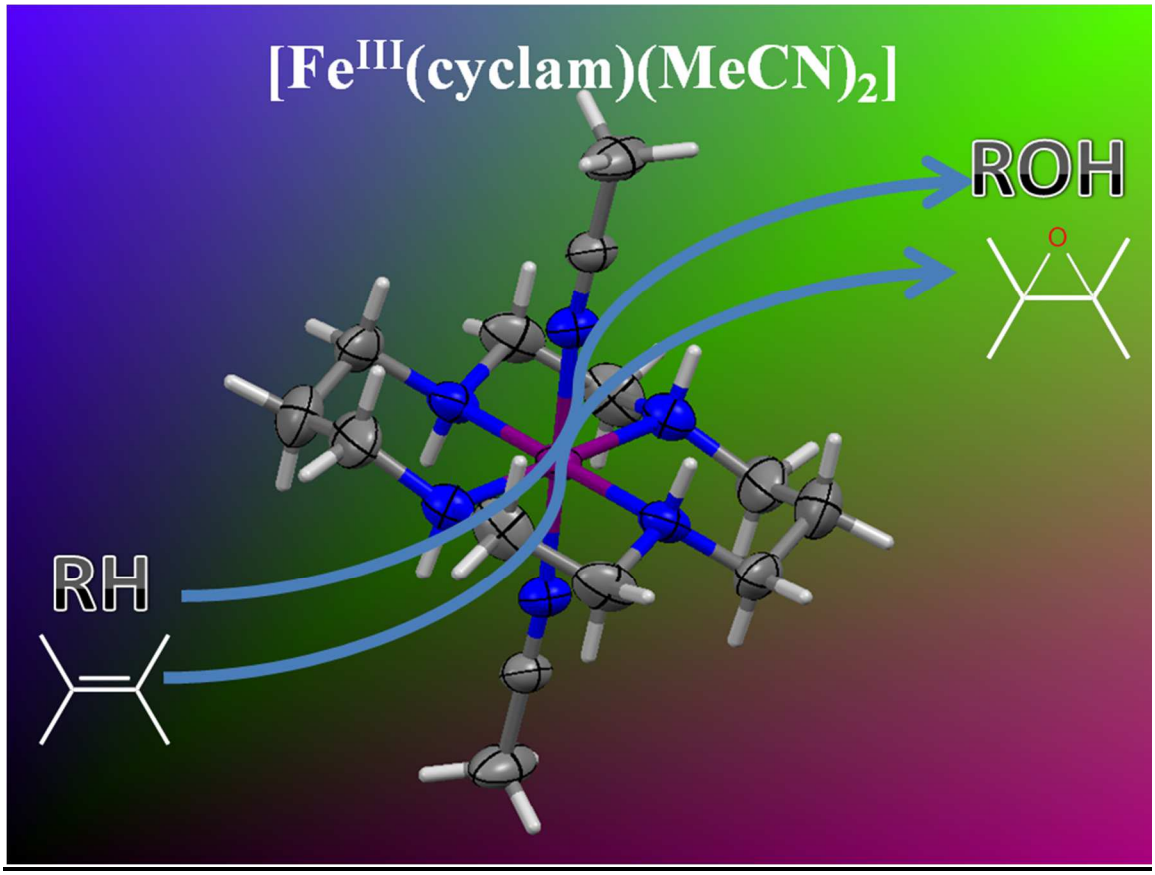
# Chapter VI

## Stereospecific Alkane Hydroxylation and Epoxidation of Olefins with Hydrogen Peroxide Catalyzed by an Iron(III)-Cyclam Complex



# Chapter VI

**Abstract**

Efficient and selective hydroxylation of cycloalkanes and epoxidation of olefins catalyzed by high-spin mononuclear non-heme iron(III) cyclam complex, *trans*[$Fe^{III}$(cyclam)$(CH_3CN)_2$]$(OTf)_3$ (**1**) with hydrogen peroxide under mild condition has been reported. The structure of the complex (**1**) has been elucidated by single crystal X-ray crystallography. Efficient and selective hydroxylation of alkanes and epoxidation of olefins has been achieved under mild condition. The epoxidation of olefins has also been reported under the most economical and synthetically useful reaction condition at room temperature.

## VI.1. Introduction

The selective functionalization of saturated C-H bonds is one of the most challenging goals in basic and industrial chemistry [1]. The inertness of saturated hydrocarbons toward chemical conversion makes them one of the most difficult substrates for selective oxidation. The CH activation or more specifically oxyfunctionalization of alkanes *in vitro* often relies on the application of high temperature and pressure, requires stoichiometric oxidants and suffers from nonselectivity and production of toxic waste [2]. Thus, development of rapid, scalable and inexpensive catalytic systems capable of activating target CH bond under ecofriendly mild condition constitutes one of the most attractive areas of contemporary chemical research. Nature has evolved several efficient iron enzymes that carry out alkane hydroxylation, olefin epoxidation, and olefinic *cis*-dihydroxylation selectively under physiological conditions [3-6]. Understanding the biochemistry of the heme (most notably cytochrome P-450) [7] and non-heme (e.g., methane monooxygenase [8], bleomycin [9], Rieske dioxygenase [6], *etc.*) iron enzymes has proved useful in the development of model catalytic systems for oxyfunctionalization of organic molecules. The pioneering work of Que *et al*. on several non-heme iron(II) complexes together with hydrogen peroxide have been identified as efficient functional models for these enzymes [10]. Majority of the investigations undertaken in this direction, involve iron(II) complexes of TPA (tris-2-pyridylmethyl amine) or closely related ligands. The iron(II) catalysts react with $H_2O_2$ and form low spin iron(III) hydroperoxo complex ($Fe^{III}$-OOH) which undergo either homolytic or heterolytic cleavage to generate reactive iron-oxo intermediates [10-11].

