^{-1}: 3055–3019 (Ar-H), 2931–2879 (Aliph. C–H), 2232 (C<ce:glyph name="tbnd"/>N), 1728, 1669, 1600, 1575, 1505, 1400, 1349, 1157, 1143, 1000, 1021, 1024, 973, 873, 769, 667, 571, 524. ^1H NMR. ($CDCl_3$), (δ: ppm): 8.08 (d, 2H, Ar-H), 7.84 (d, 2H, Ar-H), 7.66 (m, 11H, Ar-H), 6.89 (d, 2H, Ar-H), 5.41 (t, 1H, O–CH), 4.61 (m, 4H, O–CH_2). ^{13}C NMR. ($CDCl_3$), (δ: ppm): 162.48, 155.32, 136.74, 134.58, 127.88, 127.08, 126.68, 126.12, 124.48, 123.76, 121.22, 117.87, 116.52, 115.91, 115.36, 112.57, 107.48, 106.05, 79.85, 67.30. MS (ESI), m/z: 470 $[M]^+$.

2.1.2. 4-{2-(2-Naphthyloxy)-1-[(2-naphthyloxy)methyl]ethoxy} phthalonitrile (5)

Synthesized similarly to **4** from **2**. Yield: 0.3 g (15%). IR (KBr pellet), n_{max}/cm^{-1}: 3054–3017 (Ar-H), 2928–2877 (Aliph. C–H), 2231 (C<ce:glyph name="tbnd"/>N), 1728, 1628, 1596, 1508, 1462, 1317, 1253, 1240, 1178, 1157, 1102, 1020, 972, 874, 836, 792, 771, 667, 570. ^1H NMR. ($CDCl_3$), (δ: ppm): 7.77 (m, 6H, Ar-H), 7.53–7.18 (m, 11H, Ar-H), 5.27 (m, 1H, O–CH), 4.53 (m, 4H, O–CH_2). ^{13}C NMR. ($CDCl_3$), (δ: ppm): 162.56, 156.04, 135.51, 134.50, 130.11, 129.57, 127.98, 126.99, 124.47, 121.40, 120.90, 118.61, 117.73, 116.38, 115.61, 112.56, 107.13, 104.72, 79.45, 67.39. MS (ESI), m/z: 470 $[M]^+$.

2.1.3. Cobalt(II) phthalocyanine (6)

A mixture of compound **4** (300 mg, 0.64 mmol), anhydrous CoCl (41.5 mg, 0.32 mmol) and dry DMAE (3 mL) was irradiated in a microwave oven at 175 °C 350 W for 7 min. Then dark green product was filtered and solid raw accomplished by column chromatography which is placed aluminum oxide (Al_2O_3) using $CHCl_3$:CH_3OH (5:1) as solvent system. The yield: 210 mg, (68%) mp: >300 °C. IR (KBr tablet) ν_{max}/cm^{-1}: 3053 (Ar-H), 2953–2852 (Aliph. C–H), 1722, 1595, 1579, 1508, 1460, 1385, 1267, 1238, 1178, 1156, 1102, 1020, 967, 790, 770, 570. UV–vis (THF): λ_{max}, nm (log ε): 671 (4.59), 605 (4.02), 320 (4.67). MALDI-TOF-MS: m/z: 1941 $[M + H]^+$.

2.1.4. Cobalt(II) phthalocyanine (7)

Synthesized similarly to **6** from **5**. Yield: 92 mg (40%). mp: >300 °C. IR (KBr tablet) ν_{max}/cm^{-1}: 3058 (Ar-H), 2957–2855(Aliph. C–H), 1727, 1628, 1599, 1510, 1463, 1390, 1254, 1217, 1182, 1120, 1071, 965, 837, 750, 623, 471. UV–Vis (THF): λ_{max}, nm (log ε): 669 (4.32), 604 (3.74), 328 (4.27). MALDI-TOF-MS: m/z: 1941 $[M + H]^+$.

