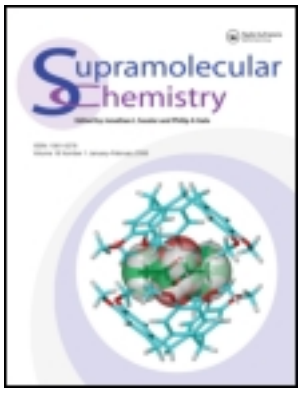

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Synthesis and application of new Schiff base Mn(III) complexes containing crown ether rings as catalysts for oxidation of cyclohexene and cyclooctene by Oxone

Seyed Mohammad Seyedi [a], Gholam Hossein Zohuri [a] & Reza Sandaroos [a]
[a] Department of Chemistry, Faculty of Science, Ferdowsi University of Mashhad, Mashhad, Iran

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Synthesis and application of new Schiff base Mn(III) complexes containing crown ether rings as catalysts for oxidation of cyclohexene and cyclooctene by Oxone

Seyed Mohammad Seyedi*, Gholam Hossein Zohuri and Reza Sandaroos*

Department of Chemistry, Faculty of Science, Ferdowsi University of Mashhad, Mashhad, Iran

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Six catalysts $MnClL^1$–$MnClL^6$, containing two crown ether rings, were synthesised and characterised by IR spectroscopy and CHN microanalysis. A combination of Oxone, as oxidant, and these catalysts was used for the oxidation of cyclohexene and cyclooctene. Among the prepared catalysts, $MnClL^3$ and $MnClL^4$ exhibited the best catalytic efficiency. Catalysts $MnClL^1$, $MnClL^2$ and $MnClL^6$ showed a moderate efficiency and $MnClL^1$ showed the lowest efficiency. Comparison of $MmclL^1$–$MnClL^4$ and $MnClL^6$ containing crown ether rings with an identical mixture of uncrowned complex $MnClL^7$ [manganese *N*,*N*′-bis(salicylidene)ethylenediamine chloride] and crown ether 2 (4′-hydroxybenzo-15-crown-5), revealed a more important role for the crown ether than increasing solubility of Oxone in the organic phase. The effect on reaction times and chemical yields of temperature, pyridine as the axial base, and different alkali metal salts was also investigated.

Keywords: crown ether; Schiff base; Oxone

Introduction

Oxidation of alkenes to epoxides is very important in organic synthesis and has been of immense interest in the area of transition metal complex-mediated reactions over the past decades (*1–9*). In this regard, metalloporphyrins have been used extensively owing to their direct relationship to enzymatic oxidation with cytochrome P-450 (*10–12*). Parallel to the porphyrin chemistry, the same catalytic reactions are mimicked by various transition metal complexes, in particular, Schiff base complexes. Such complexes are of interest because of their cheap and easy synthesis and their chemical and thermal stability (*13–19*). Application of Schiff base complexes containing crown ether rings in aerobic oxidation of various organic compounds is a topic of much current interest (*20–22*). Complexation of a hard cation in the crown cavity of these catalysts, close to the transition-metal centre, perturbs oxygen-binding properties of the metal centre which results in improved catalytic behaviour of some catalysts in comparison with their uncrowned analogues (*23*).

Catalytic oxidation of alkenes has been carried out using a variety of oxidants such as PhIO, NaOCl, H_2O_2, alkyl hydroperoxides, percarboxylic acids, magnesium monoperoxyphthalate, molecular oxygen and potassium peroxymonosulphate ($KHSO_5$). Potassium peroxymonosulphate ($KHSO_5$), which is commercially named Oxone, is a stable oxidising agent, which is easy to handle, is non-toxic, generates non-polluting byproducts, and is relatively inexpensive. Oxone has been widely studied as a routine reagent for epoxidation reactions, oxidation of aldehydes to carboxylic acids, and in many other oxidation processes (*24*). Oxone is an efficient oxidising agent that has low solubility in organic solvents, but is far more soluble in aqueous media. The use of Oxone in an aqueous medium for the epoxidation of alkenes leads to extensive hydrolysis of the reaction products. Mixtures of water–methanol (or ethanol) or water–ethanol–acetic acid overcome the low solubility of Oxone in organic solvents, but ethanol is also oxidised, and a large excess of Oxone is needed to obtain good yields of epoxides (*25–37*).

Oxidation of alkenes by Oxone, in a biphasic mixture of water, a ketone (usually acetone), dichloromethane and a phase-transfer catalyst, has been reported several times (*29–33*). The active oxidant in this system is a dioxirane generated by the reaction of Oxone with the ketone. Without the ketone no epoxidation occurs. In these kinds of systems, control of pH was necessary to avoid Baeyer–Villiger oxidation of the ketones. The maximum yield of cyclohexene oxide (calculated based on initial cyclohexene) was 78%, which was obtained at pH 7.5 and after 3 h reaction time (*29*). Ford and co-workers obtained cyclooctene oxide in 97% yield using Oxone as oxidant and without an added catalyst after 5 h in an unbuffered aqueous medium; control of pH was needed to obtain high yields of more aqueous soluble epoxides such as cyclohexene oxide and styrene oxide (*38*). The maximum yield of cyclohexene oxide (based on initial cyclohexene)

*Corresponding authors. Emails: smseyedi@yahoo.com; r_sandaroos@yahoo.com

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was 95% obtained at pH > 7.5 after 5 h reaction time. Epoxidations of alkenes with Oxone catalysed by manganese porphyrins (*34, 35*) and platinum complexes (*36*) have also been reported, but are impractical since these organometallic complexes decompose rapidly during the epoxidation. Compared with manganese porphyrins, manganese hemiporphyrazines showed better stability in epoxidation reactions (*39*). The highest yield of cyclohexene oxide reported using homogenous manganese hemiporphyrazines was 51%. It is believed that oxo manganese (V) generated by the reaction of Oxone and hemiporphyrazines-manganese (III) is the active oxidant for the oxidation of alkene.