The 14-membered macrocyclic tetraamine ligand, 1,4,8,11-tetraazacyclotetradecane (cyclam), offers a similar N4-ligand environment. Both iron(II) and iron(III) complexes of cyclams are known, where the coordinated ligands can adopt either *trans* (or planar) and *cis*-topologies that demonstrates the flexibility of these ligand frames. Interestingly, *cis* and *trans* isomers of iron(III) cyclam are known to exist in high-spin and low-spin configuration, respectively [12]. The iron(II)(cyclam)$(CF_3SO_3)_2$ was reported to catalyze the epoxidation of olefins with

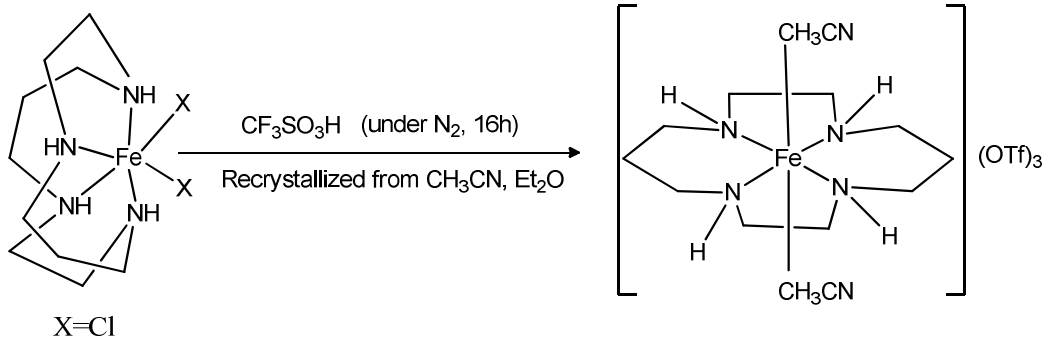
30% aqueous hydrogen peroxide [13, 14]. However, the catalytic property of iron(III)(cyclam) system has not been explored so far.

Herein, we report the synthesis and characterization of non-heme iron(III) cyclam complex with axially coordinated acetonitrile molecules (**1**). The catalytic activity of the complex towards oxygenation of alkanes, alkylbenzenes and alkenes with mild and benign $H_2O_2$ as the terminal oxidant has been studied at room temperature. Attempt has also been made to explore the catalytic activity of the complex in the epoxidation of olefins at room temperature under more economical and preparative scale synthesis.

**VI.2. Results and discussion**

**VI.2.1. Synthesis and characterization of the mononuclear iron(III) complex (1)**

The synthesis of *trans*-[$Fe^{III}$(cyclam)($CH_3CN)_2$]$(OTf)_3$ (**1**) was carried out by stirring the hitherto known complex, *cis*-[Fe(cyclam)$Cl_2$]Cl with trifluromethanesulfonic acid (triflic acid) acid for 16 h at room temperature under a nitrogen atmosphere. A bright yellow precipitate was obtained upon treating the orange solution with diethyl ether (Scheme VI.1) [15].




**Scheme VI.1** Synthesis of iron(III) cyclam complex (**1**)

The complex is fairly stable in air and quite soluble in common organic solvents. Crystals suitable for X-ray crystallography was obtained by the vapour diffusion of diethyl ether into the acteonitrile solution of the complex.

**VI.2.2. Characterization:**

**VI.2.2.1. Electronic spectra**

The electronic spectra of the complex **1** were recorded in acetonitrile. The representative spectra is shown in FigVI. 1.

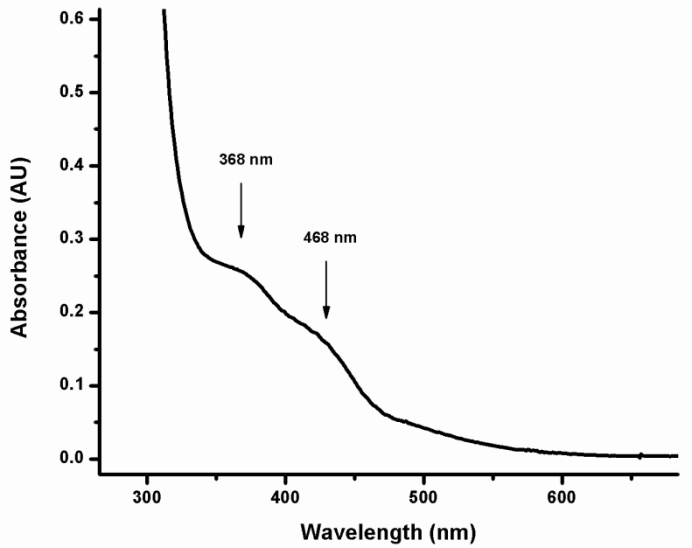



**Fig VI.1** Electronic spectrum of complex **1** in acetonitrile (conc 1mM)

The spectral data are given in the Table VI.1

**Table VI.1** Electronic spectral data of complex **1** in acetonitrile.

| | $\lambda_{max.}$ (nm) | ε ($M^{-1}$ $cm^{-1}$) |
|---|---|---|
| Complex **1** | 368 | 156 |
| | 427 | 38 |

The complex exhibit very broad low intensity absorption bands between the regions 300-500 nm due to d-d transitions. Another interesting feature of this complex is that the complex has no absorption near 334 nm which arises from the ligand to metal charge transfer transition This observation further confirms the replacement of triflate anions by acetonitrile in solution..

**VI.2.2.2. Crystal structure of the iron(III) complex (1)**

Single crystals were obtained by vapour diffusion of diethyl ether into an acetonitrile solution of complex **1** in presence of excess $NaClO_4$. As a result, the perchlorate salt of the complex (**1**-$ClO_4$) has been found to crystallize out of the solution. The asymmetric unit of **1**-$ClO_4$ contains the halves of two independent cations. The structural plot and the metric parameters of an independent cation are presented in Fig VI.2 and Table VI.2, respectively. The selected bond lengths and bond angles are compiled in Table VI.3.