2.2. Measurements

FT-IR spectra were obtained on a Perkin–Elmer 1600 FT-IR spectrophotometer with the samples prepared as KBr pellets. Optical spectra in the UV–visible region were recorded with a Perkin–Elmer Lambda 25 spectrophotometer. ^1H and ^{13}C NMR spectra were recorded on a Varian Mercury 200 MHz spectrometer in $CDCl_3$, and chemical shifts were reported (d) relative toMe_4Si as internal standard. Mass spectra were measured on a Micromass Quatro LC/ULTIMA LC–MS/MS spectrometer. MALDI-MS of complexes was obtained in dihydroxybenzoic acid as MALDI matrix using nitrogen laser accumulating 50 laser shots using Bruker Microflex LT MALDI-TOF mass spectrometer. Melting points were measured on an electrothermal apparatus. A domestic microwave oven was used for all syntheses of phthalocyanines.

2.3. General procedure for the oxidation of cyclohexene

All reactions were performed in a thermostated Schlenk vessel equipped with a condenser and stirrer. The solution of cyclohexene and catalyst in solvent were purified with bubbling nitrogen gas to remove the oxygen. A mixture of cyclohexene (0.78×10^{-3} mol), catalysts (2.57×10^{-6} mol) and solvent mixture (0.01 L) were stirred in a Schlenk vessel for few minutes at room temperature. Then, the oxidant TBHP (1.28×10^{-3} mol) was added and the reaction mixture was stirred for the desired time. The samples (0.005 L) were taken at certain time intervals. Each sample was injected at least twice in the GC, 1 μL each time. Formation of products and consumption of substrates were monitored by GC.

