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Synthesis, characterization and investigation of homogeneous oxidation activities of peripherally tetra-substituted Co(II) and Fe(II) phthalocyanines: Oxidation of cyclohexene

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ABSTRACT

The synthesis and characterization of novel peripherally tetra-substituted iron(II) **4** and cobalt(II) **5** phthalocyanines are described for the first time in this study. All the new compounds are characterized by a combination of IR, ^{1}H and ^{13}C NMR, mass and UV–vis spectroscopy techniques. Complexes **4** and **5** served as catalyst for the oxidation of cyclohexene using different types of oxidants, such as *tert*-butyl hydroperoxide (TBHP), *m*-chloroperoxybenzoic acid (*m*-CPBA), aerobic oxygen and hydrogen peroxide (H_2O_2). During the oxidation process the products formed are 2-cyclohexene-1-ol, 2-cyclohexene-1-one and cyclohexene oxide. The selectivity for 2-cyclohexene-1-ol is favored when iron(II) and cobalt(II) phthalocyanine catalysts are employed. The higher conversion is obtained as catalyst iron(II) phthalocyanine (96%). TBHP was determined as the successful oxidant with the minimum demolition of the catalyst, superior selectivity and conversion in the oxidation products.

1. Introduction

Phthalocyanines are a kind of N_4-macrocycles known for their very interesting industrial applications due to their high stability, structural flexibility, diverse coordination properties, excellent spectroscopic characteristics, and rich and reversible redox chemistry. Phthalocyanines have been extensively studied in many applications such as catalysts, liquid crystals, electrochromic and photochromic substances, data storage systems, photodynamic cancer therapy agents, photoactive units, chemical sensors, and nonlinear optical devices [1–3].

Due to π-stacking unsubstituted phthalocyanines are insoluble in common organic solvents which limits the processability, derivatization and the characterization of this type of compounds. By introduction of bulky substituents at the ligand periphery intermolecular interaction of the p systems can be reduced, phthalocyanines become soluble and ^{13}C NMR spectra are available in common organic solvents. As a result, a variety of phthalonitriles bearing alkyl, alkoxy and other functional groups have been synthesized and employed in cyclotetramerization reactions [4–14].

In the oxidation of cyclohexene, transition metal complexes as catalysts have attracted much attention in recent years, mainly for the oxidation products of cyclohexene and derivatives of cyclohexene that present highly reactive carbonyl groups in cycloaddition reactions [15]. Of the currently available various ligands, remarkable examples include porphyrin derivatives, phthalocyanine, and Schiff base [16–19]. Among these substrates, metallophthalocyanine complexes are attractive oxidation catalysts and can be prepared simply and cheaply for industrial applications. The catalytic oxidation of cyclohexene is attracting attention because its oxidation products (e.g. 2-cyclohexen-1-one, 2-cyclohexen-1-ol, epoxide) are very useful synthetic intermediates [20].

Synthetic metalloporphyrins, that are similar structure as cytochrome P-450, are highly efficient homogeneous and heterogeneous catalysts for cyclohexene oxidation by various oxidants such as iodosylbenzene [21], hydrogen peroxide and *tert*-butyl hydroperoxide [22]. The aerobic oxidation of olefins catalyzed by metalloporphyrins and metallophthalocyanines is earning interest from economic and environmental visions [23]. In addition, cobalt(II) phthalocyanines have been used catalysts for the oxidation of aromatic compounds [24]. Oxidation products of these aromatic compounds are probably aldehyde, ketones and alcohols that are commonly applied in the industrial factories and in the scientific area. In this work, cyclohexene is handled as aromatic compound and its oxidation products are stated as 2-cyclohexene-1-one, 2-cyclohexene-1-ol and cyclohexene oxide. The oxidation products of cyclohexene carry big value due to their usage in industrial field and chemical workings. Because of the importance of both

