



Original Research Article

Synthesis and Characterization of a Novel Crowned Schiff Base Ligand Linked to Ionic Liquid and Application of Its Mn(III) Complex in the Epoxidation of Olefins

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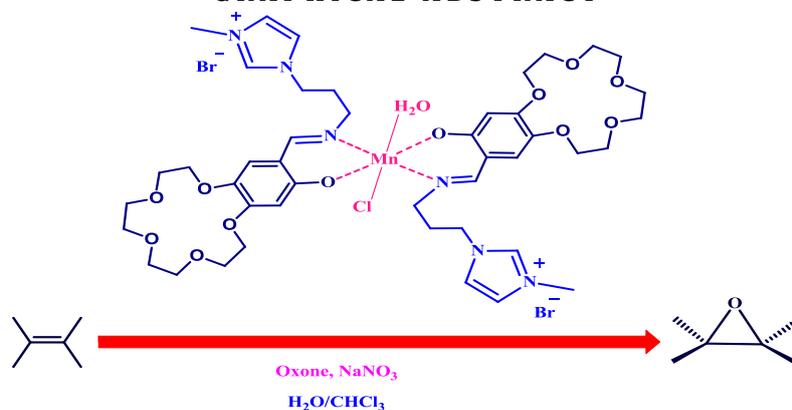
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Crown ether
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ABSTRACT

A new Schiff base ligand bound to ionic liquid and crown ether was synthesized and complexed with Mn (III) metal. Manganese complex was used in the vicinity of oxone oxidant and the absence of an axial base in water-chloroform biphasic oxidation to oxidize different alkenes, the corresponding epoxides were obtained with 70-96% yields. The lowest efficiency is related to alkenes with electron-withdrawing groups.

GRAPHICAL ABSTRACT



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Introduction

Supramolecular compounds of crown ethers are the most famous host group, which was first introduced by Pedersen. These supramolecules have been used in several scientific fields, including chemistry, medicine, biology, physics, etc. due to their special structures and the supramolecular communities they form. Likewise, if the ligands of these compounds have additional donor atoms in the side chain, their sensitivity and selectivity will increase [1-5]. To link two crown ether units using aliphatic or aromatic chains, ester [6], amide [7], calixarene [8], and type Schiff base [9] are usually used.

Schiff bases are a very important class of organic compounds that contain an azomethine group (-CH=N-) and have wide applications in many biological aspects, proteins, visual pigments, enzymatic aldolization, and decarboxylation reactions. Due to their well-known coordination ability, they are one of the most important ligands used in the coordination of metal complexes chemistry. Schiff bases complexes are further utilized as catalysts in the dyes and polymer industries, along with some cases as antifertility and enzymatic agents [10-20]. Metal-based complexes are known to have broad-spectrum antimicrobial [21] and DNA-degrading activities.

Ionic liquids (ILs) are colorless liquid salts with low melting points that are used as media for various applications in various chemical processes. This group of materials consists of two parts, negative and positive ions. Ionic liquids are good solvents for catalytic reactions and have many advantages such as easy separation, very low vapor pressure, non-flammability, high thermal stability, and low toxicity [22, 23]. Ionic liquids are currently under extensive investigation for a wide range of solvent and electrolyte applications due to the attractive combination of properties that some members of the family possess [24-32].

The catalytic process of epoxidation of alkenes in the presence of metals is of great interest due to the value of epoxide compounds as building blocks in organic chemistry syntheses. In this

important process, which is the focus of much research, we can mention the formation of epoxide in electron-deficient alkenes, which are used as intermediates in chemical and pharmaceutical materials [33]. Among various metal-containing epoxidation catalysts, Mn(III) complexes are one of the most effective catalysts for these important transformations, such as the epoxidation of electron-deficient anions [34].

Therefore, in the continuation of the work of organic reactions in the presence of homogeneous and heterogeneous catalysts [34-45], and given that the importance of the synthesis of epoxide compounds in the present research, a new Schiff base ligand linked to the ionic liquid, crown ether and complexed with manganese(III) was synthesized and it was used for the oxidation of different alkenes in the presence of oxone oxidant.