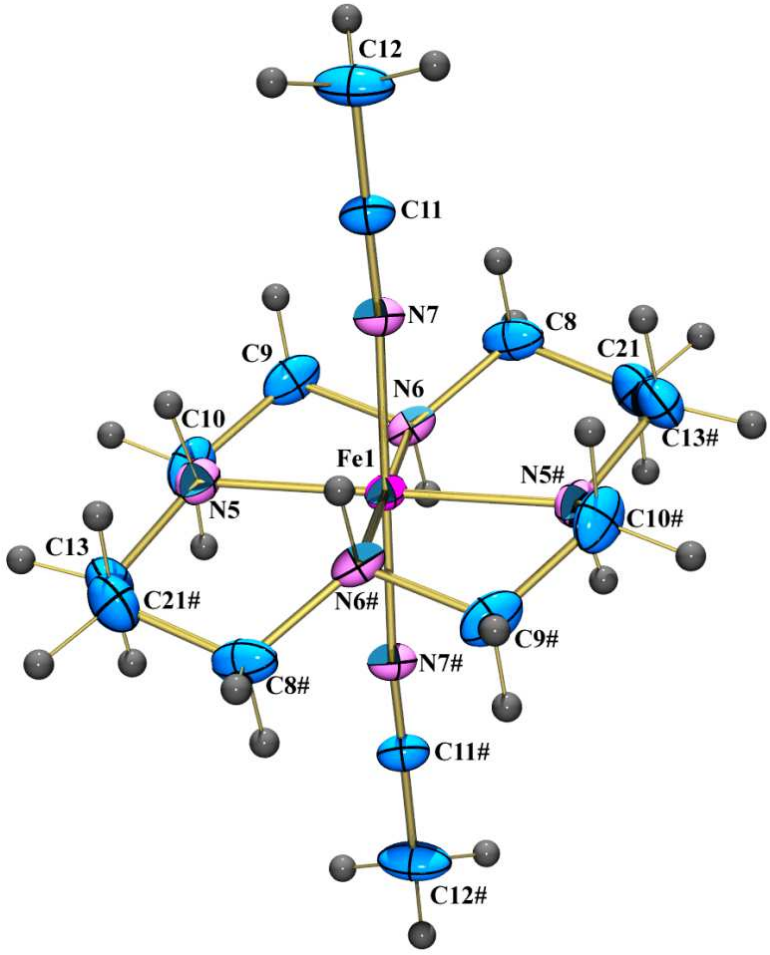



**Fig VI.2** ORTEP plot of an independent cation (**$1^{3+}$**) at 50% probability level. The perchlorate anions were omitted for clarity. The atoms marked with # are symmetry generated.

As evident from Fig VI.2, the iron(III) lies almost at the centre of the plane formed by the four N donor atoms of cyclam and is axially coordinated to two acetonitrile molecules. Thus, the coordination environment around the iron(III) is pseudo-octahedral with the N(2)-Fe(1)-N(4) vector approximately orthogonal to the plane defined by the four N-atoms.

**Table VI.2** Crystal data and structure of refinement for the complex (**1**-$ClO_4$).

| | |
|---|---|
| Empirical Formula | $C_{14}\ H_{30}\ Cl_3\ Fe\ N_6\ O_{12}$ |
| Formula weight | 583.46 |
| Temperature | 220(2) K |
| Wavelength (Å) | 0.71073 |
| Crystal System, Space group | Orthorhombic, P n m a |
| Unit cell dimensions | a = 16.914(5) Å α = 90° |
| | b = 30.937(10) Å β = 90° |
| | c = 9.866(3) Å γ = 90° |
| Volume | 5163(3) |
| Z, Calculated density ($Mg/m^3$) | 8, 1.501 |
| Absorption coefficient | 0.805 |
| F(000) | 2428 |
| Crystal size | 0.20 x 0.10 x 0.06 mm |
| Theta range for data collection | 2.48 to 28.37° |
| Limiting indices | -22<=h<=22, -41<=k<=41, -13<=l<=13 |
| Reflections collected / unique | 60947 / 6498 [R(int) = 0.1364] |
| Data / restraints / parameters | 6498 / 0 / 347 |
| Goodness-of-fit on $F^2$ | 1.075 |
| Final R indices [I>2sigma(I)] | R1 = 0.0928, wR2 = 0.2505 |
| R indices (all data) | R1 = 0.1569, wR2 = 0.2967 |
| Largest diff. peak and hole | 1.383 and -0.910 $e.A^{-3}$ |

The Fe-N distances (ca. 2.0 Å) are comparable to the optimum Fe-N distances found in related *trans*-complexes such as *trans*-[$Fe^{III}$(cyclam)(C≡CR)$_2$](OTf) [15]. The crystal packing diagram of **1**-$ClO_4$ is shown in Fig VI.3. The solid state structure has been found to get stabilized by several non-covalent interactions (Table VI.4).

**Table VI.4** Selected bond lengths (Å) and bond angles (°) for complex **1**-$ClO_4$.

| Bond lengths /Å | | | |
|---|---|---|---|
| Fe(1)-N(1) | 2.000(5) | Fe(1)-N(3) | 1.994(5) |
| Fe(1)-N(2) | 1.926(7) | Fe(1)-N(4) | 1.917(7) |
| Fe(1)-N(1)# | 2.000(5) | Fe(1)-N(3)# | 1.994(5) |
| C(15)-N(2) | 1.131(10) | C(17)-N(4) | 1.147(10) |
| C(15)-C(16) | 1.456(11) | C(17)-C(18) | 1.424(11) |
| Bond angles (°) | | | |
| N(2)-Fe(1)-N(4) | 179.0(3) | N(3)-Fe(1)-N(4) | 89.13(19) |
| N(1)-Fe(1)-N(2) | 88.44(19) | N(1)-Fe(1)-N(3) | 85.9(2) |
| N(1)-Fe(1)-N(4) | 90.88(19) | N3(1)-Fe(1)-N(3)# | 94.3(3) |
| N(3)-Fe(1)-N(2) | 91.54(18) | | |

