Chapter IV

Manganese (III) Cyclam Catalyzed Epoxidation of Alkenes under Ambient Condition

Abstract:

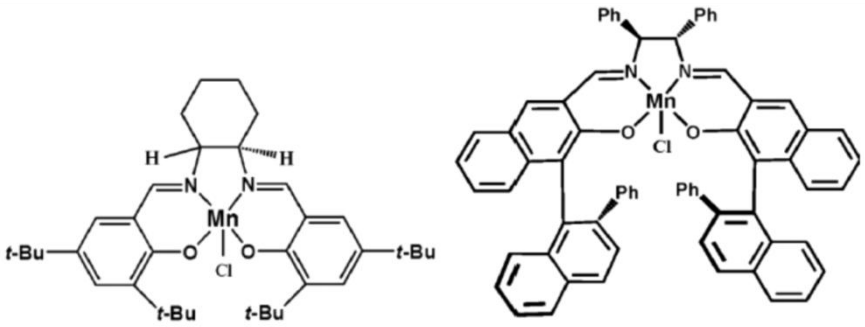
Complex *trans*-[$Mn^{III}L(OTf)_2$](OTf) has been synthesized from *trans*-[$Mn^{III}LCl_2$]Cl ,where L is 1, 4, 8, 11-tetraazacyclotetradecane or cyclam. This complex has been characterised by ESI Mass spectroscopy and elemental analysis. The EPR study of *trans*-[$Mn^{III}L(OTf)_2$](OTf) shows that the complex is EPR silent, which establishes the presence of manganese (III) centre. Further characterization has been done with the help of X-ray crystallography. This complex has been employed to catalyze the epoxidation of various alkenes under ambient condition. The iodobenzene diacetate, $PhI(OAc)_2$ was used as a terminal oxidant.

IV.1 Introduction

Olefin epoxidation is an important chemical transformation as the epoxides are important intermediates for a number of organic transformations [1-3]. Selective epoxidation of alkenes under mild condition still demands considerable attention in chemical science.

Manganese with wide range of accessible oxidation states plays versatile role in various important biological redox reactions such as Mn-dependent dioxygenases [4], oxalate oxydase [5], manganese superoxide dismutase [6], manganese catalase [7] and oxygen evolving centre in photosystem II [8]. Therefore, the investigation on the catalytic behaviour of manganese complexes in redox reactions constitutes an important area of chemistry.

The manganese (III) complexes of salen (N2O2 donor ligands) have been extensively studied for asymmetric epoxidation of alkene. The chiral manganese salen complexes, which were first reported by Jacobsen [9] and Katsuki [10], are well known for their reactivity in asymmetric epoxidation of *cis*-olefins using with various oxidants like iodosylarenes (ArIO), NaOCL, H_2O_2, $NaIO_4$, peracetic acid and even molecular oxygen in combination with aldehyde. However, in contrast to the immense success of manganese (III) salen complexes as catalysts, the manganese (III) complexes of macrocyclic non-heme N-donor ligands as efficient epoxidation catalyst are less known.



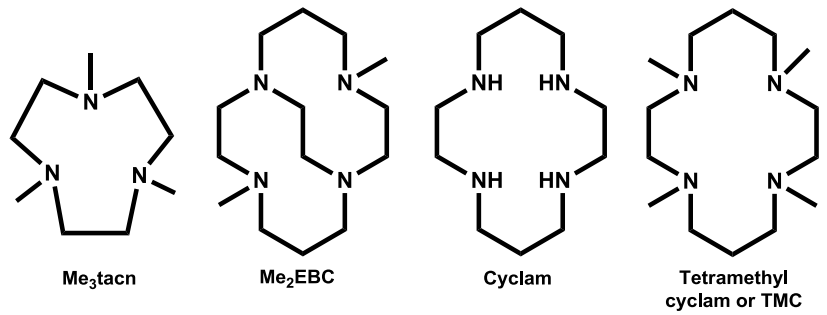
(a) (b)

Scheme IV.1. Structure of Jacobsen catalyst (a) and Katsuki's catalyst (b).