In this contribution, we report the synthesis, characterisation and application of new Schiff base catalysts $MnClL^1$–$MnClL^6$ (Figure 1), including two crown ether rings, for epoxidation reaction in the presence of Oxone as oxidant. We investigated the effect of the crown ether rings, the structure of the ligands and the reaction conditions on the efficiency of the prepared catalysts. Our epoxidation system showed better performance compared with other methods (*38, 39*).

Experimental

All chemicals and solvents were supplied by Merk Chemical Co. (Darmstadt, Germany) and Fluka Co. and were used as received. ^{1}H NMR and IR spectra were recorded on a Bruker BRX-100 AVANCE and a Shimadzu spectrometer, respectively. 4′-Aminobenzo-15-crown-5 (**1**) and $MnClL^6$ named as manganese *N*,*N*′-bis(salicylide-

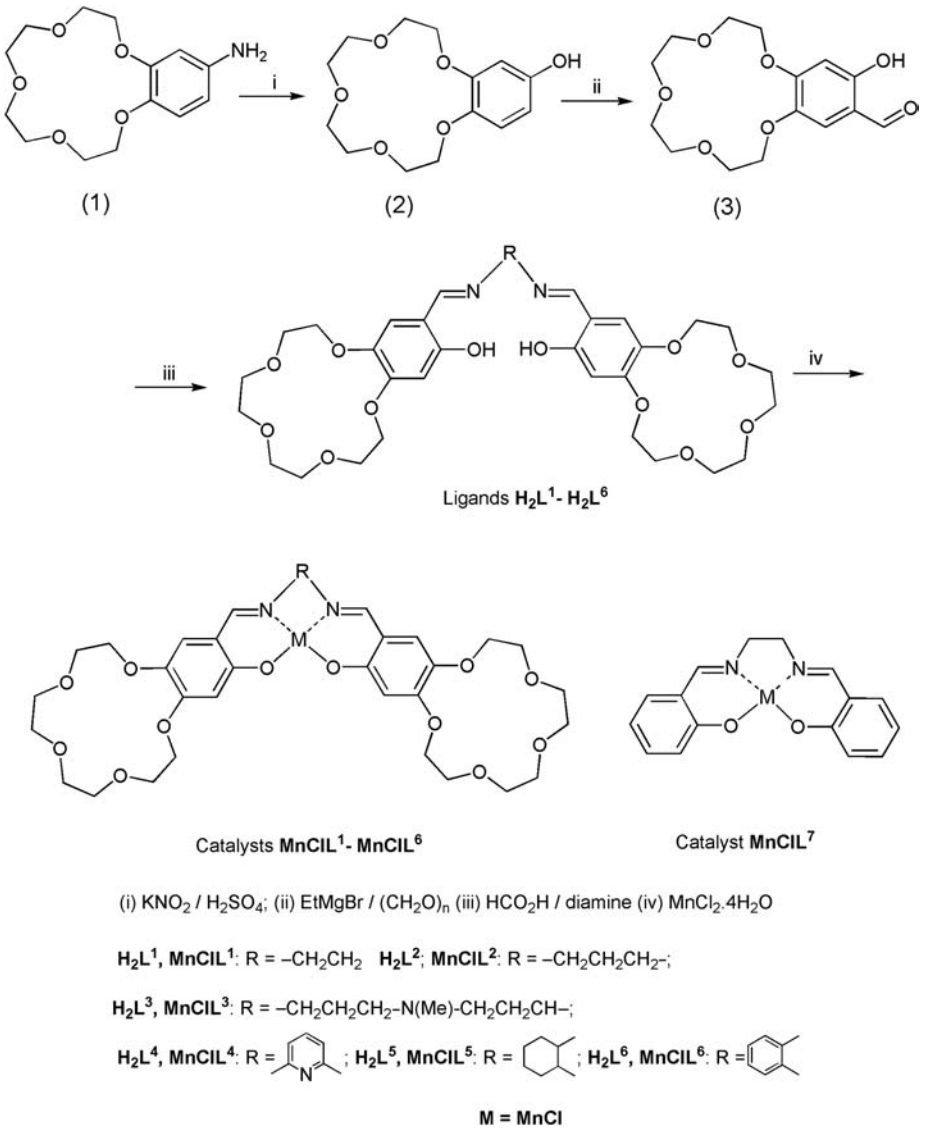


Figure 1. Synthesis of complexes $MnClL^1$–$MnClL^6$ and ligands H_2L^1–H_2L^6.

ne)ethylenediamine chloride (EUK-8) were prepared according to the literature (*40, 41*).

DFT calculations were done with Gaussian 03 program and the B3LYP/lan2Dz level of theory was used to optimise the geometry of molecule (*42*).

Synthesis of 4′-hydroxybenzo-15-crown-5 (2)

To a warm solution of concentrated sulphuric acid (5 ml) in water (40 ml), 4′-aminobenzo-15-crown-5 (40.0 mmol, 11.4 g) was added slowly with vigorous stirring. The mixture was cooled and 20 g of ice was added. A solution of potassium nitrite (31.7 mmol, 3.2 g) in water (20 ml) was added in small quantities, with stirring, to the initial solution, until all the amine groups were diazotised, which was determined by testing the solution for nitrous acid. The mixture was heated at 40°–50°C on a water bath for 2 h. The mixture was saturated with potassium chloride and extracted with ether (3 × 100 ml). The solvent of the combined extracts was removed by reduced pressure and 4′-hydroxybenzo-15-crown-5 was collected in 68% yield (27 mmol, 7.8 g). ^{1}H NMR ($CDCl_3$, 100 MHz): δ 3.77 (s, 8H, CH_2—O), 3.95 (m, 4H, CH_2—O), 4.19 (m, 4H, CH_2—O), 6.61–7.02 (m, 3H, ArH), 12.28 (s, 1H, OH). Anal. Calcd for $C_{14}H_{20}O_6$: C, 59.14; H, 7.09%. Found: C, 59.01; H, 7.00%.