Materials and Methods

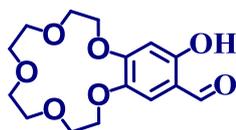
All chemicals and solvents used were purchased from Merck and Sigma-Aldrich. FTIR spectra were recorded using a Thermo Nicolet 370 device with a KBr tablet. ¹H-NMR and ¹³C-NMR spectra were measured with Bruker DPX-500 and DPX-250 devices, respectively, and chloroform and deuterium dimethyl sulfoxide were selected as solvents and TMS as internal standards. TGA was recorded using a Q600 TA device in the temperature range of 30 to 700°C with a heating rate of 20 °C/min in an argon atmosphere. ICP-OES analysis was measured using a Simultaneous VISTA-PRO device.

Synthesis of 4'-formyl-5'-hydroxybenzo-15-crown-5

To prepare 4'-hydroxybenzo-15-crown-5, first 4'-acetylbenzo-15-crown-5 [46], 4'-acetoxybenzo-15-crown-5 [46], and 4'-hydroxybenzo-15-crown-5 [47] were synthesized, respectively, with the help of the method available in the published manuscripts.

In the next step, a mixture of 5 mmol 4'-hydroxybenzo-15-crown-5, and 5 mmol (0.7 g) of hexamethylene tetraamine was dissolved in 15 ml of trifluoroacetic acid with vigorous stirring at

80 °C and refluxed for 20 hours. The resulting thick green-yellow solution was added to 80 ml of ice water and stirred for 4 hours at 25 °C. The resulting mixture was extracted with chloroform (3×30 mL) and dried with Na₂SO₄. After removing the solvent, the crude product was crystallized by n-heptane to obtain the product (85% yield) with a melting point of 109-110 °C (Scheme 1) [48].



Scheme 1: 4'-formyl-5'-hydroxybenzo-15-crown-5

4'-acetylbenzo-15-crown-5: ¹H-NMR (CDCl₃) δ: 2.41 (s, 3H), 3.86-4.30 (m, 16H), 6.72-7.24 (m, 3H).

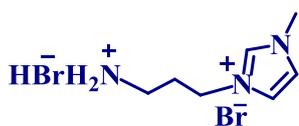
4'-acetoxybenzo-15-crown-5: ¹H-NMR (CDCl₃) δ: 2.21 (s, 3H), 3.86-4.30 (m, 16H), 6.54-6.74 (m, 3H).

4'-hydroxybenzo-15-crown-5: ¹H-NMR (CDCl₃): δ 3.65-4.31 (m, 16H), 6.11-6.88 (m, 3H), 6.94 (bs, 1H)

4'-formyl-5'-hydroxybenzo-15-crown-5: ¹H-NMR (CDCl₃): δ 3.7-4.19 (m, 16H), 6.62-7.12 (m, 2H, Ar), 9.81 (s, 1H), 6.94 (s, 1H).

Synthesis of 1-aminopropyl-3- methylimidazolium bromide hydrogenbromide ([3-apmim] Br.HBr)

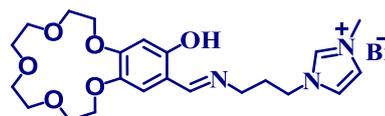
The mixture containing (5 mmol, 0.41 g) 1-methylimidazole and (5 mmol, 1 g) 3-bromopropylamine hydrogenbromide was stirred in 15 mL of acetonitrile for 4 hours at 80 °C. After the end of the reaction and removal of the solvent, the remaining mixture was crystallized in ethanol and a white precipitate (89% yield) of the desired product was formed (Scheme 2) [49].



Scheme 2: [3-apmim] Br.HBr

General synthesis method of supported ionic liquid ligand on Schiff bases attached to benzo-15-crown-5 (IL@Schiff base@benzo-15-crown-5)

3 mL of sodium hydroxide solution (1N) was added to the mixture of [3-apmim] Br.HBr (3 mmol) and 4'-formyl-5'-hydroxybenzo-15-crown-5 (3 mmol, 0.94 g) in 20 mL of ethanol, and then the mixture was refluxed for 5 hours. The yellow product was filtered and dried under a vacuum (81% yields) (Scheme 3).