The manganese complexes of tridentate ligand 1, 4, 7-triazacyclotridecane (tacn) and 1, 4, 7-triazacyclotridecane (Me_3tacn) have been reported as effective epoxidation catalysts by De Vos *et al*. [11] (Scheme IV.2). Binuclear manganese (IV) complex $[(Me_3tacn)Mn^{IV}(O)(Me_3tacn)](PF_6)_2$, was reported by Wieghardt *et al*. as a

highly selective catalyst for the epoxidation of alkene in combination with H_2O_2 [12]. Apart from the tridentate macrocyclic ligand tacn, a cross bridged macrobicyclic tetradentate N4 ligand, Me_2EBC (4, 11-dimethyl-1, 4, 8, 11-tetraazabicyclo[6.6.2]hexadecane) (Scheme IV.2) has been explored as a suitable ligand framework for various manganese complexes by Busch and co-workers. In the year 2000, Hubin *et al*. reported the first dichloro manganese (II) complex of Me_2EBC [$(Me_2EBC)MnCl_2$], which catalyzes the epoxidation of alkene using H_2O_2 in aqueous solution [13]. Later, Yin *et al*. reported olefin epoxidaion catalyzed by hydroperoxide adduct of [$(Me_2EBC)MnCl2$] generated from the reaction of [$(Me_2EBC)MnCl_2$] and 50% H_2O_2 [14]. The [$(Me_2EBC)MnCl_2$] complexes has also been reported by Busch *et al*. to catalyze the epoxidation reaction by employing ^{t}BuOOH as terminal oxidant [13(a), 14 (a-c)]. Therein they have reported the mechanistic pathway for the generation of high valent manganese species using spectroscopic methods [13(a), 14 (a-c)]. In most of the cases terminal oxidants such as iodosyl arenes [20], *m*-chloroperbenzoic acid (*m*-CPBA) [21(a) and (b)], organic peroxides [22], peracetic acid (AcOOH) [22 (a), 23], hydrogen peroxide [2 (a), 24] have been used for the epoxidation of alkenes. $PhI(OAC)_2$ is the synthetic precursor of PhIO and is a cheap and commercially available oxidant. This oxidising agent has been used earlier for epoxidation of alkenes catalyzed by several manganeseporphyrin systems [25] in ionic liquid media and in case of iron porphyrin catalysts [26].

The manganese complexes of 1,4,8,11-tetramethyl-1,4,8,11-tetraazacyclotetradecane (TMC) (Scheme IV.2) fail to exhibit any catalytic properties towards epoxidation reactions [15]. However, cyclam (1,4,8,11-tetraazacyclotetradecane) (scheme IV.2) offers a promising ligand frame due to its flexibility, particularly in absence of any N-alkyl group or ethyl bridge.



Scheme IV.2. Structures of Me_3tacn, Me_2EBC and cyclam (L) and TMC.

The first Mn(III) complex of cyclam ($[Mn^{III}LCl_2]Cl$) was reported by Poon [16] and Bryan [17]. Due to the flexibility of the ligand framework, Mn(III) complex of this ligand is capable of adopting both *cis* and *trans* geometries. The *trans* isomer is thermodynamically more stable [18]. Although the iron complex of L, $[Fe^{II}L(OTf)_2]$ is known to catalyze the selective epoxidation of styrene with H_2O_2, no report related to the catalytic behaviour of manganese (II/III) cyclam complexes is available in the literature [19].

Here, we wish to report the synthesis of *trans*-$[Mn^{III}L(OTf)_2](OTf)$ complex. This complex has been characterised on the basis of spectroscopic and elemental analysis data. The complex in acetonitrile medium is EPR inactive, which confirms the presence of a manganese (III) ion. Further the complex has been characterized by Single Crystal X-ray diffraction. This complex has been employed to catalyze the epoxidation of various alkenes with iodobenzene diacetate, $PhI(OAc)_2$ as a terminal oxidant in acetonitrile at ambient condition.

IV.2. Results and discussion

IV.2.1. Synthesis of the catalyst, $[Mn^{III}L(OTf)_2](OTf)$

Complex *trans*-$[Mn^{III}L(OTf)_2](OTf)$ has been synthesized using the following method. Complex *trans*-$[Mn^{III}LCl_2]Cl$ is treated with excess amount of trifluoromethane sulphonic acid (Triflic acid or HOTf) and stirred for 12 h at room temperature (298 K) under nitrogen atmosphere. The resulting the purple coloured reaction mixture is poured into dry diethyl ether and the product is obtained as a purple solid. The complex has been characterized by a sharp signal appearing at m/z 403.0851, corresponding to molecular ion fragment $\{[Mn^{III}L(OTf)_3]^+ - H^+\}$ in the HR MS spectrum (Fig.IV.4 in experimental section).