Synthesis of 4′-formyl-5′-hydroxybenzo-15-crown-5 (3)

To a stirred ethylmagnesium bromide (3.0 M in Et_2O, 27.0 mmol, 9 ml), 25.0 mmol of 4′-hydroxybenzo-15-crown-5 (2) (7.72 g) in 30 ml of THF, was added dropwise over 15 min at 0°C. The mixture was stirred for 2 h at room temperature. Dried toluene (40 ml) and a mixture of triethylamine (35.0 mmol, 3.5 g) and paraformaldehyde (purity 94%, 60.0 mmol, 1.92 g) were added and the mixture was stirred for further 2 h at 80°C. After this time, the reaction mixture was cooled to 0°C and then acidified to pH 3 by HCl (2 N). The organic phase was separated, dried over $MgSO_4$, and the solvent was removed. The yield of the reaction was about 75% (18.75 mmol, 5.89 g). ^{1}H NMR ($CDCl_3$, 100 MHz): δ 3.74 (s, 8H, CH_2—O), 3.92 (m, 4H, CH_2—O), 4.19 (m, 4H, CH_2—O), 6.82 (s, 1H, Ar), 7.32 (**s,** 1H, Ar), 10.0 (s, 1H, CHO), 12.8 (s, 1H, OH). Anal. Calcd for $C_{15}H_{20}O_7$: C, 57.69; H, 6.45%. Found: C, 57.64; H, 6.39%.

General procedure for ligands H_2L^1–H_2L^6

Compound **3** (0.01 mol) was dissolved in ethanol (20 ml) and mixed with the diamine (0.005 mol) and a trace amount of formic acid. The mixture was stirred at 50°C under N_2 for 6 h. The precipitate was collected by suction filtration and washed with cold ethanol. The crude product was recrystallised from ethanol to give a pure sample.

H_2L^1

^{1}H NMR ($CDCl_3$, 100 MHz) δ: 3.76 (m, 20H, CH_2—O, N═CH_2), 3.95 (m, 8H, CH_2—O), 4.17 (m, 8H, CH_2—O), 6.8–7.01 (m, 4H, ArH), 8.24 (s, 2H, CH═N), 13.10 (s, 2H, OH); IR (KBr, film) ν_{max}: 3228, 2931, 2868, 1620, 1604, 1500, 1260, 1121, 1054, 932 cm^{-1}; Anal. Calcd for $C_{32}H_{44}N_2O_{12}$: C, 59.25; H, 6.84; N, 4.32%. Found: C, 59.16; H, 6.81; N, 4.29%.

H_2L^2

^{1}H NMR ($CDCl_3$, 100 MHz) δ: 1.60–1.68 (m, 2H, CCH_2C), 3.74 (m, 20H, CH_2—O, N═CH_2), 3.92 (m, 8H, CH_2—O), 4.19 (m, 8H, CH_2—O), 6.78–7.08 (m, 4H, ArH), 8.30 (s, 2H, CH═N), 12.58 (s, 2H, OH); IR (KBr, film) ν_{max}: 3230, 2921, 2866, 1622, 1608, 1505, 1261, 1130, 1055, 930 cm^{-1}; Anal. Calcd for $C_{33}H_{46}N_2O_{12}$: C, 59.81; H, 7.00; N, 4.23%. Found: C, 59.70; H, 6.97; N, 4.20%.

H_2L^3

^{1}H NMR ($CDCl_3$, 100 MHz) δ: 1.62–1.90 (m, 4H, CCH_2C), 2.17–2.32 (t, 7H, NCH_2, NCH_3), 3.77 (m, 20H, CH_2—O, N═CH_2), 3.97 (m, 8H, CH_2—O), 4.15 (m, 8H, CH_2—O), 6.82–7.08 (m, 4H, ArH), 8.29 (s, 2H, CH═N), 13.21 (s, 2H, OH); IR (KBr, film) ν_{max}: 3224, 2931, 2861, 1618, 1601, 1500, 1261, 1129, 1048, 926 cm^{-1}; Anal. Calcd for $C_{37}H_{55}N_3O_{12}$: C, 59.56; H, 7.55; N, 5.37%. found: C, 59.51; H, 7.53; N, 5.34%.

H_2L^4

^{1}H NMR ($CDCl_3$, 100 MHz) δ: 3.74 (s, 16H, CH_2—O), 3.97 (m, 8H, CH_2—O), 4.15 (m, 8H, CH_2—O), 6.54–7.23 (m, 7H, ArH, PyH), 8.34 (s, 2H, CH═N), 13.28 (s, 2H, OH); IR (KBr, film) ν_{max}: 3223, 2930, 2867, 1621, 1602, 1505, 1251, 1124, 1051, 932 cm^{-1}; Anal. Calcd for $C_{35}H_{43}N_3O_{12}$: C, 60.25; H, 6.21; N, 6.02%. Found: C, 60.18; H, 6.17; N, 6.00%.