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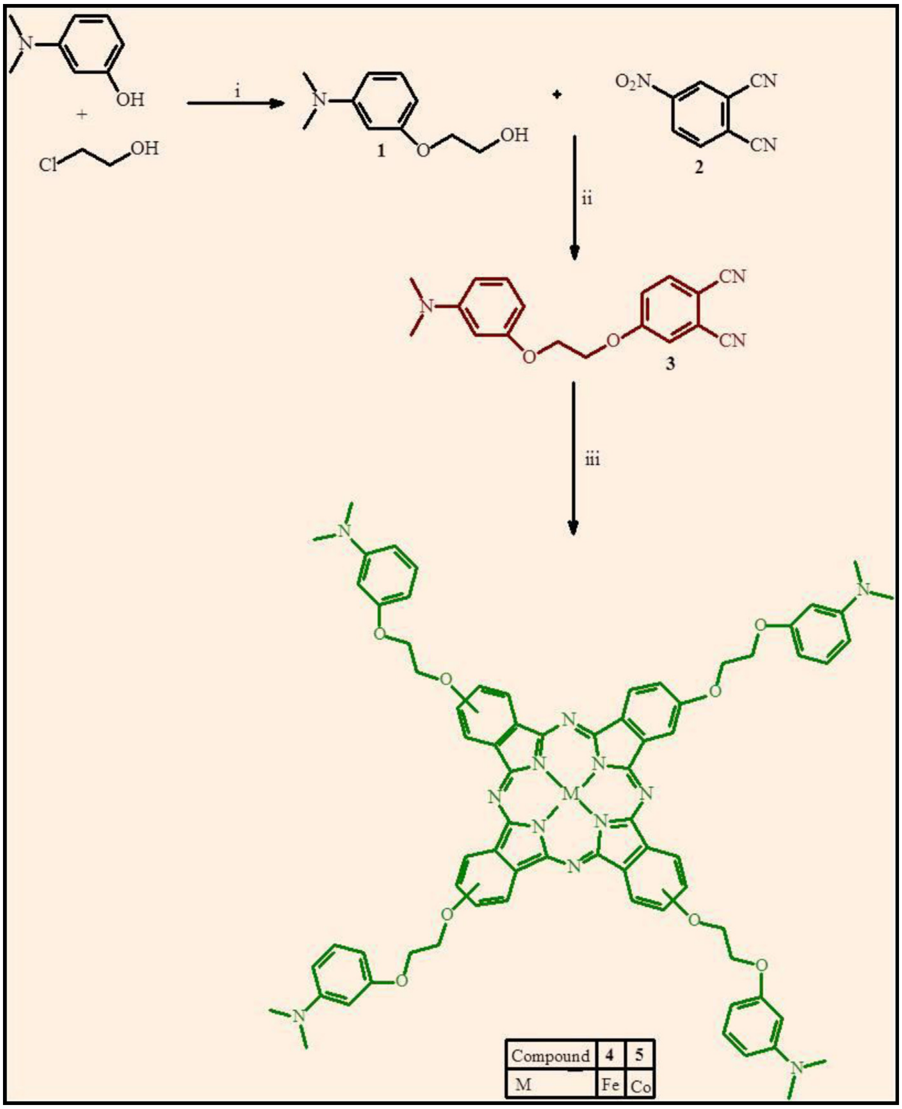

Fig. 1. The synthetic route of the phthalonitrile, cobalt phthalocyanine and iron phthalocyanine. Reagents and conditions: (i) EtOH, NaOH, 90 °C; (ii) dry DMF, K_2CO_3, 50 °C, 96 h; (ii) n-pentanol, DBU, 160 °C, $Fe(CH_3COO)_2$, $CoCl_2$.

itself and its products, phthalocyanines with different substituted groups (such as electron-acceptor groups such as halogenated and phenyl groups) have been largely worked in oxidation of cyclohexene [25].

Fe(II) and Co(II) phthalocyanines are often used as oxidation catalysts due to their oxygen transfer ability from various oxygen donors to alkanes, alkenes, phenols and thiols in various studies [26–37,25,38]. In this report, we report the synthesis and characterization of {2-[3-(dimethylamino)phenoxy]ethoxy} group-substituted iron and cobalt phthalocyanines **4** and **5**. Additionally, it is also aimed that Fe(II) and Co(II) phthalocyanines **4** and **5** are used as catalysts for the oxidation of cyclohexene, with the purpose of developing product selectivity and increasing the range of products.

2. Experimental

2.1. Synthesis

2.1.1. Synthesis of iron(II) phthalocyanine (4)

A mixture of 4-{2-[3-(dimethylamino)phenoxy]ethoxy}phthalonitrile **3** (0.2 g, 0.65 mmol) and 0.65 mmol of 1.8-diazabicyclo [5.4.0]undec-7-ene (DBU) (0.4 ml) in 3 ml of n-pentanol and anhydrous $Fe(CH_3COO)_2$ (57 mg, 0.32 mmol) was heated and stirred at 160 °C for 12 h under N_2. Then the reaction mixture was cooled precipitated by adding ethanol. The precipitated green solid product was filtered off, and then dried in vacuo over P_2O_5. The obtained green solid product was purified from the column chromatography which is placed aluminum oxide using $CHCl_3$/MeOH (100:1) as solvent system. Yield: 122 mg (58%). IR (KBr pellet) ν_{max}/cm^{-1}: 3068 (Ar—H), 2922–2870 (Aliph. C—H), 1607, 1573, 1498, 1448, 1399, 1339, 1276, 1232, 1126, 1078, 998, 958, 824, 746, 685. ^1H NMR ($CDCl_3$), (δ:ppm): 7.56 (m, 8H, Ar—H), 7.29 (m, 8H, Ar—H), 6.45 (m, 12H, Ar—H), 4.41 (m, 16H, CH_2—O), 2.94 (s, 24H, CH_3). UV–vis (THF), $\lambda_{maks}(\log \varepsilon)$ nm: 603 (4.24), 652 (4.49). MS (ESI), (*m*/*z*): 1286 $[M+H]^+$.