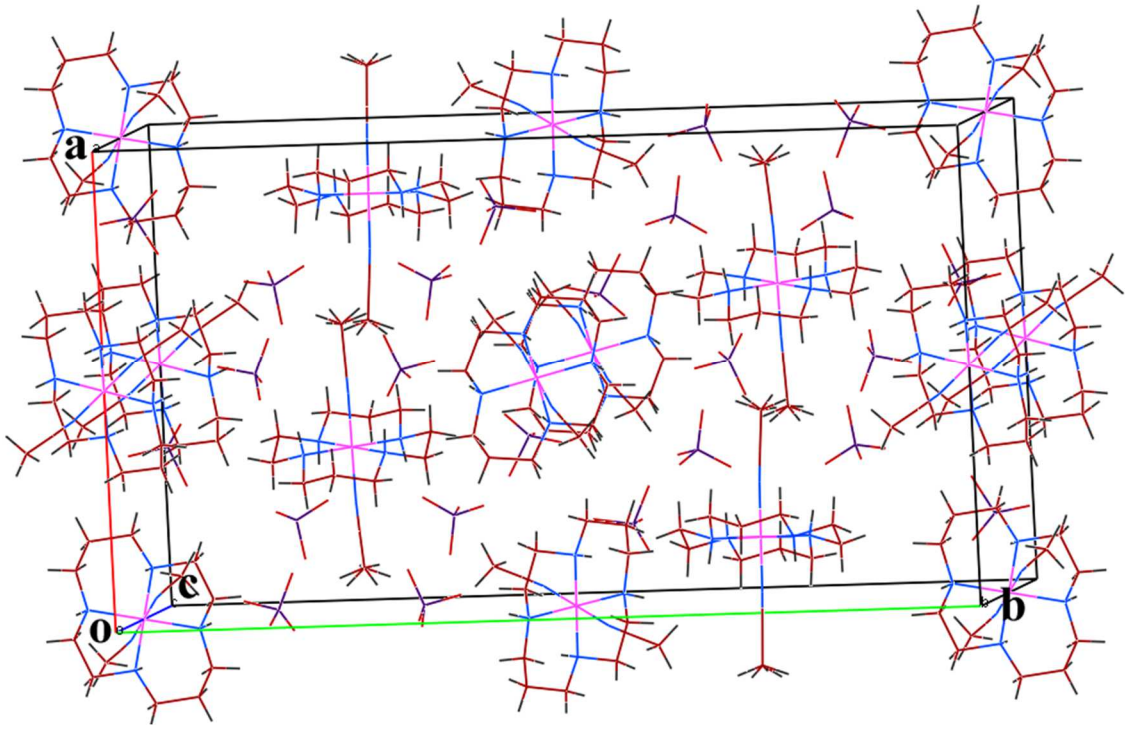



**Fig VI.3** Packing diagram of **1-$ClO_4$**

**Table VI.4** Non-covalent interactions in **1-ClO$_4$ (**Å, °).

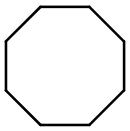
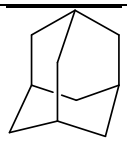
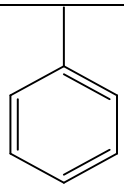
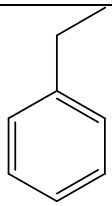
| D-H…A | D-H | H…A | D…A | D-H…A | Symmetry Code |
|---|---|---|---|---|---|
| N1-H1…O1 | 0.92 | 2.34 | 3.169 (13) | 150 | x,y,z |
| N1-H1…O3 | 0.92 | 2.45 | 3.220(16) | 142 | x,y,z |
| N3-H3…O7 | 0.92 | 2.17 | 3.021(11) | 154 | 1/2+x,y,1/2-z |
| N3-H3…O14 | 0.92 | 2.30 | 3.16 (2) | 157 | 1/2+x,y,1/2-z |
| N5-H5…O12 | 0.92 | 2.40 | 3.275 (11) | 160 | 1-x,-y,1-z |
| N5-H5…O13 | 0.92 | 2.40 | 3.048(9) | 128 | 1-x,-y,1-z |
| N6-H6…O5 | 0.92 | 1.98 | 2.884(12) | 166 | 1/2+x,y,3/2-z |
| C5-H5B…O6 | 0.92 | 2.56 | 3.249(14) | 128 | 1/2+x,y,3/2-z |
| C6-H6A…O1 | 0.92 | 2.55 | 3.335(11) | 137 | x,1/2-y,z |

### VI.2.3. Catalytic properties

#### VI.2.3.1. Oxidation of alkanes and alkylbenzenes

The catalytic property of the complex **1** containing cyclam ligand have been explored in the oxidation of alkanes under aerobic condition at room temperature using mild $H_2O_2$ as the terminal oxidant. Detailed experimental procedures for catalytic oxidation reaction are given in the experimental section. The oxidation reaction was carried under standard reaction conditions in order to compare the results with previously reported data [10, 11]. Hydrogen peroxide solution (10 equiv.) was added to an acetonitrile solution containing the catalyst (1 equiv.) and the substrate (1000 equiv.). A large excess of substrate was used in order to minimise the overoxidation of alcohol (A) to ketone (K). The addition of dilute $H_2O_2$ was carried out slowly with the use of syringe pump in order to minimise the disproportionation of $H_2O_2$. The yields are based on the amount of the oxidant converted into the oxidized products. All the individual reactions were performed at least twice and the amounts of products reported represent the average obtained. The product distributions for the catalytic oxidation of cyclohexane, cyclooctane and adamantane oxygenation reactions have been compiled in Table VI.5.

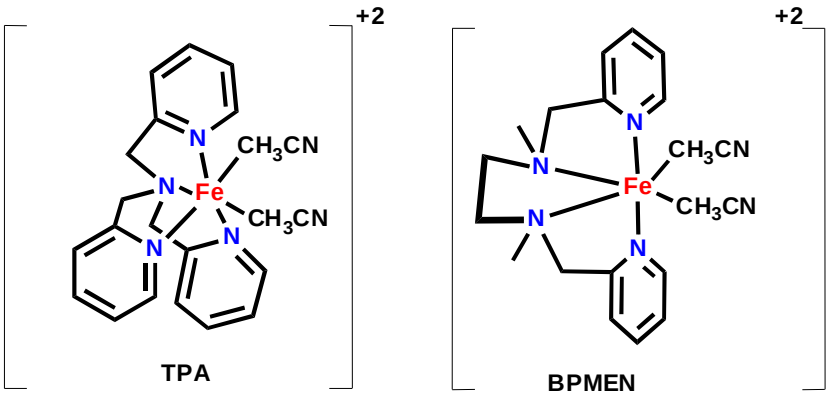
**Table VI.5** Catalytic oxidation of alkanes by **1**/ $H_2O_2$ at room temperature.

| Substrate | % of Products (TON)[a] | | | Total Yield (%) | A/K[b] |
|---|---|---|---|---|---|
| | Alcohol | | Ketone | | |
|  | 40 (4.0) | | 04 (0.4) | 44 | 10.0 |
|  | 60 (6.0) | | 05 (0.5) | 65 | 12.0 |
|  | 1-ol | 2-ol | 2-one | | 3°/2°[c] |
| | 35 (3.5) | 03 (0.3) | 01 (0.1) | 34 | 26.0 |
|  | Benzyl alcohol | | Benzaldehyde | | |
| | 33 (3.3) | | 13 (1.3) | 46 | 2.5 |
|  | 1-Phenylethanol | | Acetophenone | | |
| | 65 (6.5) | | 25 (2.5) | 90 | 2.6 |

[a] Yields are based on oxidant concentration; [c] A/K = alcohol/ketone, $3^{\circ}/2^{\circ}$= (1-ol x 3)/ (2-ol + 2-one).