H_2L^5

^{1}H NMR ($CDCl_3$, 100 MHz) δ: 1.16–1.78 (m, 8H, CyH), 3.74 (m, 18H, CH_2—O, N═CH_2), 3.92 (m, 8H, CH_2—O), 4.16 (m, 8H, CH_2—O), 6.9–7.06 (m, 4H, ArH), 8.29 (s, 2H, CH═N), 12.91 (s, 2H, OH); IR (KBr, film) ν_{max}: 3230, 2924, 2861, 1623, 1600, 1504, 1259, 1131, 1048,

924 cm^{-1}; Anal. Calcd for $C_{36}H_{50}N_2O_{12}$: C, 61.52; H, 7.17; N, 3.99%. Found: C, 61.49; H, 7.14; N, 3.92%.

H_2L^6

^{1}H NMR ($CDCl_3$, 100 MHz) δ: 3.79 (s, 16H, CH_2—O), 3.92 (m, 8H, CH_2—O), 4.11 (m, 8H, CH_2—O), 6.69–7.41 (m, 8H, ArH), 8.33 (s, 2H, CH═N), 13.07 (s, 2H, OH); IR (KBr, film) ν_{max}: 3227, 2925, 2867, 1624, 1601, 1505, 1252, 1122, 1050, 934 cm^{-1}; Anal. Calcd for $C_{36}H_{44}N_2O_{12}$: C, 62.06; H, 6.37; N, 4.02%. Found: C, 61.59; H, 6.34; N, 4.00%.

General procedure for complexes MnClL^1–MnClL^6

A solution of ligand (1.0 mmol) and $MnCl_2{\cdot}4H_2O$ (1.1 mmol) in EtOH (15 ml) was stirred for 2 h under a N_2 atmosphere at 70°C, and the mixture was then cooled, filtered and washed with EtOH to give the complexes. The pure product was obtained after recrystallisation from EtOH.

MnClL^1

IR (KBr, film) ν_{max}: 2930, 2865,1607,1602,1498, 1262, 1120, 1055, 932; Anal. Calcd for $C_{32}H_{42}ClMnN_2O_{12}$: C, 52.14; H, 5.74; N, 3.80%; found: C, 52.03; H, 5.69; N, 3.76%. Λ_m ($S\,cm^2\,mol^{-1}$): 117.12, Molar magnetic susceptibility $\chi_M = 1.08 \times 10^{-1}\,J\,mol^{-1}\,T^{-2}$, magnetic moment $\mu_m = 4.80 \times 10^{-23}\,J\,T^{-1}$.

MnClL^2

IR (KBr, film) ν_{max}: 2923, 2864, 1611, 1609, 1506, 1261, 1132, 1054, 931; Anal. Calcd for $C_{33}H_{44}ClMnN_2O_{12}$: C, 52.77; H, 5.90; N, 3.73%; found: C, 52.64; H, 5.87; N, 3.69%. Λ_m ($S\,cm^2\,mol^{-1}$): 115.56, Molar magnetic susceptibility $\chi_M = 1.06 \times 10^{-1}\,J\,mol^{-1}\,T^{-2}$, magnetic moment $\mu_m = 4.86 \times 10^{-23}\,J\,T^{-1}$.

MnClL^3

IR (KBr, film) ν_{max}: 2929, 2863, 1604, 1600, 1500, 1261, 1128, 1049, 928; Anal. Calcd for $C_{37}H_{53}ClMnN_3O_{12}$: C, 54.05; H, 6.50; N, 5.11%; found: C, 54.00; H, 6.49; N, 5.08%. Λ_m ($S\,cm^2\,mol^{-1}$): 117.02, Molar magnetic susceptibility $\chi_M = 1.10 \times 10^{-1}\,J\,mol^{-1}\,T^{-2}$, magnetic moment $\mu_m = 4.73 \times 10^{-23}\,J\,T^{-1}$.

MnClL^4

IR (KBr, film) ν_{max}: 2920, 2867, 1608, 1604, 1506, 1253, 1126, 1051, 930; Anal. Calcd for $C_{35}H_{41}ClMnN_3O_{12}$: C, 53.48; H, 5.26; N, 5.35%; found: C, 53.41; H, 5.21; N, 5.32%. Λ_m ($S\,cm^2\,mol^{-1}$): 116.71, Molar magnetic susceptibility $\chi_M = 1.07 \times 10^{-1}\,J\,mol^{-1}\,T^{-2}$, magnetic moment $\mu_m = 4.81 \times 10^{-23}\,J\,T^{-1}$.

MnClL^5

IR (KBr, film) ν_{max}: 2926, 2860, 1611, 1601, 1505, 1261, 1131, 1050, 922; Anal. Calc. for $C_{36}H_{48}ClMnN_2O_{12}$: C, 54.65; H, 6.12; N, 3.54%; found: C, 54.59; H, 6.09; N, 3.51%. Λ_m ($S\,cm^2\,mol^{-1}$): 115.98, Molar magnetic susceptibility $\chi_M = 0.98 \times 10^{-1}\,J\,mol^{-1}\,T^{-2}$, magnetic moment $\mu_m = 4.70 \times 10^{-23}\,J\,T^{-1}$.

MnClL^6

IR (KBr, film) ν_{max}: 2927, 2865, 1613, 1602, 1507, 1250, 1122, 1052, 936 cm^{-1}; Anal. Calcd for $C_{36}H_{42}ClMnN_2O_{12}$: C, 55.07; H, 5.39; N, 3.57%. Found: C, 54.87; H, 5.34; N, 3.53%.

Catalyst characterisation

Catalysts MnClL^1–MnClL^6 have nearly similar IR spectra compared with the IR spectra of the free ligands except for the C═N stretching vibration which shifted slightly (11–14 cm^{-1}) to lower frequency and increased in intensity relative to the free ligand. Additionally, the characteristic vibration of OH at $\approx$3225 cm^{-1} disappeared but the C—O—C stretching vibration remained without change. These observations demonstrate that the manganese only interacts with OH and C═N (*43*).