2.1.2. Synthesis of cobalt(II) phthalocyanine (5)

Synthesized similarly to **4** from **3** by using anhydrous $CoCl_2$. Purification was achieved using column chromatography with basic alumina as column material and chloroform:methanol (100:3) solvent system as eluent. Yield: 160 mg (51%). IR (KBr tablet) ν_{max}/cm^{-1}: 3068 (Ar—H), 2922–2870 (Aliph. C—H), 1610, 1573, 1500, 1480, 1447, 1349, 1280, 1233, 1127, 1095, 1065, 998,

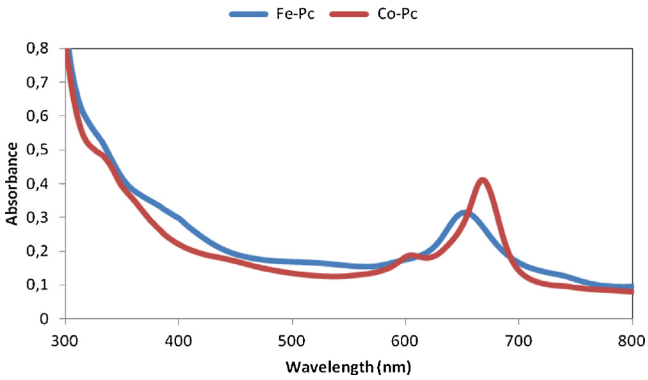

Fig. 2. UV–vis spectrum in THF for complexes **4** and **5**. (For interpretation of the references to color in this figure legend, the reader is referred to the web version of this article.)

822, 751, 685. UV–vis (THF), λ_{maks}(log ε) nm: 333 (4.68), 605 (4.27), 668 (4.61). MS (ESI), (m/z): 1168 [M-C_6H_4-$N(CH_3)_2$]$^+$.

3. Results and discussion

3.1. Synthesis and characterization

The synthesis route for the compounds is described in Fig. 1. In this study, the initial phthalonitrile derivative **3** [39] was obtained from the reaction between 2-[3-(dimethylamino)phenoxy]ethanol **1** and 4-nitrophthalonitrile **2** [40] in dry DMF at 50 °C [41,42]. Dry K_2CO_3 was used to supply the basic reaction conditions. Cyclotetramerization of the phthalonitrile derivative **3** to the iron(II) and cobalt(II) phthalocyanines **4** and **5** was accomplished in the presence of anhydrous $Fe(CH_3COO)_2$, $CoCl_2$ in n-pentanol and DBU and the crude product chromatographed on basic alumina. The structures of the target compounds were confirmed using UV–vis, IR, ^{1}H NMR, ^{13}C NMR, MS spectroscopic data. The analyses are consistent with the predicted structures as shown in Section 2.

The IR spectrum of the iron and cobalt phthalocyanines **4** and **5** clearly indicates the cyclotetramerization of the phthalonitrile derivative **3** with the disappearance of the C≡N peak at 2232 cm^{-1}, respectively. The ^{1}H NMR spectrum of iron(II) phthalocyanine **4** indicated the aromatic protons at 7.56, 7.29, 6.45 ppm and aliphatic protons at 4.41, 2.94 ppm. The ^{1}H NMR spectrum of cobalt phthalocyanine **5** could not be taken due to the paramagnetic cobalt(II) centers [43,44]. The mass spectra of tetra-substituted phthalocyanines **4** and **5** confirmed the proposed structure, with the molecular ion being easily identified at 1286 [M+H]$^+$, 1168 [M−C_6H_4-$N(CH_3)_2$]$^+$, respectively.

The metallophthalocyanines display typical electronic spectra with two strong absorption regions, one of them in the UV region at about 300–350 nm (B band) and the other one in the visible region at 600–700 nm (Q band). The electronic absorption spectra of the iron and cobalt phthalocyanines **4** and **5**, in THF at room temperature are shown in Fig. 2. UV–vis spectra of iron phthalocyanine **4** (in THF) split Q bands appeared at 652, 603 nm. UV–vis spectra of cobalt phthalocyanine **5** (in THF) split Q bands appeared at 668, 605 nm, while the split B band remained at 333 nm.