As shown in Table VI.5, catalyst **1** (1 equiv.) catalyzes the oxidation of cyclohexane with 10 equiv. $H_2O_2$ to afford cyclohexanol and cyclohexanone with turnover numbers (TN) of 4.0 and 0.4 respectively within 15 min (Table VI. 5, Entry 1). The result corresponds to the 44% conversion of the oxidant into organic products with A/K ratio of 10. Under identical condition, the two best known non-heme iron catalysts, *viz.*, $[Fe(TPA)(CH_3CN)_2](ClO_4)_2$ (**I**) and $[Fe(BPMEN)(CH_3CN)_2](ClO4)_2$ (**II**) are known to yield 3.7 TN and 6.3 TN of oxygenates respectively. The alkane hydroxylation ability of **1**, is thus, found to be superior to that of (**I**). Moreover,

selectivity towards alcohol formation, as judged by the A/K value of 10.0 for **1** is found to be better than both **I** (A/K=4.3) and **II** (A/K=8.0). Taken together, the data indicate that complex **1** is an excellent catalyst for alkane hydroxylation with $H_2O_2$.




**I** **II**

**Fig VI.4** Structure of iron (II) complexes of TPA and BPMEN

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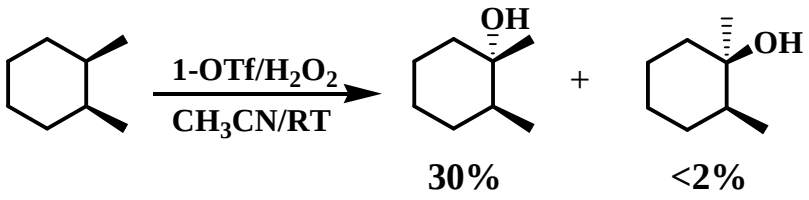
Under identical reaction condition, **1**/$H_2O_2$ catalyzed the hydroxylation of cyclooctane with an alcohol-to-ketone ratio (A/K) of 12 (Table VI. 5, Entry 2). The oxygenates are obtained in 65% overall yield (based on $H_2O_2$) providing cyclooctanol and cyclooctanone with 6.0 and 0.5 catalytic turnovers, respectively.

Adamantane was hydroxylated preferentially at the electron rich tertiary C-H bonds with normalized $3^o/2^o$ ratios of around 26.0 by **1**/$H_2O_2$. This value is comparable to those of cytochrome P450 [16] and heme [17] catalysts and much larger than those of non-heme iron catalysts examined so far [18, 11a]. To further diagnose the catalytic efficiency of **1**/$H_2O_2$ combination in comparison to the non-heme iron catalysts **I** and **II**, oxidation of *cis*-1,2-dimethyl cyclohexane has been investigated. The oxidation of the *cis*-alkane with **1**- /$H_2O_2$ afforded 3.0 TN of *cis*-1,2-dimethylcyclohexanol with a trace amount of the isomeric *trans*-alcohol product (0.2 TN). Thus, the present system is also found to be capable of stereospecific alkane hydroxylation and the results are comparable to that of catalytic systems **I**/ $H_2O_2$ and **II**/ $H_2O_2$.




**Scheme VI.2** Stereospecific hydroxylation of *cis*-1-2 dimethylcyclohexane

Oxidation of alkylbenzenes is important chemical transformations in chemical synthesis, which usually suffers from low selectivity and mostly it is accompanied by the formation of various products [19]. For example, oxidation of toluene usually affords benzaldehyde, benzyl alcohol, cresols, benzoic acid and dibenzyl. Thus, design of efficient process for the selective oxidation of of alkylbenzenes is highly desirable [20-21]. The present catalytic system can efficiently catalyze the oxidation of alkyl benzenes such as toluene and ethylbenzene. The results are summarized in Table VI.5 **1**/$H_2O_2$ system oxidizes toluene to afford benzyl alcohol (33%) as the major product and benzaldehyde (13%) as the minor product with A/K ratio of 2.5. Ethylbenzene, on the other hand, is oxidized by **1**/$H_2O_2$ system to afford mainly 1-phenylethanol (65%) along with acetophenone as the minor product (25%) with A/K ratio 2.6. Complex **1** manifested moderate selectivities towards oxidation of alkylbenzene compared with the other non-heme model systems which normally afforded benzylic alcohol as main product with A/K ratio ranging from 1.1-7.9 [22], although a secondary oxidation pathway such as the oxidation of initially formed alcohol to its oxidation product ketone cannot be ruled out in that case.

**VI.2.3.2. Role of acetic acid in C-H oxidation by 1/$H_2O_2$**

The catalytic activity of the complex **1** has been studied in the oxidation of alkanes with $H_2O_2$ in the presence of acetic acid at room temperature. Preliminary reaction was carried out using cyclohexane as substrate. In order to study the effect of acetic acid, three different amounts of acetic acid have been used with fixed substrate: $H_2O_2$: catalyst ratio. The results are summarized in Table VI.6. No alteration in the total yield as well as no alteration in the A/K ratio has been observed even when stoichiometric amount of acetic acid was used with respect to $H_2O_2$ as well as when large excess than stoichiometric amount of acetic acid was used.

**Table VI.6** Effect of acetic acid in the catalytic oxidation of cyclohexane by **1**/$H_2O_2$ system

| Substrate: $H_2O_2$:catalyst | Acetic acid (equv.) | Total yield (A/K) (%) | A/K |
|---|---|---|---|
| 1000:10:1 | 0 | 44(40+4) | 10 |
| 1000:10:1 | 1 | 45(41+4) | 10.25 |
| 1000:10:1 | 10 | 42(38+4) | 9.5 |
| 1000:10:1 | 100 | 44(36+4) | 9.1 |

We, therefore, hypothesize that the AcOH is not participating on the reactivity of the generated oxidant or it does not reversibly deactivating it, as no product alteration is observed in presence of it.

### VI.2.3.3. Mechanistic consideration

Taken together all these data discussed above, it can be inferred that complex **1** significantly differ from the other non-heme iron systems which generates OH• in presence of $H_2O_2$ that reacts with alkane to afford long-lived alkyl radicals. The participation of alkyl radical during catalytic pathway is indicated by the following symptoms [23]:

1. alcohol-to-ketone (A/K) ratio of 1.0;
2. change product distribution profile to the presence of $O_2$;
3. low 3°/2° ratio in case of adamantane oxidation;
4. low stereoselectivity in the oxidation of *cis*-1,2-dimethylcyclohexane due to the epimerization of long-lived tertiary alkyl radicals [24].