The observed molar conductance of all complexes in the DMF solution ($1.0 \times 10^{-3}\,mol\,l^{-1}$) at 25°C also showed that they were electrolytes (*44*). The molar Magnetic Susceptibility χ_M and magnetic moment μ_m of all complexes indicated that manganese has four non-paired electrons. Combining this phenomenon with the results of the molar conductances and magnetic moments of the complexes indicates that manganese in the complexes is trivalent. The elemental analysis of the complexes indicated that H_2L^1–H_2L^6 formed 1:1 (ligand/metal) complexes.

Procedure of epoxidation

In a typical experiment of two-phase epoxidation, a required volume of aqueous solution of potassium peroxomonosulphate (1.5 M) was added to a stirred mixture of chloroform (5 ml), the required amount of Schiff base complex and the alkene at room temperature. The progress of reactions was monitored by TLC. At the end of the reaction, the chloroform layer was separated and the aqueous phase was extracted with chloroform

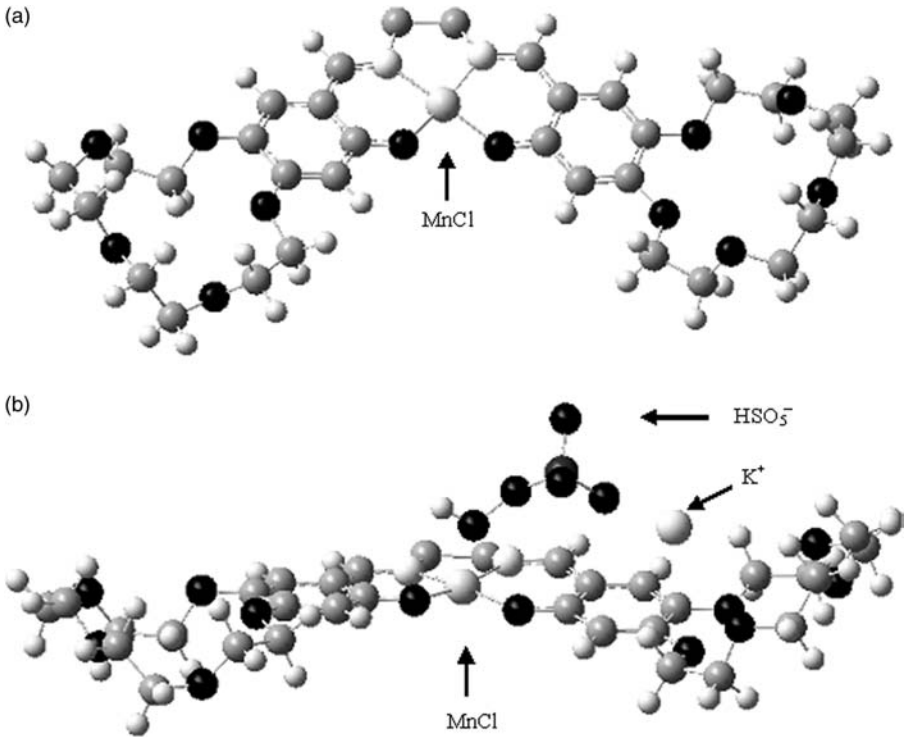


Figure 2. (a) Structure for $MnClL^1$ obtained by DFT calculation. (b) Proposed structure for co-complexation of $MnClL^1$ and $KHSO_5$. Some H and Cl atoms were omitted for clarity.

(3 × 10 ml). The combined chloroform extracts were dried ($MgSO_4$), and after the removal of the solvent *in vacuo*, the residue was purified by column chromatography (silica gel, *n*-hexane-Et_2O, 4:1).

Results and discussion

We initially synthesised $MnClL^1$–$MnClL^6$ because we anticipated that the presence of crown rings bonded to these complexes would not only increase the solubility of the oxidant ($KHSO_5$) in the organic phase, but also may facilitate bringing the $KHSO_5$ into the vicinity of the manganese, leading to faster oxidation of manganese (III) to oxo manganese (V) which is a better oxidant than $KHSO_5$ (Figure 2b). DFT studies for $MnClL^1$ gave the structure illustrated in Figure 2a. We envisioned that $MnClL^1$–$MnClL^6$ would bind $KHSO_5$ as sketched in Figure 2b (geometry not DFT optimised).

Accordingly, complexes $MnClL^1$–$MnClL^6$ as catalysts and Oxone as oxidant were employed for the oxidation of cyclohexene and cyclooctene in a biphasic medium including water and $CHCl_3$ at normal pressure and room temperature. In order to elucidate the importance of complex-crown incorporation in the efficiency of the oxidation system, an identical mixture of uncrowned complex $MnClL^7$ and crown 2 (4′-hydroxybenzo-15-crown-5) was also used for the oxidation of cyclohexene (Table 1).

The non-catalytic system (Table 1, run 1) afforded only a trace amount of epoxide, which must be due to the low solubility of $KHSO_5$ in the organic phase. On the other hand, catalytic systems containing $MnClL^1$–$MnClL^4$ or $MnClL^6$ decreased the reaction times significantly and enhanced chemical yields (Table 1, runs 2–5 and 7). Compared with $MnClL^1$–$MnClL^4$ or $MnClL^6$, the mixture of crown ether 2 and uncrowned complex $MnClL^7$ did not exhibit desirable efficiency (Table 1, run 8). This observation is consistent with our hypothesis that incorporation of crown ether and Schiff base complex is

Table 1. Oxidation of cyclohexene (1.0 mmol) by $KHSO_5$ (2.0 ml, 1.5 M, 3.0 mmol), in the presence of $MnClL^1$–$MnClL^6$ (6.0 μmol) or an identical mixture of $MnClL^7$ (6.0 μmol) and crown (**2**) (6.0 μmol) in $CHCl_3$ (5 ml) at room temperature and normal pressure.