The complex has been further characterized by Single Crystal X-ray diffraction study. The X-ray structure solution of the complex reconfirmed its formulation as well as its geometry. The central Mn(III) is found to be coordinated to the neutral ligand, cyclam (1,4,8,11-tetraazacyclotetradecane) and two acetonitrile molecule (Fig.IV.1). The complex as a whole is tricationic and the crystallographic asymmetric unit contains three triflate (OTf^-) as counter anions.

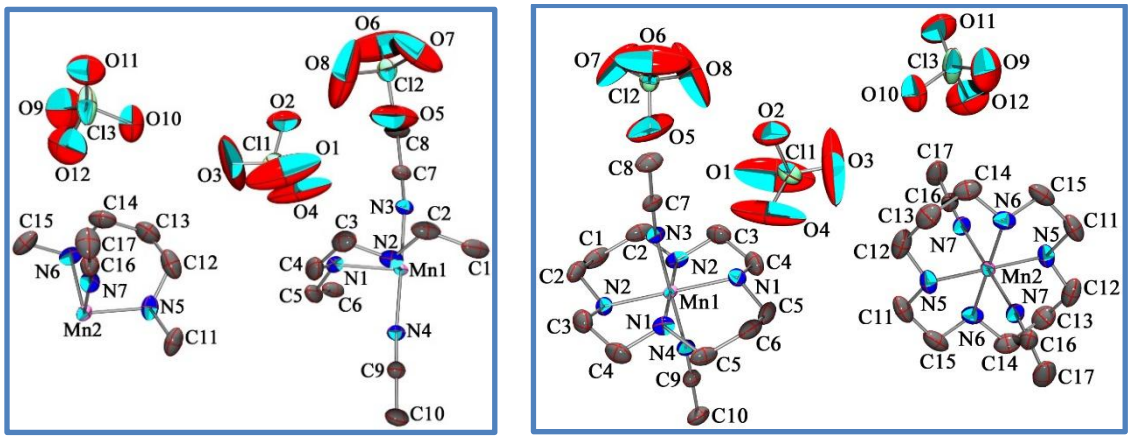


Fig.IV.1. The crystallographic asymmetric unit of the complex *trans*-$Mn^{III}L(OTf)](OTf)_2$ (Left) and the ORTEP view of the complete unit (right). All hydrogen atoms are omitted and only non-hydrogen atoms are labelled for clarity.

Table IV.1. Crystal data and structure refinement for the complex *trans*-$[Mn^{III}L(OTf)](OTf)_2$

Identification code	Mncyclam
Empirical formula	$C_{14}H_{30}Cl_3MnN_6O_{12}$
Formula weight	635.73
Temperature/K	230(2)
Crystal system	Orthorhombic
Space group	Pnma
a/Å	16.943(5)
b/Å	30.991(9)
c/Å	9.873(3)
α/°	90.00
β/°	90.00
γ/°	90.00
Volume/$Å^3$	5184(3)
Z	8
$\rho_{calc}g/cm^3$	1.629
μ/mm^{-1}	0.886
F(000)	2624.0
Crystal size/mm^3	0.50 × 0.13 × 0.08
Radiation	MoKα (λ = 0.71073)
2Θ range for data collection/°	4.32 to 50
Index ranges	-19 ≤ h ≤ 20, -36 ≤ k ≤ 36, -11 ≤ l ≤ 11
Reflections collected	33842
Independent reflections	4402 [R_{int} = 0.0494, R_{sigma} = N/A]
Data/restraints/parameters	4402/0/343
Goodness-of-fit on F^2	1.054
Final R indexes [I>=2σ (I)]	R_1 = 0.0778, wR_2 = 0.2120
Final R indexes [all data]	R_1 = 0.0902, wR_2 = 0.2256
Largest diff. peak/hole / e $Å^{-3}$	1.60/-0.67

Table IV.2. Selected bond lengths (Å) and angles (°) for complexes $Mn^{III}L(OTf)](OTf)_2$