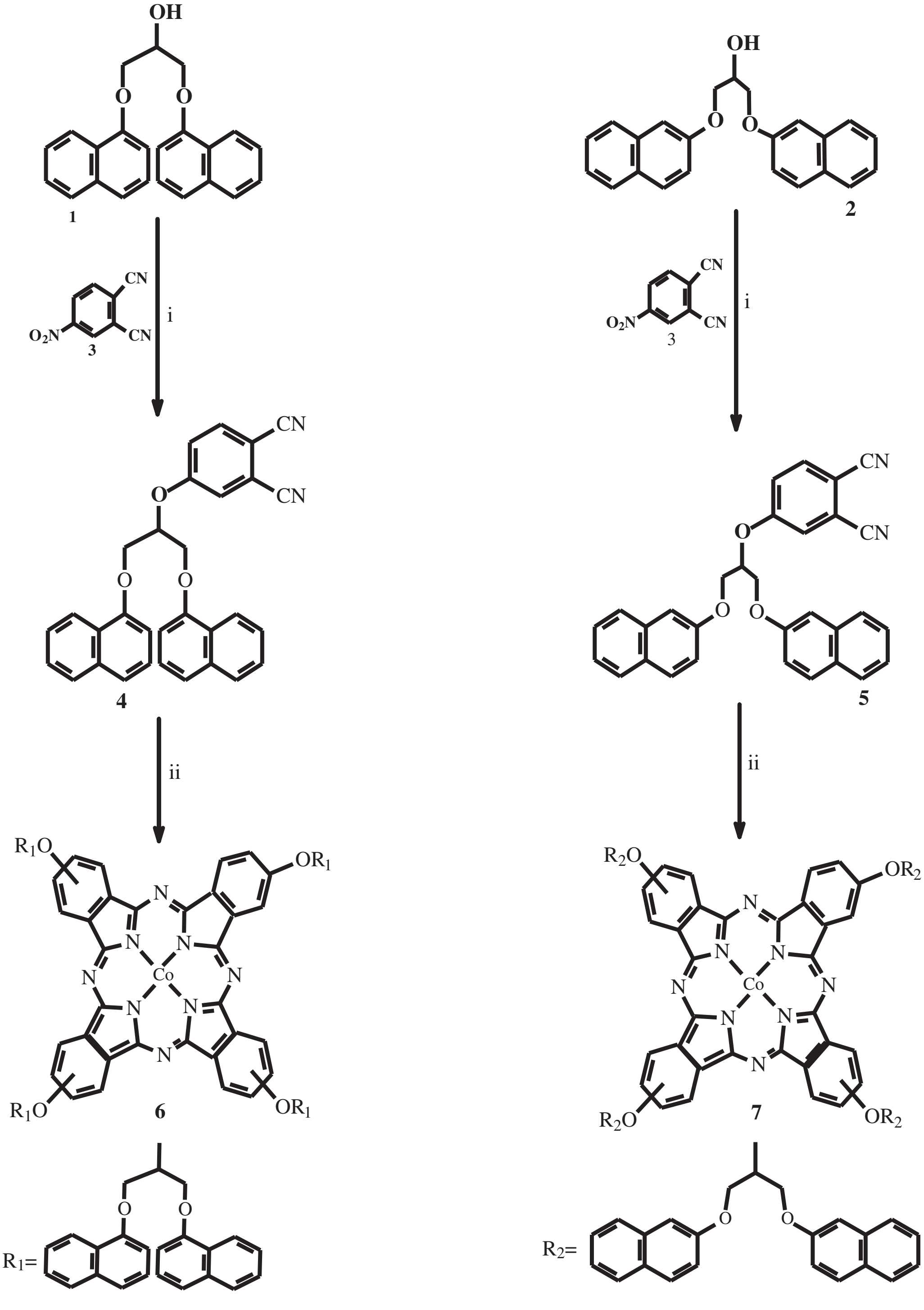
3. Results and discussion

3.1. Synthesis and characterization

Scheme 1 shows a brief schematic for the synthesis of peripherally tetra-substituted cobalt phthalocyanine complexes **6** and **7**. The phthalonitrile derivatives **4** and **5** were synthesized from the 1,3-bis(naphthalen-1-yloxy)propan-2-ol **1** and 1,3-bis(naphthalen-2-yloxy)propan-2-ol **2** by nucleophilic reaction with 4-nitrophthalonitrile **3** in the presence of K_2CO_3 and in dry DMF at 50 °C, respectively. After, in a microwave oven, cobalt phthalocyanines **6** and **7** were obtained in the presence of metal salt ($CoCl_2$) in DMAE at 175 °C, 350 Watt in average 6 min.

In the IR spectra, the formation of compounds **4** and **5** was clearly confirmed by the disappearance of the OH and NO_2 band at ~3410 and ~1538–1355 cm^{-1} and appearance of a single intense peak (C<ce:glyph name="tbnd"/>N) at 2232 and 2231 cm^{-1}, respectively. In the ^1H NMR spectrum of **4** and **5**, OH group of compounds **1** and **2** disappeared as expected. In the ^1H NMR spectrum of compounds **4** and **5** the aromatic protons appear at 8.08 (d), 7.84 (d), 7.66 (m), 6.89 (d) ppm for compound **4**, 7.77 (m), 7.53–7.18 (m) ppm for compound **5**. Also nitrile carbon atoms were observed at 115.36, 112.57 ppm for compound **4**, 115.61, 112.56 ppm for compound **5**. The MS spectrum of compounds **4** and **5**, which shows a peak at $m/z = 470$ $[M]^+$ supports the proposed formula for these compounds.

The IR spectra of the cobalt(II) phthalocyanines **6** and **7** which are very similar each other, show no the sharp C<ce:glyph



Scheme 1. The synthetic phthalonitriles and cobalt phthalocyanine complexes. Reagents and conditions: (i) dry DMF, K_2CO_3, 60 °C; (ii) $CoCl_2$, DMAE, 175 °C, 350 W.

name="tbnd"/>N vibration peak (2232–2231 cm^{-1}) which was observed in the IR spectra of **4** and **5**. The ^1H NMR spectra of metallophthalocyanines **6** and **7** could not be taken because of the paramagnetic cobalt(II) center. In the mass spectrum of Co phthalocyanines, the presence of molecular ion peaks at $m/z = 1941$ $[M + H]^+$, confirmed the proposed structures.

The UV/vis spectra of the cobalt(II) phthalocyanine complexes **6** and **7** in DMF at room temperature are shown in Fig. 1. In UV–vis spectra of the cobalt(II) phthalocyanines Q-bands were observed at around 671 nm for **6**, 669 nm for **7** with the shoulders at around 605 nm for **6**, 604 nm for **7** and the B bands were observed between 328 and 320 nm.