3.2. Aggregation studies

Aggregation is usually depicted as a coplanar association of rings progressing from monomer to dimer and higher order complexes. It is dependent on the concentration, nature of the solvent, nature of the substituents, complexed metal ions and temperature [45–47]. In this study, the aggregation behavior of the iron and cobalt phthalocyanine complexes **4** and **5** are investigated in different solvents ($CHCl_3$, CH_2Cl_2, THF, DMF, DMSO, EtOAc) (Fig. 3 for complex **4**). While iron phthalocyanine **4** showed little aggregation in $CHCl_3$, CH_2Cl_2, THF, DMF, EtOAc, DMSO showed full aggregation. The absence of aggregated species in solution of **4** in DMSO, DMF may be attributed to the axial coordination ability of Fe(II) center. It is well known that the nature of solvent has a great influence on the aggregation behavior of phthalocyanines [48,49]. On the other hand, the complex **5** showed little aggregation only in EtOAc but cobalt phthalocyanine **5** did not show any aggregation in $CHCl_3$, CH_2Cl_2, THF, DMF, and DMSO.

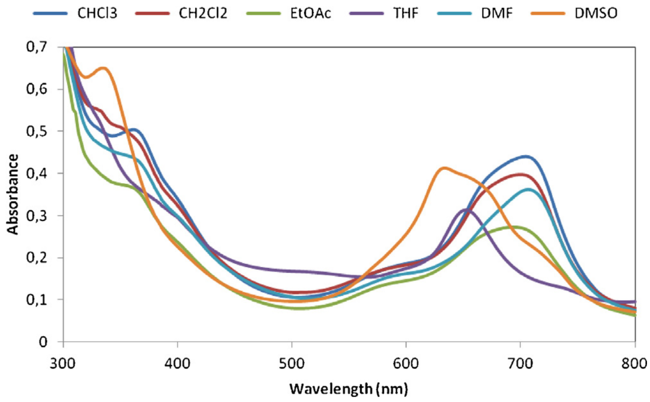

Fig. 3. UV–vis spectrum of iron(II) phthalocyanine **4** in different solvents (concentration = 10 × 10^{-6} mol dm^{-3}). (For interpretation of the references to color in this figure legend, the reader is referred to the web version of this article.)

The aggregation behavior of iron and cobalt phthalocyanine complexes **4** and **5** were also investigated at different concentrations in DMSO. In DMSO, as the concentration increased, the intensity of absorption of the Q band also increased and there were no new bands (normally blue shifted) due to the aggregated species for all phthalocyanines (Fig. 4 for complex **4**). Beer–Lambert law was obeyed for all of the compounds in the concentrations ranging from 12 × 10^{-6} to 2 × 10^{-6} mol dm^{-3}.

3.3. Catalytic studies

3.3.1. Oxidation of cyclohexene with **4** and **5**

As shown in Tables 1–4, all oxidation experiments to evaluate the catalytic effect of complexes **4** and **5** on the oxidation of cyclohexene were performed under different reaction conditions. Schlenk tube was filled with cyclohexene (1.16 × 10^{-3} mol), complex **4** (3.88 × 10^{-6} mol) or complex **5** (3.89 × 10^{-6} mol) and

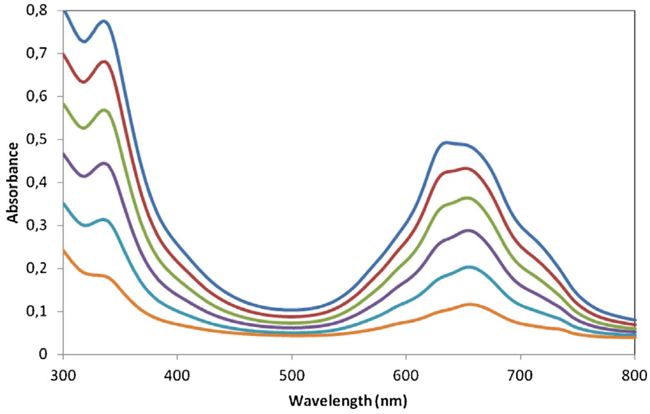

Fig. 4. UV–vis spectrum of cobalt phthalocyanine **5** in DMSO at different concentrations, 12 × 10^{-6}, 10 × 10^{-6}, 8 × 10^{-6}, 6 × 10^{-6}, 4 × 10^{-6}, 2 × 10^{-6} mol dm^{-3}. (For interpretation of the references to color in this figure legend, the reader is referred to the web version of this article.)

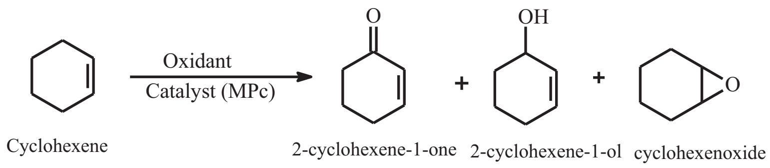

Fig. 5. Product formed through oxidation of cyclohexene by TBHP, m-CPBA and H_2O_2 in the presence of complexes **4** and **5**.