Selected bonds	(Å)	Selected bond angles	(°)
Mn(1)-N(1)	2.000(4)	N(3)-Mn(1)-N(4)	178.6(2)
Mn(1)-N(2)	1.997(4)	N(3)-Mn(1)-N(2)	91.76(15)
Mn(1)-N(3)	1.928(5)	N(4)-Mn(1)-N(2)	89.23(16)
Mn(1)-N(4)	1.928(5)	N(3)-Mn(1)-N(1)	88.24(15)

IV.2.2 Catalyzis

The catalytic behaviour of *trans*-$[Mn^{III}L(OTf)](OTf)_2$ has been studied for the oxidation of alkenes to corresponding epoxides and diols using a series of terminal oxidants such as H_2O_2, ^{t}BuOOH, *m*-CPBA, oxone and $PhI(OAc)_2$. Initially, the relative oxidising abilities of these terminal oxidants have been examined with only cyclooctene as standard substrate in presence of *trans*-$[Mn^{III}L(OTf)](OTf)_2$ as catalyst in acetonitrile (MeCN) medium at 298 K (Table IV.1). The experiments have been carried out with the ratio of oxidant (100 equivalent), catalyst (1 mM) and substrate (500 mM). The concentration of substrate was 1000 mM in the case of H_2O_2 as oxidant. No appreciable amount of oxidised products is observed when ^{t}BuOOH, *m*-CPBA, oxone have been used as terminal oxidants. In general, no trace of *cis* diols has been detected on gas chromatogram.

Table IV.3. Catalytic epoxidation of cyclooctene in presence of *trans*-$[Mn^{III}L(OTf)](OTf)_2$ as a catalyst with various oxidants.

Substrate	**Oxidant**	**Yield of product (%)**	
		1,2-epoxyoctane	**1,2-octane diol**
Cyclooctene	H_2O_2 [a]	19	-
	PhIO [b]	28	-
	$PhI(OAc)_2$ [b]	60	-

Reaction condition:
[a]For the reaction with H_2O_2: *trans*-$[Mn^{III}L(OTf)](OTf)_2$: H_2O_2: Cyclooctene; 1 mM: 100 mM: 1000 mM in acetonitrile at 298 K; [b] For PhIO and $PhI(OAc)_2$: *trans*-$[Mn^{III}L(OTf)](OTf)_2$: PhIO/$PhI(OAc)_2$: Cyclooctene; 1 mM: 100 mM: 500 mM in acetonitrile at 298 K.

With H_2O_2 as oxidant, the yield of 1,2-epoxycyclooctane is 19% (Table IV.1). The yield of epoxide is 28% in presence of PhIO as terminal oxidant. However, a much

higher yield of 1,2-epoxycyclooctane (60%) is obtained when $PhI(OAc)_2$ is used as the oxidant. The greater reactivity of $PhI(OAc)_2$ than PhIO in alkene epoxidation may be attributed to the greater Lewis basicity of $PhI(OAc)_2$, which makes it easy to bind with the electron deficient *trans*-$[Mn^{III}L(OTf)_2](OTf)$ [7].

IV.2.2.1. Optimization of reaction condition

To optimize the reaction conditions, various reaction parameters have been examined. The results under different conditions are compiled in Table IV.2.

Table IV.4. Catalytic epoxidation of cyclooctene under different conditions using $PhI(OAc)_2$ as oxidant at 298 K.

Entry	Substrate	[Cat]:[Sub]:[Ox]	Solvent	Product	Yield[a](%)
1.		0.1:500:100	MeCN		5 (0.5)
2.		**1:100:150**	**MeCN**		**58 (58)**
3.		1:100:150	DCM-MeCN (1:1, v/v)		42 (42)
4.	**Cyclooctene**	1:100:150	DCM	**1, 2-epoxyoctane**	40 (40)
5.		1: 50:100	MeCN		44 (44)
6.		1:100:100	MeCN		60 (30)
7.		1.5:50:100	MeCN		63 (21)
8.		2:50:100	MeCN		74 (19)
9.		2.5:50:100	MeCN		84 (17)

[a]Yields are calculated with respect to substrate. The values of Turn Over Number (TON) given in the parenthesis (TON= moles of product formed after complete reaction/ moles of catalyst).

The amount of 1,2-epoxycyclooctane is very low (5%) even in presence of large excess of substrate, when the amount of catalyst (0.2 μmol) is low (entry 1). By increasing the catalyst loading up to 10 times (2 μmol), the yield of epoxide increases up to 58% (Entry 2). Further increase in catalyst loading up to 5 μmol, the yield of 1,2-epoxycyclooctane gradually increases and reaches the highest yield of 84% (Entry 6-9).