3.2. *Catalytic studies*

3.2.1. *Oxidation of cyclohexene with complex **6** and complex **7***

Cyclohexene (0.77×10^{-3} mol), cobalt(II) phthalocyanine complexes (2.57×10^{-6} mol), m-CPBA (1.28×10^{-3} mol) and DMF (0.01 L) were mixed in Schlenk vessel and refluxed at 90 °C with 900 rpm stirring (Tables 1–4). The formed oxidized products were

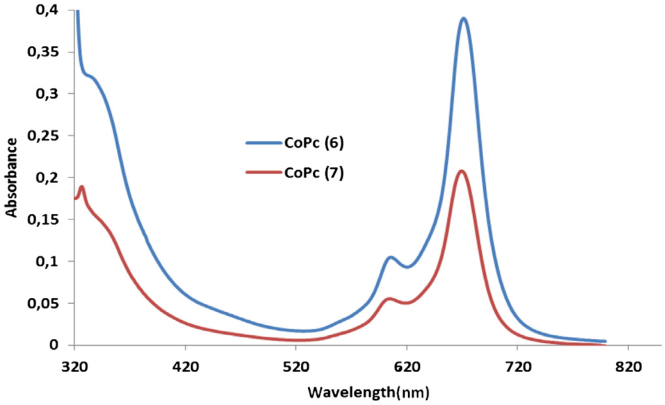


Fig. 1. UV–vis spectrum of **6** and **7** in THF.

Table 2
Temperature effect of cyclohexene oxidation with complexes **6** and **7**.

Catalyst	*T* (°C)	Alcohol[a]	Ketone[b]	Epoxide[c]	Tot. conv. (%)	TON[d]	TOF[e] (h^{-1})
6	25	25	17	5	47	141	47
7		24	20	4	51	153	51
6	50	36	27	6	69	207	69
7		33	23	14	70	210	70
6	70	47	27	7	81	243	81
7		41	23	14	78	234	78
6	90	54	29	8	97	291	97
7		49	26	19	94	282	94

Conversion was determined by GC.
Reacion time = 3 h.
[a] 2-Cyclohexene-1-ol.
[b] 2-Cyclohexene-1-one.
[c] Cyclolohexene oxide.
[d] TON = mole of product/mole of catalyst (all products).
[e] TOF = mole of product/mole of catalyst × time(3 h).

monitored with GC by spotting and comparing with standards. Blank experiments were done without the catalysts to observe vital mission on the cyclohexene oxidaition. In Tables 1–4, different operation conditions were evaluated to compare the catalytic activity of **6** and **7**. Then, the results show that for oxidation of cyclohexene these complexes are active catalyst in DMF. Three types of oxidized product were obtained. They are 2-cyclohexene-1-ol as dominant product and 2-cyclohexen-1-one and cyclohexene epoxide (Fig. 2). To improve the conversion of cyclohexene, the parameters such as substrate/catalyst ratio, the reaction temperature, oxidant ratio and type of oxidants were investigated.

Surprisingly the conversion was reached the highest value after 3 h when complexes **6** and **7** were used as catalyst. But after 3 h, the conversion stayed the same value (Fig. 3a and b). Both catalysts were employed as catalyst to give same oxidized product that is 2-cyclohexene-1-ol with high yield. Table 1 shows that cyclohexene oxidation reactions were done with different the substrate/catalyst ratio (300–1500). The other reaction conditions are 1.28×10^{-3} mol m-CPBA, 0.01 L DMF, 90 °C and 3 h. The low substrate catalyst molar ratio done a remarkable acceleration effect on the reaction rate of cyclohexene oxidation. When the substrate concentration decreases, the reaction rate increases. Looking at the data in Table 1 it is easy to realize that 2-cyclohexene-1-ol as dominant product with selectivity of 54% and 49% for complexes **6** and **7** respectively. This study shows that the catalyst **6** and **7** with m-CPBA as oxidant leaned the formation of 2-cyclohexene-1-ol from the other products.