Run	Catalyst	Yield (%)[a]	Time (h)
1	–	Trace	120
2	$MnClL^1$	68	27.0
3	$MnClL^2$	70	30.0
4	$MnClL^3$	80	3.5
5	$MnClL^4$	76	6.2
6	$MnClL^5$	24	47.0
7	$MnClL^6$	73	18
8	$MnClL^7$ + crown (**2**)	31	40.0

[a] Cyclohexene oxide yields are calculated on the initial amount of cyclohexene.

a crucial requirement for $MnClL^1$–$MnClL^4$ and $MnClL^6$ to exhibit high catalytic activities. As explained, crown ether situates the oxidant adjacent to the metal through trapping the potassium ion of the oxidant in its cavity and so facilitates the oxidation of Mn (III) to M=O (V) (Figure 2). The general catalytic efficiency order of the catalysts is: $MnClL^3 > MnClL^4 >> MnClL^6 > MnClL^1 > MnClL^2 >> MnClL^7$ and crown ether $2 > MnClL^5$. This trend might be due to the electron density of central metal ion being enhanced by the electron-donating effect of the ligands which facilitates the oxidation of Mn (III) to Mn=O (V). Accordingly, $MnClL^3$ and $MnClL^4$ including an additional electron donating N atom on their ligands showed the highest catalytic performance. Additionally, steric congestion around the coordinated metal in $MnClL^5$, originating from chair conformation of cyclohexyl ring, prevents either the substrate or the oxidant from approaching the central metal of $MnClL^5$. Therefore, the reaction catalysed by $MnClL^5$ exhibited the lowest chemical yield and the longest reaction time (Table 1, run 6). Furthermore, the N ∩ N bridge group in $MnClL^6$ is phenyl, which contributes to the formation of the π-extended coordination structures. This contribution might facilitate the oxidation and so afford better catalytic performance of $MnClL^6$ compared to $MnClL^1$ and $MnClL^2$ (Table 1, run 7).

Among typical catalyst components, ligands play a predominant role in the oxidation process. During electron exchange between metal and substrate, ligand aids metal to balance its electron density with releasing electrons, when required to facilitate oxidation of the metal, and with receiving electrons during the oxidation of the substrate. Accordingly, to obtain a highly active catalyst, existence of ligands with notable balance between their electron donating and withdrawing properties, evidenced by the calculation of energy gap between the highest occupied molecular orbital (HOMO) and the lowest unoccupied molecular orbital (LUMO) of them, is a predominant requirement. Accordingly, the energy gap between HOMO and LUMO of H_2L^1–H_2L^6 was studied using the DFT calculation (Table 2). As can be seen, H_2L^6 and H_2L^4 own the lowest energy gaps while $MnClL^3$ which was obtained from the complexation of H_2L^3 with manganese ion showed the highest activity. To find a reasonable relationship between the catalytic performances and ligand structures, the density of positive charge on the central metal of catalysts $MnClL^1$–$MnClL^6$ was measured using DFT studies (Table 2). This study revealed that $MnClL^3$ and $MnClL^4$ possessed the lowest positive charge on their central metal, which made them more susceptible to be oxidised compared to their analogues.

Table 2. Energy gap (eV) between HOMO and LUMO of H_2L^1–H_2L^6; positive charge on the central metals of catalysts obtained by DFT studies.

Catalyst	Positive charge	Ligand	Energy gap (eV)
$MnClL^1$	1.2351	H_2L^1	3.9
$MnClL^2$	1.2364	H_2L^2	4.0
$MnClL^3$	1.0631	H_2L^3	4.0
$MnClL^4$	1.1002	H_2L^4	3.1
$MnClL^5$	1.2237	H_2L^5	4.3
$MnClL^6$	1.1124	H_2L^6	2.9

It is worthy of mention that a colour change from brown to orange occurred upon adding oxidant to the reaction mixture when there was not any alkene, which might be due to a variation of the oxidation level of manganese.

It is known that the addition of an axial base such as pyridine is necessary to promote the catalytic activity of manganese complexes since it increases electron donation of the ligands in the complex and subsequently improves the susceptibility of manganese (III) to be oxidised to manganese (V) (*39*). Accordingly, the experiments reported in Table 1 were repeated in the presence of pyridine as an axial base (Table 3). The addition of pyridine improved the chemical yields of all the reactions to some extent. Furthermore, the reaction times of $MnClL^3$ and $MnClL^4$ showed less sensitivity to the addition of pyridine and $MnClL^5$, which remained nearly constant, whereas those of $MnClL^1$, $MnClL^2$ and $MnClL^6$ were dramatically reduced (Table 3, runs 1–6). It is concluded that the additional N atom on the bridge groups of $MnClL^3$ and $MnClL^4$ itself might play the role of axial base, therefore, the presence of pyridine as an external axial base only slightly improves corresponding reaction times in these cases. We decided to examine the effect of pyridine

Table 3. Effect of axial base (6 mmol) on the oxidation of cyclohexene by $KHSO_5$ in the presence of $MnClL^1$–$MnClL^6$.