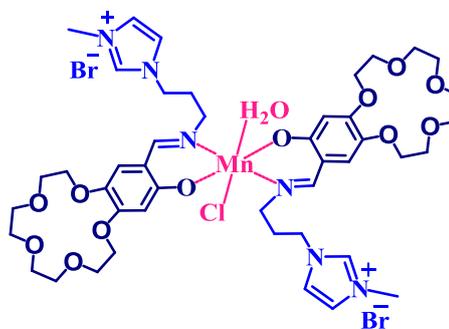


Scheme 3: IL@Schiff base@benzo-15-crown-5

¹H-NMR (DMSO) δ: 1.42 (m, 2H), 2.49 (t, 2H), 3.51 (t, 2H), 3.74-4.12 (m, 16H), 4.28 (s, 3H), 6.21 (s, 1H), 6.91 (s, 1H), 7.62-7.63 (m, 2H), 7.70 (s, 1H), 9.30 (s, 1H), 10.18 (bs, 1H); IR (KBr, ν/cm⁻¹): 3429, 2939, 3075, 1660, 1293.

Synthesis of Mn(III) complex

To the solution of ligand (IL@Schiff base@benzo-15-crown-5) (0.2 mmol) in 20 mL of ethanol, 20 ml of ethanol solution containing manganese (II)acetate tetrahydrate (Mn(OAc)₂·4H₂O) (1.0 mmol, 0.17 g) and LiCl (1.0 mmol, 0.042 g) were added and refluxed for about 7 hours. Then, the mixture was cooled to 25 °C, and the light brown precipitate was separated by filtration. The desired light brown precipitate (72% yield) was separated by filtration and washed with cold ethanol (Scheme 4).

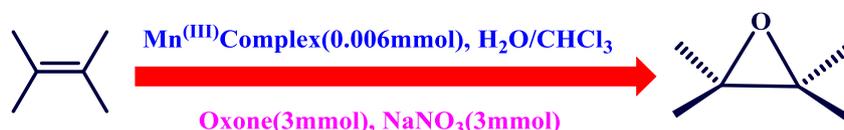


Scheme 4: Mn(III) complex

Alkene epoxidation by Mn complex bound to ionic liquid and crown ether in water-chloroform medium

In the epoxidation reaction of alkenes, 3 mmol (0.45 g) of oxone (KHSO₅), 3 mmol (0.25 g) of NaNO₃, 2 mmol of alkene, and 0.006 mmol of Mn

complex were added to 5 mL of H₂O, and 1 mL of chloroform at temperature of 50 °C and stirred. The progress of the reaction was followed by TLC. The reaction yields were calculated as 18-96% by injecting the crude product into the gas chromatography (GC) column (Scheme 5).



Scheme 5: Epoxidation of alkenes by Mn complex

Results and Discussion

Identification of Mn complex

For this purpose, the FT-IR spectra of ligand and complex (Figures 1 and 2) were compared. In the FT-IR spectrum of the broad-band ligand (which is due to the hydrogen bond) OH, it can be seen in the 3563 cm⁻¹ regions. Compared with cobalt complex, the decrease in the intensity of this band after coordination with manganese can be caused by the presence of water of crystallization in the complex structure. The band related to C=N of the ligand appeared at 1651 cm⁻¹, which was shifted to lower frequencies (1630 cm⁻¹) after being coordinated with manganese. In FT-IR, the bands at 568 cm⁻¹ and 697 cm⁻¹ are related to stretching vibrations of Co-N and Co-O,

respectively. In addition, the common bands in the spectra of ligand and complex are around 1100-1250, 1400-1600, 2900, and 3100 cm⁻¹, respectively, corresponding to C-O, C=C, -C-H, and =C-H vibrations.

XRD analysis of ligand and complex was further investigated. Due to the crystal structure of the ligand, it gives much sharper peaks than the corresponding complex (Figures 3 and 4). By comparing the elemental analysis (ICP and CHN) of ligand and complex, the ratio of ligand metal was revealed as 1:2 in the complex. In addition, the results of elemental analysis of the complex have partially made possible the presence of at least one water molecule in the complex structure.