TBHP (1.94×10^{-3} mol) in DMF (0.01 L) and refluxed at 90 °C with 900 rpm stirring in a typical catalytic reaction. The oxidation experiments were done again with the oxidants without using complexes **4** and **5** as catalyst to prove significant of the catalyst in cyclohexene oxidation. In Tables 1–4, the workings of the catalytic activity of **4** and **5** were clearly demonstrated for oxidation of cyclohexene. These workings in DMF show that both complexes are successfully active catalysts in cyclohexene oxidation. At the end of the cyclohexene oxidation, 2-cyclohexene-1-ol is observed as the main product and 2-cyclohexen-1-one and cyclohexene epoxide as minor product by using gas chromatography by both spotting and comparison with standards (Fig. 5). Some parameters were studied for getting maximum conversion of cyclohexene such as varying the reaction temperature, time and different oxidants, subst./cat. ratio.

Fig. 6a and b shows the variation of product yield with reaction time. Among the oxidation products 2-cyclohexene-1-ol was obtained with superior yield than the other both products. The conversion from cyclohexene to these three products has increased with the increasing time. But after 3 h, no yields of the products were observed. This situation is probably due to the degradation of the FePc and CoPc catalyst by oxidant, with time.

For the influence of the substrate to iron(II) and cobalt(II) phthalocyanines, the molar ratio was carried out in the range of 300–1500 while other parameters were kept constant. The constant parameters were 90 °C, 1.94×10^{-3} mol TBHP, 0.01 L DMF for 3 h. Table 1 demonstrates the experimental outcomes. As it is seen, decreases in the substrate/catalyst molar ratio increases the reaction rate. According to Table 1, both catalysts give same main product (2-cyclohexene-1-ol) with selectivity of 65% for complex **4** and 60% for complex **5**.

Catalytic activity of metallophthalocyanines and metalloporphyrins can be effected with replacing the central metal in the oxidation reactions. Nam et al. used iron porphyrin with nitrate or perchlorate as axial ligands with m-CPBA for the oxidation of cyclohexene. They obtained cyclohexene oxide as main product with yield (68–78%). On the other hand, same study was carried out with chloride axial ligands, and not more than 2% yield was obtained [50]. A few studies were also done with porphyrins. More elevated yields of cyclohexene oxide were obtained by using chloroperoxybenzoic acid and iodosylbenzene [51,52]. However, photooxygenation of cyclohexene was achieved with titanium porphyrins, and cyclohexene hydroperoxide as a main product and cyclohexene oxide as the side product were determined [53]. Additionally, 2-cyclohexene-1-ol was achieved as main product (55% and 67%) with TBHP as oxidant and cobalt phthalocyanines as in Ref. [54]. In our study, owing to the usage of complexes **4** and **5**, 2-cyclohexene-1-ol was obtained main product with TBHP as an oxidant.

To investigate the effect of oxidant type, different oxygen sources were used on cyclohexene oxidation (TBHP, m-CPBA, aerobic oxygen and H_2O_2). Keeping the other parameters of the oxidation experiments, only the amount of oxidant was changed. The data are given in Table 2 and Fig. 7.

When H_2O_2 was immediately added to the reaction media, the color of reaction solution of the **4** or **5** catalyst turned from the blue-green color to colorless. This means that complexes **4** and **5** were not employed as catalysts in the oxidation with H_2O_2. Thus, it can be said that fast degradation of the phthalocyanine rings **4** and **5** was observed with H_2O_2 as an oxidant. Moreover, degradation of the phthalocyanine rings **4** and **5** was also determined with m-CPBA. As TON values were compared, activity with m-CPBA (TON: 420) is