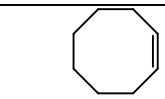
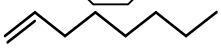
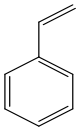
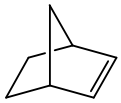
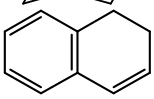
High A/K and 3°/2° ratio in **1**/ $H_2O_2$ system point to a mechanism similar to that of the rebound mechanism operated in cytochrome p-450 and related enzyme cycle. This catalytic cycle initially proceed by the abstraction of aliphatic hydrogen by a ferryl intermediate (Cpd1) followed by an oxygen rebound to form the alcohol coordinated to the iron center [25]. In full agreement with these evidences pointed above and the non-existence of alternative oxidation pathway such as desaturations or secondary transformation such as intramolecular rearrangement of the carbon–

centered radicals [26, 27] it is obvious that short-lived alkyl radicals and hence viability of rebound mechanism is operating in the oxidation pathway by **1**/$H_2O_2$ system.

**VI.2.3.4. Oxidation of olefins**

The catalytic activity of [Fe(cyclam)$(CH_3CN)_2$]$(OTf)_3$ was further investigated in the oxidation of various olefins at room temperature with environmentally benign and inexpensive $H_2O_2$ as the oxidant. To allow direct comparison with published data, reactions were conducted using the conditions previously used for the complexes derived from the ligands tpa, bpmen and related systems [10, 11, 13, 14]. To achieve high conversion of $H_2O_2$ into olefin oxidation products, a large excess of substrate was used and the $H_2O_2$ solution was delivered to the reaction system by syringe pump over a period of 30 min to avoid its disproportionation. Detailed experimental procedures for catalytic oxidation reaction are given in the experimental section. Table VI.7 summarizes the results of alkene oxidation by **1**/ $H_2O_2$.

**Table VI.7** Catalytic oxygenation of olefins by **1**/ $H_2O_2$ at room temperature[a].

| Entry | Substrate | Product | Yield(%)[b] |
|---|---|---|---|
| 1 |  | Cyclooctene oxide | 80 |
| 2 |  | 1,2-epoxyoctane | 60 |
| 3 |  | Styrene Oxide<br>Benzaldehyde | 36<br>6 |
| 4 |  | Exo-epoxide | 70 |
| 5 |  | Oxide | 80 |
| 6 | *Cis* stilbene | *Cis* oxide<br>*Trans* oxide | 90<br>5 |
| 7 | *Tert*-butyl acrylate | Epoxide | 5 |

[a] 10 mM (10 equiv. *w.r.t.* substrate) of $H_2O_2$ was delivered by a syringe pump over 30 min at a rate of 0.8 mL/h; [b] Yield is expressed with respect to the initial concentration of the oxidant.

Under the reaction conditions employed, oxidation of cyclooctene affords 80% epoxide without formation of a trace amount of diol (Table VI.7, entry 1).With 1-octene as substrate, it affords 1,2-epoxy octane upto 60% (Table VI.7, entry 2).
Styrene has been efficiently oxidized to styrene oxide and benzaldehyde. Under the reaction conditions employed, the total yield is 42% with 36% for styrene oxide and 6% for benzaldehyde (Table VI.7, entry 3). Norbornene is regiospecifically oxidised to its *exo*-epoxide only with the yield of 70%. The present catalytic system is also effective in catalyzing the epoxidation of dihydronaphthalene at room temperature (Table VI.7, entry 5) and the total amount of epoxide is 80%.
*Cis*-stilbene is a useful probe substrate because it can form *cis*- and / or *trans* configured products, depending upon the reaction pathway followed. [% RC is used to represent the percentage of retention of configuration in the products of oxidation, expressed as 100 X (A – B) / (A + B), where A= yield of *cis*-epoxide with retention of configuration and B = yield of the epimer]. In our study, the oxidation of *cis*-stilbene yielded the major cis oxide product with 99% retention of configuration with 90% yield of *cis*-stilbene oxide (Table VI.7, entry 6). For the oxidation of electron poor olefins such as tert-butyl acrylate and dimethyl fumarate, the yield of epoxide is very low, as for instance in case of tert-butyl acrylate the yield of epoxide decreased to 5% (Table VI.7, entry 7). Thus, at room temperature, $[Fe(cyclam)(CH_3CN)_2](OTf)_3$ exhibits better catalytic activity towards the oxidation of electron-rich olefins at room temperature in presence of $H_2O_2$ as the terminal oxidant in comparison to that of poor ones. This type of catalytic behaviuor is indicative of the involvement of electrophilic oxidant. [28, 29]
The experiments discussed above all involved $H_2O_2$ as the limiting reagent (Fe/substrate/$H_2O_2$ = 1/1000/10). However, Jacobsen and co-workers [19d] previously reported excellent epoxidation yields using 3 mol% of Fe(II)BPMEN catalyst at 4°C under substrate limiting conditions (Fe/$CH_3COOH$/$H_2O_2$/substrate =1:10:50:33.3). Considering this precedent, we have also applied the same protocol where $H_2O_2$/olefin ratio was maintained at 1.5:1 and found that the catalyst was still effective at 5 mol% of catalyst with the oxidant delivered by syringe pump under air for 30 mins. The epoxidising ability of $[Fe(cyclam)(CH_3CN)_2](OTf)_3$ can be compared with the other best known non-heme iron catalysts such as iron(II)

complexes of the non-heme ligands such as TPA [10b, 10d], BPMEN [10b, 10d], as well as the tetraazamacrocyclic $Me_2EBC$ [14] ligand ($Me_2EBC$ = 4,11–di-methyl-1,4,8,11-tetraazabicyclo[6.6.2]hexadecane) and closely related [Fe(TMC)(OTf)](OTf) [14] complex (TMC= 1,4,8,11-tetramethyl-1,4,8,11-tetraazacyclotetradecane). The catalytic activity can well be compared with the iron complex of pyridine-containing 14-membered macrocyclic ligand (PyMAC) ligand reported by Akimova and co-workers [34], which also contain two trans oriented labile solvate molecules. The results are compiled in Table VI.8.