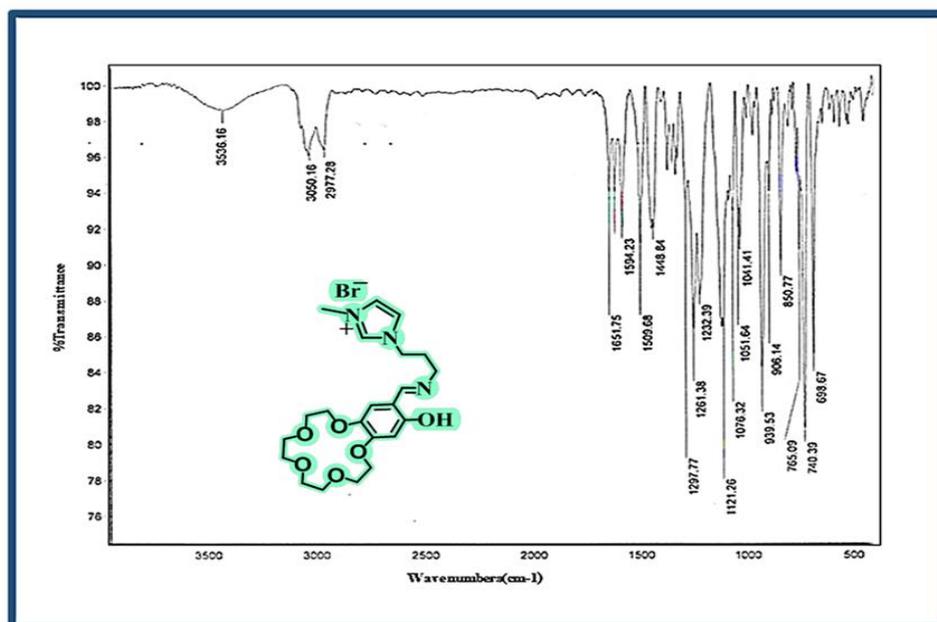


Figure 1: FT-IR spectrum of the ligand

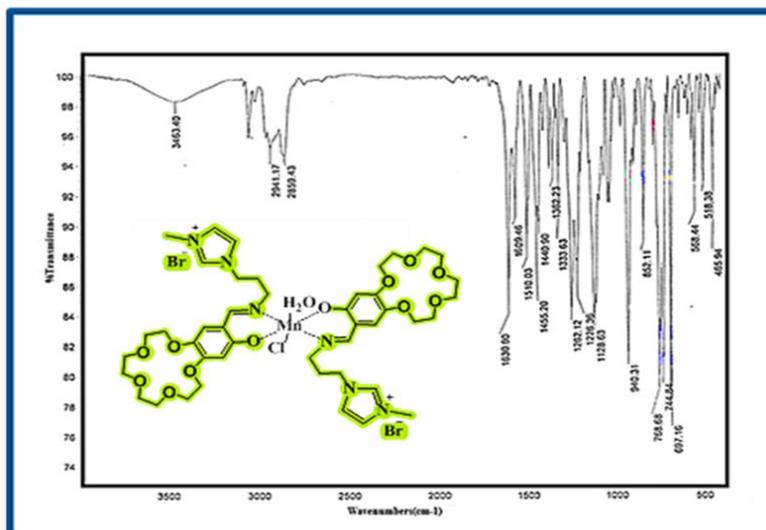


Figure 2: FT-IR spectrum of Mn complex

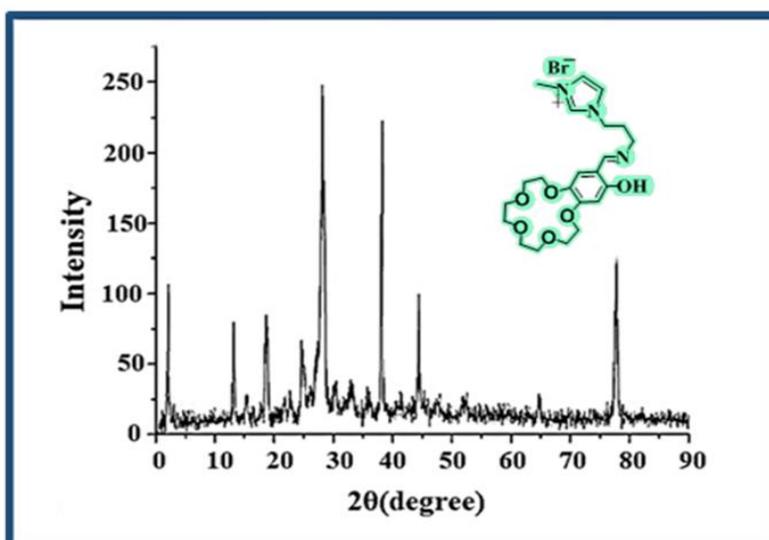


Figure 3: Ligand XRD analysis

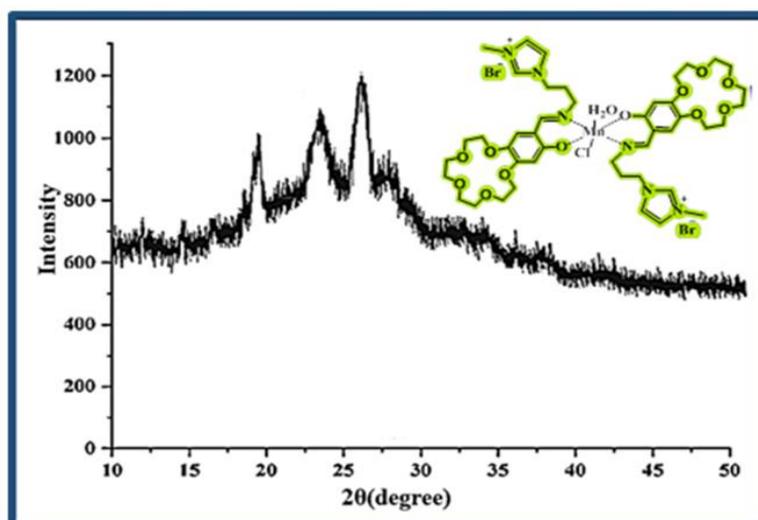


Figure 4: XRD analysis of Mn complex

The synthesized Mn complex was used as a catalyst and oxone as an oxidant in the oxidation of cyclohexene in a two-phase environment containing water and chloroform at a temperature of 50 °C, and the desired epoxide was obtained with a yield of 91 % (Table 1). It should be mentioned that the reaction was performed in other solvents such as H₂O, MeOH, EtOH, CHCl₃, CH₂=CN, and a mixture of H₂O/EtOH, which did not have great efficiency due to the low solubility of oxone or due to the high solvolysis of the product. Therefore, the mixture of water and chloroform was chosen, on the one hand, to dissolve oxone in the aqueous phase, and on the other hand, the product was formed in the environment of chloroform and its hydrolysis was minimized. To show the importance of connecting crown ether and ionic liquid to the complex in the performance of oxidation system, an equal mixture of the same complex without crown/crown ether and an equal mixture of the same complex without ionic liquid/ionic liquid were used for the cyclohexene oxidation, which after time longer resulted in lower yield (Table 1, entries 3 and 4).

These observations indicate that the binding of crown ether and ionic liquid to the Schiff base complex is an essential requirement for the