Although, high yield (84%) of the product is achieved, a considerable decrease in turnover number (TON 17) is observed. The entry 6 shows that lower substrate concentration (200 μmol) lowers the product yield to 60%, although the turnover number (TON) remains at 30, which is much higher than that observed in Entry 9. Therefore, entry 2 appears to be the best combination with turnover number of 58.
The effect of solvent in the epoxidation reaction has been examined. When a mixture of acetonitrile-dichloromethane (1:1) has been chosen as the reaction medium, 44% yield of epoxycyclooctane is obtained (entry 3). On the other hand, only 40% yield of epoxide is observed in dichloromethane (entry 4). Therefore, acetonitrile appears to be the most suitable reaction medium for *trans*-$[Mn^{III}L(OTf)](OTf)_2$ catalyzed epoxidation of alkenes (entry 2).
The catalytic reactions have been performed in presence of small amount of water as an additive but no change in the yield of epoxides is observed. It may be noted that the yield of product increases with addition of small amount of water in Fe(II)porphyrinato complex (TPFPP)Cl catalyzed epoxidation using $PhI(OAc)_2$. The present catalytic system shows that water has no role in the formation of the epoxides.

IV.2.2.2. Reactivity of *trans*-$[Mn^{III}L(OTf)_2](OTf)$ with alkenes

The optimization of reaction parameters of *trans*- $[Mn^{III}L(OTf)](OTf)_2$ catalyzed epoxidation of cyclooctene is extended to the investigation for epoxidation of various alkenes. The percentage yields of the products are summarized in table IV.3.

Table IV.5. Products obtained from the reactions of $PhI(OAc)_2$ with different alkenes in presence of *trans*-$[Mn^{III}L(OTf)_2](OTf)$ as catalyst.

Entry	Substrate	Product	Yield of product (%)
1.	1-Octene	1, 2-Epoxyoctane	13
2.	Cyclooctene	Cyclootene oxide	60
3.	Styrene	Styrene oxide	62
		Phenyl acetaldehyde	27
		Benzaldehyde	2
4.	*cis*-stilbene	*cis*-Stilbenee oxide	30
		trans-Stilbene oxide	37
5.	*trans*-Stilbene[a]	*trans*-Stilbene oxide	60
6.	Norbornene	Norbornene epoxide	22.3
7.	1, 2-Dihydronaphthalene	1, 2-Dihydronaphthalene oxide	37

[a]Reaction of *trans*-Stilbene has been carried out in acetone due to low solubility in acetonitrile.

The epoxidation of 1-octene under given condition produces only 13% of 1,2-epoxyoctane (entry 1). On the other hand, 60% of 1,2-epoxycyclooctane is obtained from cyclooctene under the same reaction condition (entry 2). These observations indicate the higher reactivity of the catalyst for electron rich alkenes. The epoxidation of styrene produces 62% of styrene oxide, 27% of phenyl acetaldehyde and 2% of benzaldehyde (entry 3). This shows the higher selectivity of the catalyst towards epoxidation products. The epoxidation of *cis*-stilbene affords both the *cis* and *trans*-isomers of stilbene oxide (30% and 37% respectively) (entry 4). However, in the epoxidation of *trans*-stilbene, only *trans*-stilbene oxide (60%) is obtained as the sole product with no trace of *cis*-stilbene oxide (entry 5). The higher yield of *trans*-stilbene oxide in cases of both *cis* and *trans*-stilbene indicates that the catalyst under investigation is stereo selective towards the *trans* isomer. Nam and his co-workers have established that manganese (II) cyclam complex, *trans*-$Mn^{II}L(OTf)_2$,], is catalytically inactive for epoxidation of alkenes[23]. Therefore, it can be inferred that the promotion of the oxidation state of manganese centre from +2 to +3 is

responsible for the catalytic reactivity of manganese complexes of cyclam. Furthermore, attempt to employ *trans*-$[Mn^{III}L(Cl)_2]Cl$ as epoxidation catalyst fails to produce any tangible result, which arises due to the less lability of Mn-Cl bond.

Table IV.6. Epoxidation of electron rich alkenes catalyzed by $[Mn^{III}L(OTf)_2](OTf)$ and other catalysts.