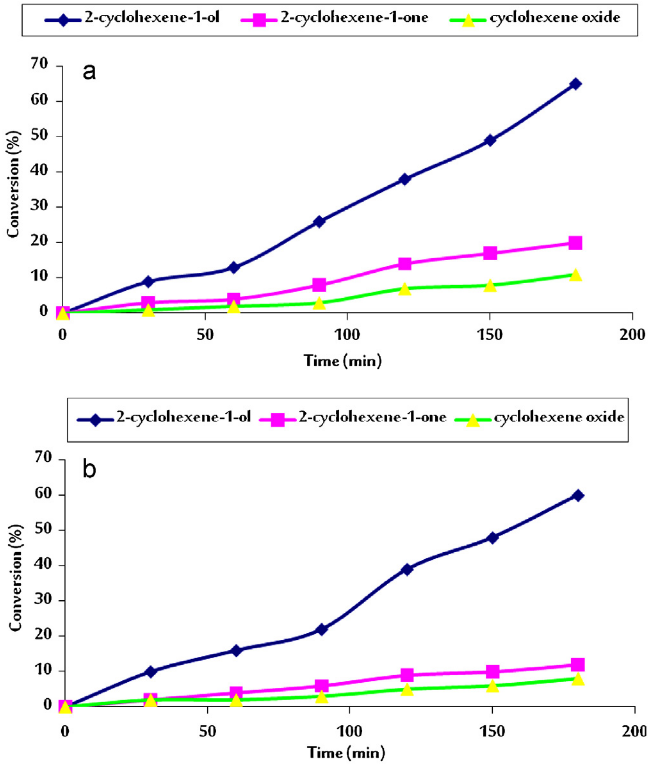

Fig. 6. Time-dependent conversion of cyclohexene oxidation for (a) catalyst **4** and (b) catalyst **5**.

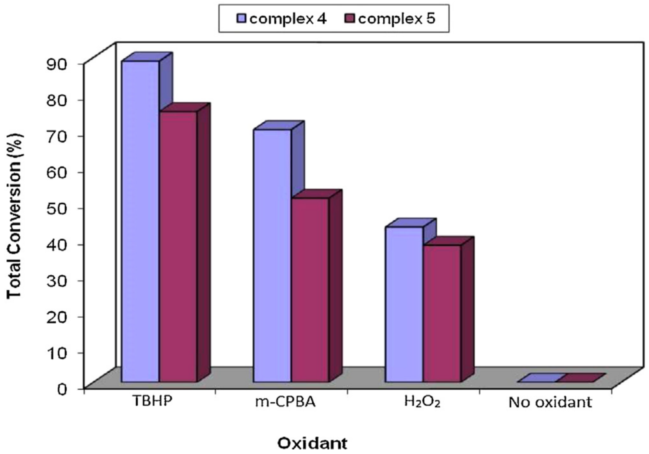

Fig. 7. The oxidant effect on cyclohexene oxidation.

Table 1
Amount of substrate effect of cyclohexene oxidation with complex **4** and **5**.

Catalyst	Subs./Cat.	Alcohol[a]	Ketone[b]	Epoxide[c]	Tot. Conv. (%)	TON[d]	TOF[e] (h^{-1})
4	300/1	65	20	11	96	288	96
5		60	12	8	80	240	80
4	600/1	60	18	11	89	534	178
5		53	12	8	75	450	150
4	900/1	53	14	6	73	657	219
5		50	11	7	68	612	204
4	1200/1	41	14	5	60	720	240
5		36	8	5	49	588	196
4	1500/1	35	10	3	48	720	240
5		28	4	4	36	541	180

[a] 2-Cyclohexene-1-ol.
[b] 2-Cyclohexene-1-one.
[c] Cyclolohexenoxide.
[d] Mole of product/mole of catalyst.
[e] Mole of product/mole of catalyst × time.
Conversion was determined by GC.

Table 2
Different oxidant effect of cyclohexene oxidation with complex **4** and **5**.

Catalyst	Oxidant	Alcohol[a]	Ketone[b]	Epoxide[c]	Tot. Conv. (%)	TON[d]	TOF[e] (h^{-1})
4	TBHP	60	18	11	89	534	178
5		53	12	8	75	450	150
4	H_2O_2	22	12	9	43	258	86
5		21	10	7	38	228	76
4	m-CPBA	49	15	6	70	420	140
5		41	7	3	51	306	102
4	Free oxidant	–	–	–	–	–	–
5		–	–	–	–	–	–

[a] 2-Cyclohexene-1-ol.
[b] 2-Cyclohexene-1-one.
[c] Cyclolohexenoxide.
[d] Mole of product/mole of catalyst.
[e] Mole of product/mole of catalyst × time.
Conversion was determined by GC.

higher than with H_2O_2 (TON: 258). When TBHP was used as oxygen source on cyclohexene oxidation, complexes **4** and **5** show the considerably exalted activity in the experimented oxidant (TON: 534 and 450 for catalysts **4** and **5**). The checking studies demonstrate that the cyclohexene cannot be oxidized without the oxidant.

Another important parameter effecting the results of catalysis is the ratio of substrate/oxidant. As it is seen in Table 3, we investigated the amount of oxidant by changing oxidant/catalyst ratio on the cyclohexene oxidation while other parameters were constant. Until the changing to 800/1, the oxidation rate raised but from this ratio, total conversion leaned to declining. At this point, the coordination of the iron(II) and cobalt(II) may change and occur inactive intermediate species.