catalyst to show high efficiency. It seems that the crown ether ring places the oxidant in the vicinity of the Mn metal by trapping the k⁺ in its cavity. In this way, it facilitates the oxidation of Mn(III) to (V) M=O, which is a much stronger oxidant than oxone. It should be mentioned that a color change from orange to brown occurs after adding the oxidant to the reaction mixture without alkene, which is probably caused by the change in the oxidation number of Mn. In addition, the crown ether ring increases the catalyst transfer to the organic phase. On the other hand, the presence of ionic liquid increases the dissolution of the catalyst in the aqueous phase to trap more oxidants. However, the influence of the polar properties of the ionic liquid on the catalyst activity is probable. It has been found that the addition of an axial base increases the catalytic activity of Mn complexes, because the axial base improves the electron density of the central metal of complex, thereby improving the oxidation of Mn(III) to Mn(V) [50].

Therefore, the effect of increasing different axial spans was investigated, which did not bring significant change (Table 2). It seems that probably the N atom of imidazole ring can play the role of an axial base and there is no need for an external axial base.

Table 1: Epoxidation of cyclohexene by Mn complex attached to crown ether and ionic liquid^a

Entry	Catalyst	Time (h)	Yield (%)
1	-	120	Trace
2	Mn complex bound to crown ether and ionic liquid	2	86
3	Mn complex without crown ether/crown ether (1:1)	5	60
4	Mn complex without ionic liquid/ionic liquid (1:1)	7	86

^a Reaction conditions: 2 mmol cyclohexane, 3 mmol KHSO₅, 0.006 mmol catalyst, 5 mL H₂O, and 1 mL chloroform, 50 °C.