Substrate	Products	Yield (%)		
		$Fe^{II}L(OTf)_2$[a]	**$[Mn^{III}L(OTf)_2](OTf)$**	**$Mn^{II}(Me_2EBC)Cl_2$**
Styrene	Styrene oxide	NR[c]	62	45 5[b]
cis-Stilbene	*cis*-Stilbene oxide	26	30	18 1[b]
	trans-Stilbene oxide	1.7	37	2 14[b]
trans-Stilbene	*trans*-Stilbene oxide	36	60	NR
	cis-Stilbene oxide	-	-	

[a]Reaction conditions: *trans*-$Fe^{II}L(OTf)_2$: 0.02 mmol, substrate 1 mmol, oxidant 1 mmol (in 4 mL MeCN at 4 °C for 2 h) [23]; [b]Reaction conditions: solvent, acetone/water (4:1), catalyst 1 mM, olefin 0.1 M, 0.53 M ^{t}BuOOH, room temp, 14 h [14 (c)]; [c]NR: not reacted.

Busch and his group have reported $Mn^{II}(Me_2EBC)Cl_2$ complexes (Me_2EBC = 4,11-Dimethyl-1,4,8,11-tetraazabicyclo[6.6.2]hexadecane) as efficient catalyst for the epoxidation of olefins with 50% H_2O_2 or ^{t}BuOOH in 1:4 water-acetone [14] (Table IV.4). Therefore, *trans*-$[Mn^{III}L(OTf)_2](OTf)$ shows better catalytic activity towards the epoxidation of electron rich alkenes compared to $Mn^{II}(Me_2EBC)Cl_2$ complexes. Therefore, complex *trans*-$[Mn^{III}L(OTf)_2](OTf)$ appears as an efficient and selective catalyst for epoxidation reaction of olefins using $PhI(OAc)_2$.

IV.3. Conclusions

1. Mononuclear Mn (III) complex of non heme macrocyclic N4 ligand, cyclam (1, 4, 8, 11-tetraazacyclotetradecane) efficiently catalyzes selective epoxidation of alkenes under ambient condition.

2. To the best of our knowledge, this is the first report of manganese (III) complex of cyclam which has been used as an efficient epoxidation catalyst.

3. The catalyst, *trans*-$[Mn^{III}L(OTf)_2](OTf)$ shows higher reactivity in comparison to other manganese complexes of similar macrocyclic N-donor ligands used for epoxidation of alkenes.

IV. 4. Experimentals

IV. 4 .1. Materials and methods

All the solvents used were of spectroscopic grade and stored over activated molecular sieve (4Å). Cyclam (1,4,8,11-tetraazacyclotetradecane), olefinic substrates, and the oxidant $PhI(OAc)_2$ were procured from Sigma Aldrich and used without further purification unless and otherwise stated. Iodosyl benzene was prepared from $PhI(OAc)_2$ following the reported method [27]. Trifluoromethane sulphonic acid (triflic acid or HOTf) was obtained from Sigma Aldrich. The products were detected by Perkin Elmer Clarus-500 GC with FID (Elite-I, Polysiloxane, 15-meter column) using naphthalene as internal standard.

IV.4.2. Synthesis of the complex $[Mn^{III}(OTf)_2](OTf)$

IV.4.2.1. Synthesis of *trans*-dichloro(1,4,8,11-tetraazacyclotetradecane) manganese(III) chloride (*trans*-$[Mn^{III}LCl_2]Cl$)

To a solution of $MnCl_2.\ 2H_2O$ (0.81 g, 5 mmol) in methanol (100 mL), a solution of cyclam (1 g, 5 mmol) in methanol (5 mL) was added drop wise. The reaction mixture was then stirred for 2 h at 25 °C. The resulting solution containing green precipitate was filtered and washed with cold methanol. To the filtrate, which assumed to contain both *cis* and *trans*-isomers, concentrated hydrochloric acid (1 mL) was added. The acidic solution was then stirred for 2 h. The mixture was left undisturbed for 6 h, after which green crystals of *trans*-$[Mn^{III}LCl_2]Cl$ started to separate out. The green product was collected, dried and weighed (1.5 g, 4.9 mmol, 98%).