Table 2 shows experimental results related to effect of temperature on cyclohexene conversion toward the products with ox./subst./cat. = 500/300/1 and m-CPBA, in DMF during 3 h. For this parameter, DMF was used as solvent due to its high boiling point. Whereby, we can study different temperature effect on cyclohexene oxidation. According to Table 2, we can conclude that the reaction temperature on the oxidation of cyclohexene was raised when the catalytic activity of complexes **6** and **7** increased. When the reaction temperature was increased to the highest temperature, the yield of oxidized products was increased. The highest conversion at 90 °C was observed that 97% and 94% with TON = 291 and 282 for complexes **6** and **7** respectively. The overall conversion was increased 50% for

Table 1
Amount of substrate effect of cyclohexene oxidation with complexes **6** and **7**.

Catalyst	Subs./cat.	Alcohol[a]	Ketone[b]	Epoxide[c]	Tot. conv. (%)	TON[d]	TOF[e] (h^{-1})
6	300/1	54	29	8	97	291	97
7		49	26	19	94	282	94
6	600/1	48	29	8	85	510	170
7		45	25	10	80	480	160
6	900/1	37	29	8	74	666	222
7		34	25	10	69	621	207
6	1200/1	30	22	5	57	684	228
7		27	18	6	51	612	204
6	1500/1	18	19	3	40	630	210
7		16	16	4	36	540	180

Conversion was determined by GC.
Reacion time = 3 h.
[a] 2-Cyclohexene-1-ol.
[b] 2-Cyclohexene-1-one.
[c] Cyclolohexene oxide.
[d] TON = mole of product/mole of catalyst (all products).
[e] TOF = mole of product/mole of catalyst × time(3 h).

Table 3
Different oxidant effect of cyclohexene oxidation with complexes **6** and **7**.

Catalyst	Oxidant	Alcohol[a]	Ketone[b]	Epoxide[c]	Tot.Conv. (%)	TON[d]	TOF[e] (h^{-1})
6	TBHP	33	26	6	65	195	65
7		34	23	10	67	201	67
6	H_2O_2	22	22	6	50	150	50
7		14	26	12	52	156	52
6	m-CPBA	54	29	8	97	291	97
7		49	26	19	94	282	94
6	Free oxidant	–	–	–	–	–	–
7							

Conversion was determined by GC.
Reacion time = 3 h.
[a] 2-Cyclohexene-1-ol.
[b] 2-Cyclohexene-1-one.
[c] Cyclolohexene oxide.
[d] TON = mole of product/mole of catalyst (all products).
[e] TOF = mole of product/mole of catalyst × time(3 h).

complex **6** and 43% for complex **7**, when the temperature was raised 25–90 °C. The low reaction temperature did not favor the oxidation of cyclohexene. At the lowest temperature (25 °C), the conversion of cyclohexene to oxidized products only 47% for complex **6** and 51% for complex **7**.

Table 3 shows that the data were obtained from the results of oxidation experiments with different types of oxygen sources (such as TBHP, m-CPBA, aerobic oxygen and H_2O_2). For these experiments, 1.28×10^{-3} mol m-CPBA, TBHP, H_2O_2 were used. During these experiments, m-CPBA was found most effective oxidant on the oxidation of cyclohxene with complexes **6** and **7** (Fig. 4). For the blank experiments, all reactions were done again without m-CPBA and we deduced that cyclohexene oxidation reactions did not progress. The other oxygen sources like TBHP or hydrogen peroxide were not found suitable oxidant for our catalytic system. The reason of observation the lowest conversion with H_2O_2 is fast degradation of the phthalocyanine ring **6** and **7**. The color of solution immediately turned from the blue-green color of to colorless after adding H_2O_2. Because of this, complexes **6** and **7** were not employed effectively as catalyst during the oxidation. When comparing the performance of TBHP and H_2O_2, decomposition of phthalocyanine ring of complexes **6** and **7** with THBP was lower than H_2O_2. The highest activity of complexes **6** and **7** with m-CPBA (TOF:97 and 94) and other oxidant activity can be seen in Table 3.

Table 4 shows the results getting from cyclohexene oxidation reaction with changinge substrate-to-oxidant ratio. This ratio effect was worked in the range of 300/1–1200/1. When the ratio was increased from 300 to 500, total conversion was increased from %69 to %97 for complex **6** and %57 to %94 for complex **7**. But from this ratio until to 1200/1, the total conversion tended to decrease. We cannot easily tell oxidant role at this stage, but this situation may explain as changing coordination of cobalt and iron ion and create nonactive species.