Table 2: Axial effect on the oxidation of cyclohexene

Entry	Axial base	Time (h)	Yield (%)
1	Pyridine	2	86
2	pyridine-N-oxide	2	87
3	N-methylimidazole	2	83

^a Reaction conditions: 2 mmol cyclohexane, 3 mmol KHSO₅, 0.006 mmol catalyst, 5 mL water, and 1 mL chloroform, 50 °C

Next, the effect of the reactants ratio on cyclohexene epoxidation reaction was investigated (Table 3). By increasing the amount

of oxidant (up to 3 mmol) compared with the amount of cyclohexene and catalyst, the reaction efficiency improves to some extent, further

increase of this ratio does not create a noticeable change (Table 3, entries 1-3). It seems that a large amount of oxone causes the destruction of epoxide due to its acidic property, and its small amount reduces the rate of Mn oxidation. Increasing the amount of cyclohexene up to 2 mmol improves the efficiency of the catalytic system, but higher amounts decrease the efficiency and prolong the reaction time (Table 3, entries 4-7). Checking the amount of catalyst further determined that the best results are obtained when the amount of 0.006 mmol of catalyst is used (Table 3, entry 2 is compared with entries 8 and 9). Probably, the Lewis acid property of the catalyst prevails in amounts

higher than 0.006 mmol and causes the epoxide degradation.

The noteworthy point is the NaNO₃ addition to the catalytic system decreases the time and increases the yield of the reaction, while the addition of Ba(NO₃)₂ and LiNO₃ was almost ineffective (Table 4). It is possible that the greater matching of benzo-15-crown-5 cavity size (d=0.18-0.22 nm) and the Na⁺ ion size (d=0.19 nm) leads to a better transfer of HSO₅⁻ to the aqueous environment. Likewise, the size of Li⁺ (d=0.136 nm) is too small and the size of Ba²⁺ and K⁺ (d=0.266 nm) is too big to fit in the cavity of benzo-15-crown-5.

Table 3: Effect of molar ratio of reactants on chemical efficiency and reaction time of cyclohexene epoxidation

Entry	KHSO ₅ : Cat: Cy	Time (h)	Yield (%)
1	1: 0/006: 2	2	68
2	3 :0/006: 2	2	86
3	6 :0/006: 2	2	87
4	3 :0/006: 1	3	78
5	3 :0/006: 2	2	86
6	3 :0/006: 3	3	70
7	3 :0/006: 4	3/2	69
8	3 :0/012: 2	2/6	48
9	3 :0/002: 2	2/5	67

^aReaction conditions: 5 mL water and 1 mL chloroform as solvent, and temperature 50 °C

Table 4: Efficacy of alkali salts (3 mmol) on cyclohexane oxidation

Entry	Alkali metal salts	Time (h)	Yield (%)
1	LiNO ₃	2	87
2	NaNO ₃	0.25	91
3	Ba (NO ₃) ₂	2	86
4	-	2	86

^a Reaction conditions: 2 mmol cyclohexane, 3 mmol KHSO₅, 0.006 mmol catalyst, 5 mL water, and 1 mL chloroform, 50 °C

Table 5: Comparison of the epoxidation system of this project with other reported researches

Entry	KHSO ₅ (mmol)	Alkene (mmol)	Time (h)	Yield (%)
1	0.44	Cyclohexene (0.35 mmol)	5	95 ^a [51]
2	3.2	Cyclohexene (1.6 mmol)	0.75	51 ^b [52]
3	3	Cyclohexene (2 mmol)	0.25	This work ^c
4	0.6	Cyclooctene (0.35 mmol)	5	97 ^a [51]
5	3.2	Cyclooctene (1.6 mmol)	16	60 ^b [52]
6	3	Cyclooctene (2 mmol)	0.3	This work ^c

^aThe reactions were carried out in 5 mL of dichloroethane at a temperature of 25 °C using 8 mmol of hemiporphyrine complex and in the presence of 2,4,6-trimethylpyridine (8 mmol). ^bThe reactions were carried out at a temperature of 23 °C in an aqueous environment without a catalyst. ^c Reactions at 50 °C, 2 mmol of cyclohexane, 3 mmol of KHSO₅, 0.006 mmol of catalyst, 5 ml of H₂O, and 1 mL of chloroform.

To demonstrate the value of epoxidation system designed in this project, this system is compared with another reported research works (Table 5). In general, the catalytic system reported in this research more efficient, has a shorter reaction time, and in some cases, it had both advantages. Finally, to expand the scope of reaction, the catalyst was used for the oxidation of other alkenes (Table 6). As can be seen, the conjugated alkene with the electron-withdrawing group has little or no tendency to be epoxidized. In addition, trans-alkenes are more easily oxidized compared with the cis type, because in the transition state, the distance between the substitutions of the cis-alkene is much less than that of the trans-alkenes, which causes the instability of transition state, so the reaction rate decreases.