**Table VI.8** Oxidation of c*is*-cyclooctene catalyzed by nonheme iron(II) complexes with $H_2O_2$ at room temperature[a].

| Entry | Complex | Yield[c] | | Ref. |
|---|---|---|---|---|
| | | Epoxide | *cis*- Diol | |
| 1 | [Fe(TPA)$(OTf)_2$] | 32% | 37% | 10d |
| 2 | [Fe(bpmen)$(OTf)_2$] | 63% | 6% | 10d |
| 3 | [Fe($Me_2EBC$)$(OTf)_2$] | 10% | 13% | 14 |
| 4 | [Fe(cyclam)$(CH_3CN)_2$]$(OTf)_3$ | 56% | 0% | This work |
| 4[b] | [Fe(cyclam)$(CH_3CN)_2$]$(OTf)_2$ | 38% | 0% | This work |
| 5 | [Fe(PyMAC) $(OTf)_2$] | 36% | n.d | 31 |
| 6 | [Fe(TMC)$(OTf)_2$] | 1% | 0% | 14 |

[a]Reaction conditions: $H_2O_2$ was added by syringe pump at a rate of 0.8 mL/hr (30 equiv. with respect to catalyst) in air to a $CH_3CN$ solution containing 1.0 mM catalyst, 20 mM *cis*-cyclooctene. After sringe pump addition was completed, the reaction was stirred for another 30 min. [b]Oxidant is injected all at once. [c]Yield is based on the substrate.

We explored more synthetically practical reaction conditions using 20 mM *cis*-cyclooctene and 30 mM $H_2O_2$, where substrate was the limiting reagent (Table VI. 5, entry 4). With 5 mol% catalyst, 56% of epoxide was obtained (TON = 11.20) within 15 mins. Longer reaction times did not increase the product yield, suggesting that epoxidation of olefins with $H_2O_2$ in the presence of **1** is rapid. The reaction exhibited high selectivity with respect to epoxides other identified side products included diol is not obtained.

With catalyst:substrate:oxidant ratio of 1:200:300, the reported complex derived from the ligands TPA and BPMEN yielded 32% epoxide and 37% diol and 63% epoxide and 6% diol respectively(Table VI.8, entries 1, 2). The complex [Fe($Me_2$EBC)($OTf)_2$], which is structurally similar to the cyclam, afforded 13% *cis*-diol and 10% epoxide (Table VI.8, entry 3) under the assume reaction conditions employed for our system. Interestingly, the too closely related [Fe(TMC)($OTf)_2$] complex is inactive as a catalyst for olefin oxidation as no *cis*-dihydroxylation of *cis*-cyclooctene was observed and at best one turnover number of the epoxide product was obtained under the similar reaction conditions (Table VI.8, entry 6). As [Fe($Me_2$EBC)($OTf)_2$] and [Fe(TMC)($OTf)_2$] differ primarily in the orientation of the two potential labile sites at the iron center, the difference in their catalytic activity supports the notion that the two *cis*-labile sites are needed to promote this type of catalytic behaviour. Likewise, the pyridine azamacrocycle system [Fe(PyMAC)] [31] complex under the same condition yielded 36% epoxide and not any trace amount of diol (Table VI.8, entry 5). Its fully oxidized macrocycle i.e. having methyl groups to all nitrogens does not afford any epoxide.

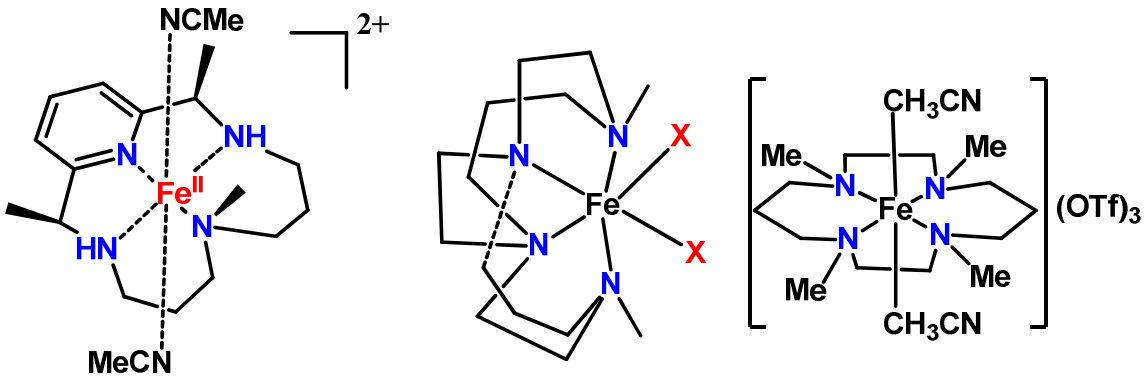



**Fig VI.5** Structures of iron (II) complexes of PyMAC, $Me_2$EBC, TMC. [14, 30]

Therefore, it can be concluded from the above discussion that not only *cis* orientation but as well as -NH group in the ligand moiety is essential criteria for $H_2O_2$ activation. In the previous study by Valentine and co-workers [13] on iron (II) complex of cyclam ligand claimed the hypothesis that $HOO^-$ complex of iron cyclam may be an intermediate because the preferred conformation of the cyclam ligand

presents the $HOO^-$ ligand with an axial N-H bond that is well suited for hydrogen bonding. Comparison of these values with those obtained with related iron complexes under analogous experimental conditions further reinforces the initial conclusions that the cyclam ligand architecture gives rise to mononuclear iron(III) complex with remarkable catalytic activity.

Experiments were devised to investigate whether the synthesized (**1**) complex could catalyze the epoxidation of olefins on a preparative scale. Therefore substrate concentration was increased keeing the substrate:oxidant ratio 1:1.5. Under this condition, the catalytic activity of the complex **1** has been examined initially in the epoxidation of cyclooctene by mild $H_2O_2$ as oxidant at room temperature. In order to achieve the maximum yield in the epoxidation reaction, a broad screening was done using different reaction conditions.

**Table VI.9** Oxidation of cyclooctene under syringe pump addition of $H_2O_2$

| Entry | Cat: Sub::$H_2O_2$ | Yeild(%)[a] |
|---|---|---|
| 1 | 1:100:150 | 36 |
| 2 | 1:100:(150x2)[b] | 38 |
| 3 | 2:100:150 | 53 |
| 4 | 2.5:100:150 | 55 |
| 5 | (1x5):100:(150x5)[c] | 58 |
| 6 | 5:100:150[d] | 55 |
| 7 | 5:100:750[e] | 56 |

[a]Determined by GC. Yields are based on initial concentration of substrate; [b]$H_2O_2$ (1.5 equiv) added after one iteration; [c]iterative addition of 5 mol% of 1, $H_2O_2$ (1.5 equiv) every 10-15 min; [d]slow addition of 5 mol% **1**, 1.5 equiv. $H_2O_2$ with respect to substrate via syringe pump over 30 min into a $CH_3CN$ of cyclooctene ( 100 mM); [e]slow addition of 5 mol% **1**, 7.5 equiv. $H_2O_2$ with respect to substrate via syringe pump over 30 min into a $CH_3CN$ of cyclooctene (100 mM).