Table 4
Amount of oxidant effect of cyclohexene oxidation with complexes **6** and **7**.

Catalyst	Oxidant/ catalyst	Alcohol[a]	Ketone[b]	Epoxide[c]	Tot. conv. (%)	TON[d]	TOF[e] (h^{-1})
6	300/1	40	22	7	69	207	69
7		22	19	16	57	156	52
6	500/1	54	29	8	97	291	97
7		49	26	19	94	282	94
6	700/1	49	25	8	82	246	82
7		38	24	17	79	237	79
6	1000/1	49	20	10	79	237	79
7		33	22	15	70	210	70
6	1200/1	34	19	9	62	186	62
7		22	20	14	56	168	56

Conversion was determined by GC.
Reacion time = 3 h.
[a] 2-Cyclohexene-1-ol.
[b] 2-Cyclohexene-1-one.
[c] Cyclolohexene oxide.
[d] TON = mole of product/mole of catalyst (all products).
[e] TOF = mole of product/mole of catalyst × time(3 h).

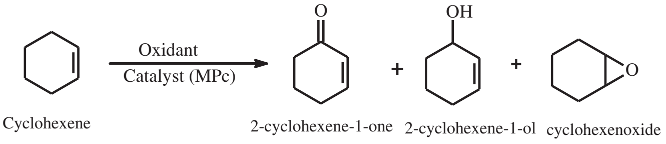


Fig. 2. Product formed through oxidation of cyclohexene by TBHP, m-CPBA and H_2O_2 in the presence of complexes **6** and **7**.

Table 5 barely demonstrate that the success of Co(II) phthalocyanine catalysts **6** and **7** by comparison of the metallophthalocyanine and metalloporphyrin catalysts. We obtained the best reported results in terms of TOF in literature for homogenous oxidation of cyclohexene with m-CPBA in the presence of Co(II) phthalocyanine catalysts.

3.3. Monitoring the oxidation system by UV–vis spectroscopy

Within the UV spectrum of the metallophthalocyanines has been observed the existence of two absorption bands assigned to the transition $n \rightarrow \pi^*$ and $\pi \rightarrow \pi^*$. These absorbstion bands, that are called as B and Q bands, are observed in the UV–vis spectra of Co(II) phthalocyanine complexes [28–39]. Also these bands are to be found in the spectra of the metallophthalocyanine complexes, but

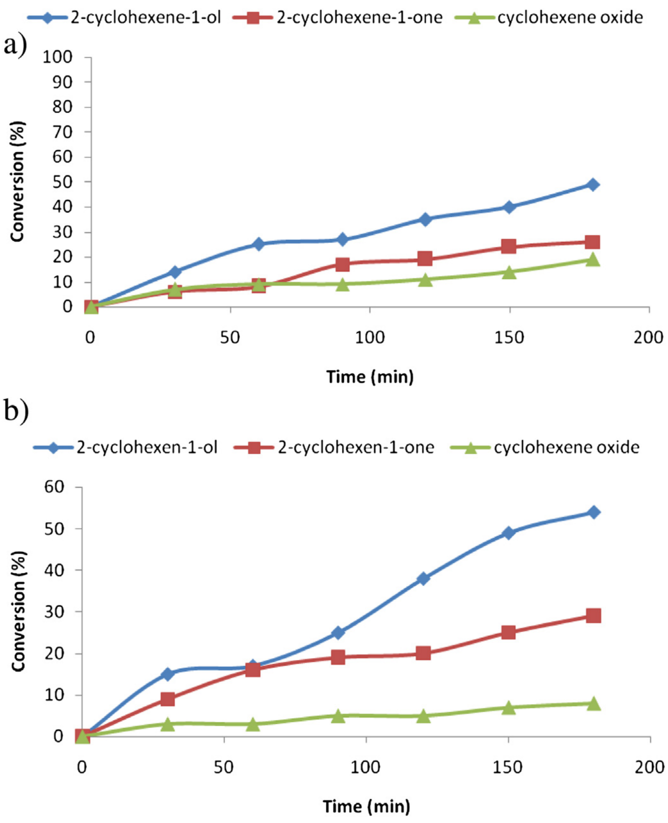


Fig. 3. Time-dependent conversion of cyclohexene oxidation a) for catalyst **6** b) for catalyst **7** [Reaction conditions: Cyclohexene (0.77×10^{-3} mol), cobalt(II) phthalocyanine complexes (2.57×10^{-6} mol), m-CPBA (1.28×10^{-3} mol), DMF (0.01 L), 3 h and 90 °C].