IV.4.2. Synthesis of *trans*-$[Mn^{III}L(OTf)_2](OTf)$

Triflic acid (1.35 g, 60 mmol) was added to solid *trans*-$[Mn^{III}LCl_2]Cl$ (0.306 g, 1 mmol) under N_2 atmosphere at 298 K. The mixture was stirred for 12 h in N_2 atmosphere. Thereafter the reaction mixture was poured into dry diethyl ether (150 mL) and the wall of beaker was scratched with a glass rod, which afforded a purple solid. The solid was filtered and washed with diethyl ether repeatedly and dried under inert atmosphere. Yield: 0.597 g (85%). HR MS: m/z 403.0851 $\{[Mn^{III}L(OTf)_2]^+ - H^+\}$. Anal. Calcd: C 49.97, H 3.82, N 12.67 found C 49.26, H 3.95, N 12.47.

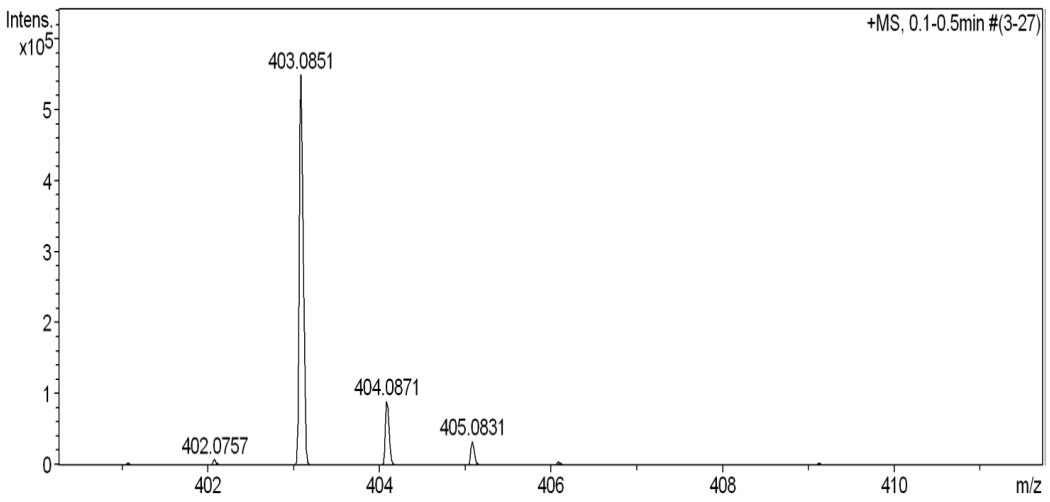


Fig.IV.2. High resolution mass spectra of $[Mn^{III}L(OTf)_2]^+$ in aceonitrile.

IV.4.2.2. X-ray crystallography

Crystallographic data and experimental details for the complex are summarized in Table IV.1. Data on the crystals have been collected on a Bruker SMART 1000 CCD area-detector diffractometer using graphite monochromated Mo Kα= 0.71073 Å) radiation by α scan. The structure was solved by direct methods using SHELXS-97 [28] and difference Fourier syntheses and refined with SHELXL97 package incorporated in WinGX 1.64 crystallographic collective package [29]. All the hydrogen positions for the compound were initially located in the difference Fourier map, and for the final refinement, the hydrogen atoms were placed geometrically and held in the riding mode. The last cycles of refinement included atomic positions for all the atoms, anisotropic thermal parameters for all non-hydrogen atoms and isotropic thermal parameters for all the hydrogen atoms. Full matrix-least-squares structure refinement against $|F^2|$. Molecular geometry calculations were performed with PLATON [30], and molecular graphics were prepared using ORTEP-3 [31].

IV.4.3. Catalytic epoxidation of olefins with *trans*-$[Mn^{III}L(OTf)_2](OTf)$

All reactions were carried out in glass vials (15 mL). In a typical reaction, $PhI(OAc)_2$ (75 mM, 150 equivalent) was added to a mixture of 50 mM of substrate (100 equivalents) and 0.5 mM of catalyst in acetonitrile. The reaction mixture was stirred for 2 h at 298 K and the colour of the solution turned to dark brown from light green. After 2 h, naphthalene solution in acetonitrile (5 μmol) was added as internal standard. Total volume of the mixture was kept fixed at 2 mL. The reaction mixture was then passed though a short silica gel column. The column was washed with

chloroform for 2-3 times. From the extracted solution 1 μL was injected into the GC. The yields of the products were calculated from the ratio of the peak area of substrate to peak area of internal standard (naphthalene).

IV. 5. References

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