In order to design the best catalytic system, the effect of different temperatures was examined on the reaction rate of oxidation of cyclohexene. Investigation of this parameter proved that as the reaction temperature was increased the catalytic activity of complexes **4** and **5** increased on the oxidation of cyclohexene. The experiments were performed in the different temperatures (25, 50, 70, 90 °C) with ox./subst./cat. = 500/300/1 and TBHP, in DMF during 3 h (Table 4). The differences in the conversion was 46% for complex **4** and 34% for complex **5** when the temperature was raised from 25 to 90 °C. The highest conversion (96%) was obtained with TOF = 96 for complex **4** and (80%) with TOF = 80 for complex **5** at 90 °C. Based on the results, temperature of the cyclohexene oxidation with both complexes (molar ratio subs/ox/cat: 300/500/1) was determined as 90 °C.

Table 5 contains the oxidation studies in the literature. Based on the performances of the Fe-Pc and Co-Pc catalysts **4** and **5** towards the cyclohexene oxidation, it can be said that they are more successful catalysts than some other metallophthalocyanine and metalloporphyrin catalysts. The best reported results are obtained in terms of TOF in literature for homogeneous oxidation of cyclohexene with TBHP as oxidant and FePc and Co-Pc as catalyst. FePc was determined as successful catalyst on our study by comparing with Co-Pc.

Lastly, we monitored the oxidation system by UV–vis spectroscopy in order to investigate the catalytic mechanism for the metal-catalyzed cyclohexene in DMF and the results are illustrated in Fig. 8. The UV–vis spectrum of metal–phthalocyanine (MPc) complexes is commonly known and they consist of an intense band called the Q band in the visible region [55]. The spectrum in Fig. 8 shows the typical spectrum of monomeric form of CoPc with a Q band at 665 nm and also the electronic spectral change of this catalyst during the process of the catalytic reaction in the presence of TBHP. The Q band shifts to 670 nm for complex **5** and decreases in the intensity of the Q band. Because of the oxidation state of metal ion from 2+ to 3+, the shift in the Q band is observed [34]. In the B-band religion no peak can be observed. Thus addition of TBHP to solutions of Co-Pc resulted in only metal and not ring oxidation of Co-Pc. As catalysis continued, there was a gradual decrease in the intensity of the Q band of the Co-Pc catalyst, suggesting catalyst degradation as is typical [26] of MPc catalysts in homogeneous catalysis. This degradation of the

Table 3
Amount of oxidant effect of cyclohexene oxidation with complex **4** and **5**.

Catalyst	Oxidant/catalyst	Alcohol[a]	Ketone[b]	Epoxide[c]	Tot. Conv. (%)	TON[d]	TOF[e] (h^{-1})
4	500/1	60	18	11	89	534	178
5		53	12	8	75	450	150
4	800/1	62	18	12	92	552	184
5		56	14	9	79	474	158
4	1000/1	52	15	9	76	456	152
5		50	12	7	69	414	138
4	1200/1	46	10	7	63	378	126
5		41	10	5	56	336	112
4	1500/1	38	9	4	51	306	102
5		32	7	4	43	258	86

[a] 2-Cyclohexene-1-ol.
[b] 2-Cyclohexene-1-one.
[c] Cyclolohexenoxide.
[d] Mole of product/mole of catalyst.
[e] Mole of product/mole of catalyst × time.
Conversion was determined by GC.

Table 4
Temperature effect of cyclohexene oxidation with complex **4** and **5**.

Catalyst	T (°C).	Alcohol[a]	Ketone[b]	Epoxide[c]	Tot. Conv. (%)	TON[d]	TOF[e] (h^{-1})
4	25	32	10	8	50	250	83
5		32	9	5	46	230	76
4	50	42	12	11	65	325	108
5		49	10	5	54	270	90
4	70	52	18	10	80	400	133
5		51	11	7	69	345	115
4	90	65	20	11	96	288	96
5		60	12	8	80	240	80

[a] 2-Cyclohexene-1-ol.
[b] 2-Cyclohexene-1-one.
[c] Cyclolohexenoxide.
[d] Mole of product/mole of catalyst.
[e] Mole of product/mole of catalyst × time.
Conversion was determined by GC.

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

Catalyst	Rxn time (h)	Rxn temp. (°C)	Oxidant	Conv. (%)	Ref.
Mn(tbpcH$_2$ [a])	24	rt[g]	O_2	~45	[56]
Fe(tbpcH$_2$ [a])				~55	
Co(tbpcH$_2$ [a])				~30	
Fe(TMP[b])Cl	10 min	25	*m*-CPBA	89	[57]
Mn(PFTDCPP[c])	3	nr[h]	PhIO	93	[58]
MnTMpyP	16	rt[g]	PhIO	28	[59]
FeTMpyP				29	
MoTMpyP				0	
MnTTAPP				39	
Cl$_{16}$FePc[d]	8	nr[h]	TBHP	45.3	[26]
FePc[d]					
CoPc[d]					
Co[NÔ]$_2$ Cu[NÔ[e]]$_2$	8	75	H_2O_2	27.6	[60]
				43.50	
Cu(II)(L-prolinate)$_2$	24	22	O_2	60	[61]
		40		20	
[Mn(Me$_2$salpnMe$_2$ [f])]	8	40	TBHP	50.9	[62]
[Co(Me$_2$salpnMe$_2$ [f])]				42.7	
[Cu(Me$_2$salpnMe$_2$ [f])]				36.9	
[Ni(Me$_2$salpnMe$_2$ [f])]				23.8	
Co(salen)–POM	6	60	H_2O_2	91	[63]