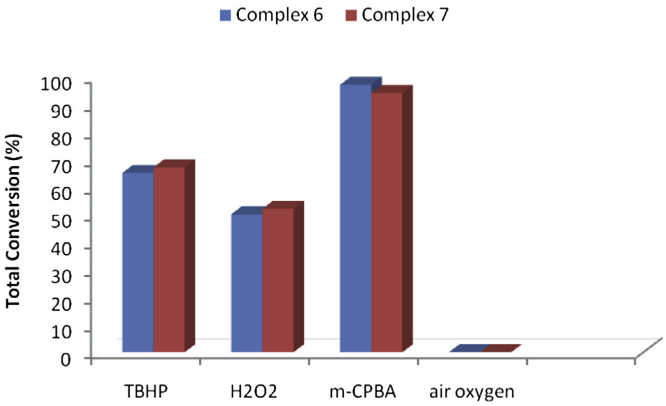


Fig. 4. The oxidant effect on cyclohexene oxidation [Reaction conditions: Cyclohexene (0.77×10^{-3} mol), cobalt(II) phthalocyanine complexes (2.57×10^{-6} mol), m-CPBA (1.28×10^{-3} mol), DMF (0.01 L), 3 h and 90 °C].

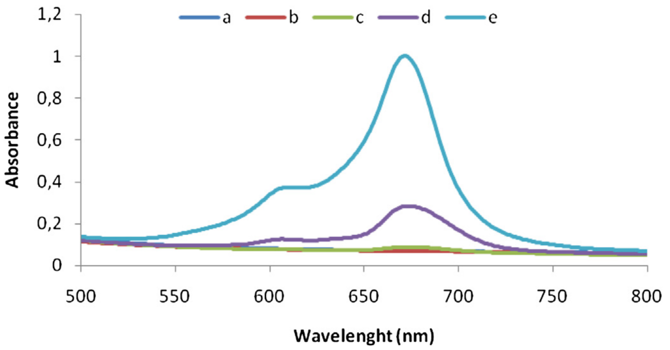


Fig. 5. Time-dependent changes in the visible spectrum of the oxidized complex **6** observed on addition of TBHP (1.28×10^{-3} mol) to a reaction mixture containing 0.77×10^{-3} mol cyclohexene and 2.57×10^{-6} mol complex **6** catalyst in 10 ml: (a) 45 min; (d) 90 min; (c) 135 min (d) 180 min after addition of m-CPBA. All spectra for the oxidized complex **6** were taken after sixfold dilution with DMF. (e) Visible spectrum of (non-oxidized) complex **6**.

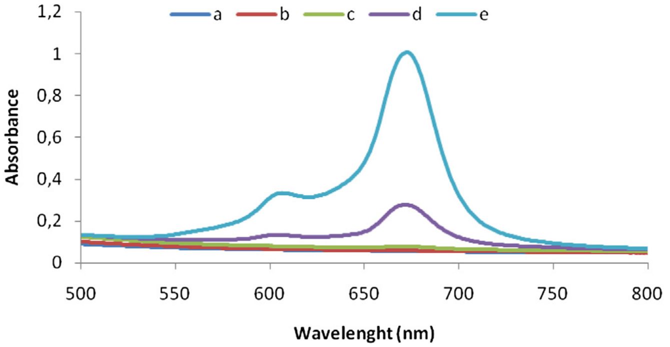


Fig. 6. Time-dependent changes in the visible spectrum of the oxidized complex **7** observed on addition of m-CPBA (1.28×10^{-3} mol) to a reaction mixture containing 0.77×10^{-3} mol cyclohexene and 2.57×10^{-6} mol complex **7** catalyst in 10 ml: (a) 45 min; (d) 90 min; (c) 135 min (d) 180 min after addition of m-CPBA. All spectra for the oxidized complex **7** were taken after sixfold dilution with DMF. (e) Visible spectrum of (non-oxidized) complex.