Run	Catalyst	Axial base	Yield (%)[a]	Time (h)
1	$MnClL^1$	Pyridine	79	3.0
2	$MnClL^2$	Pyridine	78	4.1
3	$MnClL^3$	Pyridine	89	0.9
4	$MnClL^4$	Pyridine	84	1.4
5	$MnClL^5$	Pyridine	28	42
6	$MnClL^6$	Pyridine	77	2.5
7	$MnClL^1$	pyridine-*N*-oxide	76	8
8	$MnClL^2$	pyridine-*N*-oxide	72	11
9	$MnClL^3$	pyridine-*N*-oxide	83	2
10	$MnClL^4$	pyridine-*N*-oxide	80	4
11	$MnClL^5$	pyridine-*N*-oxide	29	61
12	$MnClL^6$	pyridine-*N*-oxide	75	13
13	$MnClL^1$	*N*-methylimidazole	72	10
14	$MnClL^2$	*N*-methylimidazole	69	11.5
15	$MnClL^3$	*N*-methylimidazole	84	3.4
16	$MnClL^4$	*N*-methylimidazole	76	5
17	$MnClL^5$	*N*-methylimidazole	19	59
18	$MnClL^6$	*N*-methylimidazole	71	10

Other conditions are the same as given in Table 1.
[a]Cyclohexene oxide yields are calculated on the initial amount of cyclohexene.

N-oxide as an axial base on the epoxidation of cyclohexene. The reason of this attempt was originated by the possibility that pyridine-*N*-oxide resistance to oxidation could improve its ability for activating the manganese complex. Unfortunately, the basicity of this oxygenated ligand revealed not to be efficient enough to improve catalytic activities compared to those obtained by pyridine (Table 3, run 7–12). Similar unsatisfactory results were obtained with *N*-methylimidazole (Table 3, run 13–18).

Next, the effect of reagent ratio on the reactions performed over $MnClL^1$ was investigated (Table 4). When using an excess oxidant with respect to pyridine, yields were enhanced at the expense of longer reaction time (Table 4, compare runs 1–3). It is believed that the presence of excess amounts of oxidant leads to the loss of catalytic activity as a consequence of free pyridine exhaustion (*39*). Accordingly, excess amounts of pyridine and oxidant with respect to catalyst and cyclohexene were used in order to shorten reaction times and improve chemical yields of these reactions (Table 4, runs 4–7). As can be seen (Table 4, run 6), with a sixfold excess of pyridine and a threefold excess of oxidant with respect to catalyst and cyclohexene, the best result in terms of chemical yield and reaction time was obtained. Chemical yield and reaction time remained nearly constant after further increase in the pyridine excess (Table 4, run 7). With increasing amount of catalyst, chemical yield was adversely affected (Table 4, run 8). It is probable that $MnClL^1$ could act as a Lewis acid, which facilitates ring opening of epoxide. Additionally, an excess amount of cyclohexene decreased the reaction time somewhat, but at the expense of lower chemical yield which may be due to the increase of side reactions (Table 4, run 9). Similar results were obtained when the effect of reagent ratio on the catalytic performance of $MnClL^1$ was investigated (Table 4, runs 10–18).

Table 4. Effect of molar ratio of reagents on chemical yields and times of reactions catalysed by $MnClL^1$ and $MnClL^2$ in 5 ml chloroform.

Run	Molar ratio of reagents $KHSO_5$[a]:Cat:Py:Cy	Yield (%)[b]	Time (h)
1[c]	1:0.006:1:1	68	24
2[c]	3:0.006:1:1	74	25
3[c]	6:0.006:1:1	75	25
4[c]	3:0.006:2:1	66	11
5[c]	3:0.006:4:1	72	8
6[c]	3:0.006:6:1	79	3
7[c]	3:0.006:8:1	78	3.2
8[c]	3:0.012:6:1	48	2.6
9[c]	3:0.002:6:2	41	2.5
10[d]	1:0.006:1:1	62	27
11[d]	3:0.006:1:1	70	23
12[d]	6:0.006:1:1	69	24
13[d]	3:0.006:2:1	62	14
14[d]	3:0.006:4:1	72	9
15[d]	3:0.006:6:1	78	4.1
16[d]	3:0.006:8:1	79	4.5
17[d]	3:0.012:6:1	37	3.4
18[d]	3:0.002:6:2	34	2.5

[a] A 1.5 M solution in water.
[b] Cyclohexene oxide yields were calculated on the initial amount of cyclohexene.
[c] $MnClL^1$ was used as a catalyst.
[d] $MnClL^2$ was used as a catalyst.

In order to investigate the influence of temperature on the chemical yield of reactions that were performed over $MnClL^1$–$MnClL^4$ and $MnClL^6$, these catalysts were used between temperatures of 15–60°C for the oxidation of cyclohexene (Figure 3). As can be seen, the highest chemical yield of reactions performed over $MnClL^3$ and $MnClL^4$ were obtained at 35°C while the maximum yields of reactions performed over $MnClL^1$, $MnClL^2$ and $MnClL^6$ were obtained at 25°C. At temperatures between 35 and 60°C, chemical yields obtained for $MnClL^3$ and $MnClL^4$ as catalysts remained nearly constant; however, chemical yields obtained by $MnClL^1$, $MnClL^2$ and $MnClL^6$ were adversely affected between 25 and 60°C. The higher thermal stability of $MnClL^3$ and $MnClL^4$ might be due to the presence of more atoms contributing in the coordination sphere of the metal.

It is interesting that the addition of $NaNO_3$ to the catalytic system dramatically reduced the reaction times and slightly improved the chemical yields while the addition of $Ba(NO_3)_2$ and $LiNO_3$ was almost ineffective (Table 5). It is conceivable that there is a good match between the cavity size of 15-crown-5 ($d = 0.18$–0.22 nm) (*45*) and the dimension of the alkali metal Na^+ ($d = 0.19$ nm), resulting in a better extraction of HSO_5^- to the aqueous medium. On the other hand, the dimension of Li^+ ($d = 0.136$ nm) is too small and those of Ba^{+2} and K^+ ($d = 0.266$ nm) are too large to fit with the cavity size of the crown.