On the other hand, the efficiency of the synthesized catalyst was compared with several reported catalysts (Table 7) for the oxidation of alkene number 5 as a model reaction. As can be seen, among the catalysts, the Mn complex has the best efficiency (96%), the most suitable solvent, and the shortest reaction time (Table 7, entries 1-10).

Investigating the catalytic stability is important because the metal leaching from the catalyst is responsible for the reduction of catalytic activity in successive runs. To evaluate the stability and reusability of the Mn(III) complex, epoxidation was evaluated for model reaction. After each experiment, the catalyst was filtered, washed with H₂O, dried, and reused. The results revealed that the catalytic activity of Mn(III) complex is suitable for reuse more than five times (Figure 5).

Table 6: Epoxidation of different alkenes

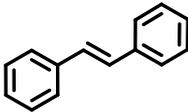
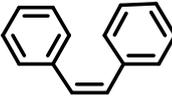
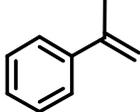
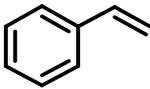
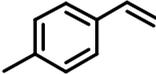
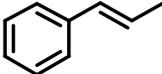
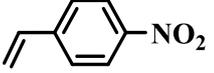
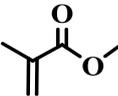
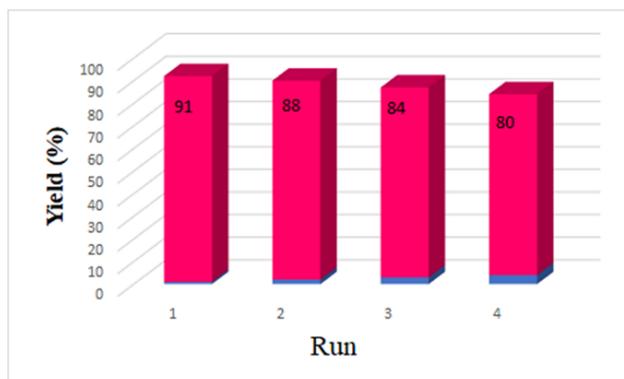
Entry	Alkene	Time (h)	Yield (%)
1		0.25	91
2		3.5	84
3		4	72
4		1,6	96
5		1	95
6		0.3	95
7		0.6	96
8		2	88
9		15	70
10		18	-

Table 7: The performance of Mn complex to compare with some other catalysts

Entry	Catalyst	Solvent	Time (h)	Yield (%)	Reference
1	Pd/ZnO nanoparticles	THF	24	82	[53]
2	MnWO ₄ (3 wt%)/SBA-16	CH ₃ CN	24	90	[54]
3	Co(acac) ₂ APTS@SBA-15	DMF	12	61	[55]
4	Cobalt(III) Schiff base complex	CH ₃ CN	24	46	[56]
5	(MOF) viz. [Nd (HCOO) ₃] n	CH ₃ CN	24	78	[57]
6	[Ln ₂ (N ₃) (nic) ₂ (OH) ₃ (Hnic)- (H ₂ O)] n (Ln = GdIII)	CH ₃ CN	24	81	[58]
7	γ-Al ₂ O ₃ -NR-400	C ₄ H ₈ O ₂	4	64	[59]
8	Mn complex (This work)	H ₂ O/ CHCl ₃	1	95	This work

**Figure 5:** Mn complex recycling test during four cycles for epoxidation reaction

Conclusion

In general, in this project, a catalyst containing crown ether, and the ionic liquid was synthesized and used in the epoxidation reaction of olefins. It was found that this catalyst shows more activity than the catalyst without ionic liquid and crown ether in this reaction. Due to the presence of nitrogen in the imidazole ring, there is no need to use an axial base, which specifies its role as an axial base. In addition, the crown ether ring connected to the Schiff base not only brings the oxidant and the central metal of catalyst closer, but also by trapping the cation with the oxone, causes the transfer of this species to the organic phase, thus increasing the efficiency of the catalytic system.

Disclosure Statement

No potential conflict of interest was reported by the authors.

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Authors' contributions

All authors contributed to data analysis, drafting, and revising of the paper and agreed to be responsible for all the aspects of this work.

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