[a] *Tetra-tert*-butylphthalocyanine.
[b] *Meso*-tetramesitylporphinato.
[c] 5-(Pentaflorophenyl)-10,15-20-tri(2,6-dichlorophenyl)porhrin.
[d] Phthalocyanine.
[e] 2-Pyrazinecarboxylic acid.
[f] *N,N*.-Bis-(α-methylsalicylidene)-2,2-dimethylpropane-1.
[g] Room temperature.
[h] Not reported.

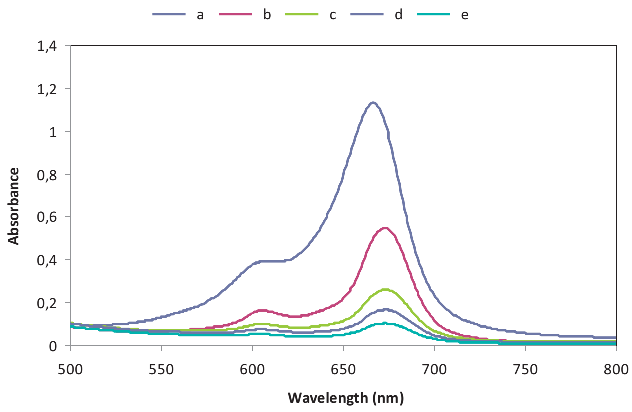

Fig. 8. Time-dependent changes in the visible spectrum of the oxidized complex **5** observed on addition of. All spectra for the oxidized complex **5** were TBHP (1.94×10^{-3} mol) to a reaction mixture containing 1.16×10^{-3} mol cyclohexene and 3.89×10^{-6} mol complex **5** catalyst in 10 ml: (b) 45 min; (c) 90 min; (d) 135 min; (e) 180 min after addition of TBHP taken after sixfold dilution with DMF. (a) The visible spectrum of (non-oxidized) complex **5**. (For interpretation of the references to color in this figure legend, the reader is referred to the web version of this article.)

catalysts is likely a consequence of RO• and ROO• radicals. These radical species that are formed by oxidant (especially TBHP) easily attack the phthalocyanine complex. This situation can easily realize to observe changing reaction color. Before the catalysis, the color of the solution was blue and then it turned to green as catalysis progressed. 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. The mechanism for Fe(II)Pc and Co(II)Pc transformation during the catalytic oxidation of cyclohexene (ROOH=THBP, m-CPBA, and H_2O_2).

$$\mathrm{PcM^{II}} + \mathrm{ROOH} \xrightarrow{-\mathrm{ROO^{\cdot}},\ \mathrm{RO^{\cdot}}} \mathrm{PcM^{III}} \xrightarrow{\mathrm{ROOH}} \mathrm{PcM^{III}\text{-}O\text{-}^{III}MPc}$$

M: Co and Fe

4. Conclusion

We have presented the synthesis and characterization of a new peripherally tetra-substituted Fe(II) and Co(II) phthalocyanines **4** and **5** using spectroscopic methods. The target symmetrical Fe(II) and Co(II) phthalocyanines **4** and **5** were separated by column chromatography and characterized by a combination of UV–vis, IR, ^{1}H NMR, ^{13}C NMR, MS spectroscopic data. This work has determined catalytic activities of Fe(II) and Co(II) phthalocyanines **4** and **5** on cyclohexene oxidation. There are few reports about catalytic studies for Fe(II) and Co(II) phthalocyanines. The results show that cyclohexene was converted to 2-cyclohexene-1-ol as major product and 2-cyclohexen-1-one, cyclohexene oxide as minor products with 96% and 80% with **4** and **5**, respectively. The most promising observation is that cyclohexenol is found to be major product in all of the catalytic tests. Substrate effect, temperature effect and oxidant effect were also discussed in this work. Control experiments were done without catalyst precursor, the corresponding metal salt as catalyst and we did not observe any product in the reaction mixture. Iron(II) and cobalt(II) phthalocyanine complexes **4** and **5** were also examined as catalyst for this reaction. Milder reaction conditions, higher yields of the products, shorter reaction time, and more inexpensive reagents make this catalytic system a useful oxidation method for cyclohexene.

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Appendix A. Supplementary data

Supplementary data associated with this article can be found, in the online version, at http://dx.doi.org/10.1016/j.molcata.2013.06.009.

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