they broadens and shifts because of μ-oxo dimeric species of Co(II)-Pc to Co(III)–Pc [40]. Figs. 5 and 6 indicate spectral changes observed for the catalysts **6** and **7** during the oxidation reaction with m-CPBA. The typical monomeric form of Co(II) phthalocyanine complexes is seen in Fig. 1 before the start of the catalytic reactions. Q band at 669 nm for complexes **6** and **7** with respectively. With adding of oxidant (such as TBHP, m-CPBA or H_2O_2), Q-band decreases in intensity and broadens at 666 and 667 nm. Around the B band religion (~480 nm) there is no peak. Thus addition of m-CPBA to solutions of Co(II) complexes resulted in only metal and not ring oxidation of Co-Pc. As catalysis proggressed, there was a proggressive decrease in the intensity of the Q band of the Co(II) phthalocyanine catalyst, suggesting catalyst degradation as is typical of MPc catalysts in homogenous catalysis [41]. The reason of this degradation can be explained as a result of the attack of the phthalocyanine ring by the alkoxy and alkylperoxide radicals which are produced from m-CPBA. It is noted the change of reaction color that from blue to green as catalysis continued. However, the reaction products continued to form even after the catalyst had turned yellow, suggesting that once reaction intermediates are formed, the reaction can still progress in the presence or absence of the original form of the catalyst. Both phthalocyanine complexes were degragaded by the oxidant. These degradation were monitored changing color by UV–vis spectroscopy. When we used m-CPBA as an oxidant, the reaction color changed from blue to green and the oxidation progressed, the catalyst turned yellow. This indicates that complexes **6** and **7** can exist a long time in reaction media and catalyzed effectively without degradation on cyclohexene oxidation.

Table 5
Catalytic activities toward the homogeneous oxidation of cyclohexene of some previously reported catalyst.

Catalyst	Rxn time (h)	Rxn temp. (°C)	Oxidant	Conv. (%)	Ref.
Co(tbpcH$_2$[a])	24	Rt[h]	O_2	~45 ~55 ~30	[42]
CoPc[b]	8	nr[i]	TBHP	45.3	[41]
Co[NO]$_2$ Cu[NO[c]]$_2$	8	75	H_2O_2	27.6 43.50	[43]
[Co(Me$_2$salpnMe$_2$[d])]	8	40	TBHP	42.7	[44]
Co(salen)–POM	6	60	H_2O_2	91	[45]
CoPc[e]	3	90	m-CPBA	61	[10]
CoPc[f]	3	90	m-CPBA	80	[21]
CoPc[g]				45	

[a] $tbpcH_2$ = *tetra-tert*-butylphthalocyanine.
[b] Pc = peripherally substituted phthalocyanine.
[c] *NO* = 2-pyrazinecarboxylic acid.
[d] $Me_2salpnMe_2$ = *N*,*N*-bis-(α-methylsalicylidene)-2,2-dimethylpropane-1.
[e] Pc = 4-{2-[3-(diethylamino)phenoxy]ethoxy} group substituted phthalocyanine.
[f] Pc = 4-[2-(1,4-dioxa-8-azaspiro[4.5]dec-8-yl)ethoxy group substituted phthalocyanine.
[g] Pc = 4-(3,3-diphenylpropoxy) group substituted phthalocyanine.
[h] rt = room temperature.
[i] nr = not reported.

4. Conclusion

In conclusion, we have synthesized and characterized a new metal free phthalocyanine, cobalt(II) complexes and showed their catalytic activity in the selective oxidation of cyclohexene to 2-cyclohexen-one as dominant product, 2-cyclohexen-ol and cyclohexene oxide under homogenous conditions with TBHP in DMF. We have also investigated that UV–vis spectrum of new cobalt(II) phthalocyanine complexes in different solvents (CH_2Cl_2, $CHCl_3$, THF and DMF). The high percentage yield of reactions in the presence of cobalt(II) phthalocyanine complexes seems promising.

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