To elucidate the merit of our epoxidation system, it was compared with other systems (*38, 39*) in Table 6. Our

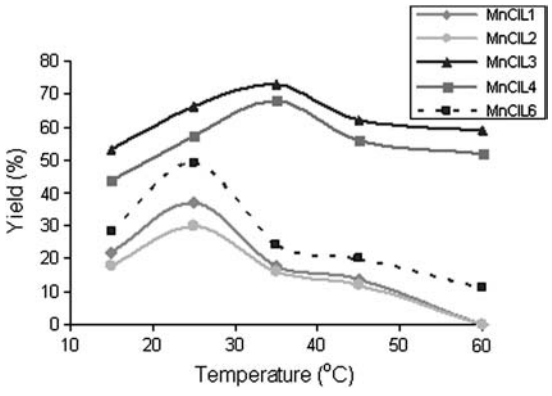


Figure 3. Effect of temperature on the yield of oxidation of cyclohexene by $KHSO_5$ in the presence of $MnClL^1$–$MnClL^4$ and $MnClL^6$. Reaction time is 30 min; other conditions are the same as given in Table 3.

Table 5. Effect of alkali metal salts (3.0 mmol) on the oxidation of cyclohexene (1 mmol) by $KHSO_5$ in the presence of $MnClL^1$–$MnClL^4$ and $MnClL^6$.

	Yield (%)[a]				Time (h)			
Catalyst	–	$Ba(NO_3)_2$	$NaNO_3$	$LiNO_3$	–	$Ba(NO_3)_2$	$NaNO_3$	$LiNO_3$
$MnClL^1$	79	79	88	80	3.0	3.1	1.7	2.8
$MnClL^2$	78	79	90	77	4.1	4.2	2.0	4.0
$MnClL^3$	89	87	95	90	0.9	0.8	0.3	0.8
$MnClL^4$	84	85	94	80	1.4	1.3	0.5	1.4
$MnClL^6$	78	80	90	77	2.5	2.6	1.2	2.4

Other conditions are the same as given in Table 3.
[a] Cyclohexene oxide yields were calculated on the initial amount of cyclohexene.

Table 6. Comparisons of epoxidations.

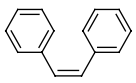
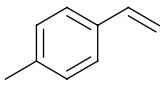
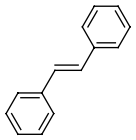
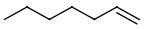
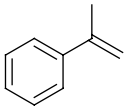
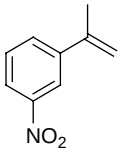
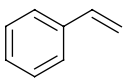
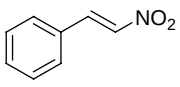
Alkene (mmol)	$KHSO_5$ (mmol)	Yield (%)[a]	Time (h)	Reference
Cyclohexene (0.35 mmol)	0.44	95	5	(*38*)[b]
Cyclohexene (1.6 mmol)	3.20	51	0.75	(*39*)[c]
Cyclohexene (1 mmol)	3.0	95	0.3	This work[d]
Cyclohexene (1 mmol)	3.0	94	0.5	This work[e]
Cyclooctene (0.35 mmol)	0.60	97	5	(*38*)[b]
Cyclooctene (1.6 mmol)	3.20	60	16	(*39*)[c]
Cyclooctene (1 mmol)	3.0	96	0.2	This work[d]
Cyclooctene (1 mmol)	3.0	95	0.4	This work[e]

[a] Cyclohexene oxide and cyclooctene oxide yields were calculated on the initial amount of alkene.
[b] Reactions were performed using manganese hemiporphyrazine complex (8.0 mmol), in the presence of 2,4,6-trimethylpyridine (8.0 mmol), in 5 ml dichloroethane, at 25°C.
[c] Reactions were performed at 23°C in an aqueous media and without catalyst.
[d] $MnClL^3$ was used as a catalyst.
[e] $MnClL^4$ was used as a catalyst; conditions were the same as given in Table 5.

catalytic system exhibited either higher chemical yield or shorter reaction time and, in some cases, exhibited both of them when compared with literature precedents.

Eventually, the reaction was extended to the different alkenes using $MnClL^3$ as a catalyst and Oxone as an oxidant (Table 7). As can be seen, conjugated π-electron-withdrawing groups with double bond of alkenes decrease the reactivity for epoxidation (Table 7, run 8); additionally, more reactivity of *cis*-alkenes in comparison with *trans*-ones may be due to the *cis*-orientation of the substituents,

Table 7. Epoxidation of different alkenes[a].

Run	Substrate	Yield[b] (%)	Time (h)	Run	Substrate	Yield[b] (%)	Time (h)
1		74	3.5	**5**		96	0.6
2		52	4.0	**6**		69	2.0
3		94	1.6	**7**		21	15
4		92	1.0	**8**		0	16

[a] $MnClL^3$ was used as a catalyst; conditions were the same as given in Table 5.
[b] Epoxide yields were calculated on the initial amount of cyclohexene.

which facilitates the approach of the alkene to the active oxidant (Table 7, runs 1 and 2).

Conclusion

We elaborated the effect of a crown ether ring bonded to Schiff base catalysts on the efficiency of these catalysts for the epoxidation of cyclohexene and cyclooctene by $KHSO_5$. The catalytic activity of such catalysts emerges completely when an aromatic nitrogen base such as pyridine as axial ligand and potassium nitrate were added to the reaction mixture. Additionally, our system, in some cases, showed better effectiveness for epoxidation compared to other methods (*38, 39*) as indicated in Table 6.

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