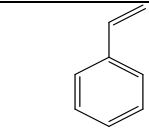
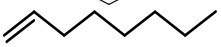
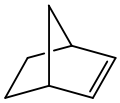
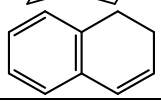
The optimization of reaction conditions reveal that 100 equiv. of cyclooctene is most effective in terms of epoxide yield with 2 mM of catalyst and 150 equiv. of $H_2O_2$ concentration in acetonitrile under air at room temperature. Under this optimized

reaction conditions, cyclooctene has been oxidized to epoxide with the yield of 56% with 100% selectivity and not even at a trace amount of diol has been detected.

While the iron (III) cyclam catalyzed epoxidation reaction enables for the first time the selective oxidation of electron rich olefinic substrates with preparatively useful yields, important challenges remain; these include improving catalyst turnovers and productive substrate conversions. Keeping this in mind, the substrate: oxidant ratio 100:150 was maintained and the catalyst concentration was increased upto 2.5 mM. In this case the yield of epoxide reaches to 55%. Adding more oxidant alone does not alter product yield (Table VI.9, entry 2) indicating that catalyst decomposition, not inefficient use of $H_2O_2$, is responsible for the modest yields observed. Currently, five iterative additions of catalyst **1** (1 mol %), hydrogen peroxide oxidant ($H_2O_2$, 1.5 equiv) in 10-15 min intervals are utilized to obtain maximum product yields (Table VI.9, entry 5) and the maximum yield in this case reaches to 58%. Significantly, with a single addition, increasing the catalyst concentration up to 5 mol% with or without increasing the amount of oxidant (Table VI.9, entries 6 & 7) affords no significant improvement in yield. These results suggest that increased catalyst concentrations are deleterious to catalyst productivity.

After optimizing the reaction conditions in case of cyclooctene epoxidation reaction, we applied the same protocol in case of other substrates such as 1-octene, styrene, norbornene and 1,2 dihydronapthalene (Table VI. 10) by keeping the catalyst: substrate: oxidant 2:100:150.

**Table VI.10** Catalytic oxygenation of alkenes by **1**/ $H_2O_2$ at room temperature under substrate limiting condition.

| Entry | Substrate | Product | Yield (%)[b] |
|---|---|---|---|
| 1 |  | Styrene Oxide | 29 |
| | | Benzaldehyde | 3 |
| 2 |  | 1,2-epoxyoctane | 8 |
| 3 |  | *Exo*-epoxide | 10 |
| 4 |  | Epoxide | 6 |

[b]Yeild are reported with respect to substrate

Styrene was epoxidized with an efficiency of 29% with concominant formation of trace amount of benzaldehyde. 1-octene proved to be poorer substrate under the similar reaction conditions and afforded only 8% epoxide product In case of norbornene and 1,2-dihydronapthalene, the conversion dropped to 10% and 6%. Taken together all the data presented above, the iron (III) cyclam with two *trans* located vacant sites has emerged as an active system for the epoxidation of alkenes at room temperature.

**VI. 3. Conclusion**

1. The mononuclear iron(III) cyclam complex with two acetonitrile molecule at the *trans* positions has been synthesized and characterized.

2. Single crystal X-ray crystallography has been employed for the molecular structure elucidation of the synthesized complex. X-ray crystallography study has proved unambiguously that two acetonitrile molecules occupy the *trans* position.

3. The catalytic activity of the complex has been examined in the oxidation of alkanes, alkylbenzenes and alkenes at room temperature using environmentally benign and inexpensive $H_2O_2$ as oxidant.

4. High A/K ratio in the oxidation of alkanes suggests the involvement of high valent metal oxo intermediates in the oxidation reaction.

5. Remarkably, no *cis*-dihydroxylation products were detected in the case of olefin oxidation reactions. This structural element raised up the essentiality of two *trans* vacant coordination sites (labile sites) otherwise the selective epoxidation is not observed.

6. In order to assess its potential for preparative scale synthesis, oxidation of olefins has also been achieved under substrate limiting conditions.

7. However, rigorous spectroscopic and dynamic studies are required to correlate the mechanism with its reactivity.

## VI.4. Experimental section

### VI.4.1. Materials and Physical Methods

All solvents were of spectroscopic grade and were used as after keeping it in 4 Å molecular sieves. Cyclam (1,4,8,11-teteraazacyclotetradecane) was supplied from Sigma Aldrich and were used as received. Other substrates, all the reaction products and $H_2O_2$ (as ~30% solution in water) were purchased from Aldrich and were used as received. The exact active oxygen content of the oxidant was determined iodometrically prior to use. The product analysis were done by Perkin Elmer Clarus-500 GC with FID (Elite-I, Polysiloxane, 15-meter column) by injecting 1 µL aliquot from the reaction mixture after passing the reaction mixture through a short plug of silica. Electronic spectra were recorded on an Agilent-5843 spectrophotometer. ESI mass spectra were obtained on a Waters-Q-Tof premier - HAB213 mass spectrometer. Elemental microanalyses (C, H and N) were done by Perkin-Elmer (Model 240C) or Heraeus Carlo Erba 1108 elemental analyzer.

### VI.4.2. Synthesis of $[Fe^{III}(cyclam)(CH_3CN)_2](OTf)_3$ (1)

A vial fitted with nitrogen bubbler charged with cis-Fe(cyclam)$Cl_2$ (0.453 g, 1.12 mmol) and 10 g (66.6 mmol) trifluromethane sulfonic acid. Nitrogen was bubbled through the solution for 16 h. The resulting orange solution was transferred to a large beaker to which was added about 150 mL of diethyl ether. Upon stirring and scratching a light yellow powder was formed and it was dried under vacuum. The ESI-MS spectrum of **1** shows a peak at m/z 554 which corresponds to $[Fe^{III}(cyclam)(OTf)_2]^+$. UV-vis, $\lambda_{max}$ (nm), ε ($M^{-1}$ $cm^{-1}$): 368 (156), 427 (38).

### VI.4.3. Catalytic oxidation of hydrocarbons

#### VI.4.3.1. Reaction condition for catalysis

In a typical reaction, 10 equiv of $H_2O_2$ (diluted from 30% $H_2O_2$ solution with $CH_3CN$ resulting in a 50 mM solution) was delivered by syringe pump under air over a period of 30 min at room temperature to a vigorously stirred $CH_3CN$ solution containing iron complex and 1000 equiv of substrate. The final concentrations were 1 mM, 10 mM $H_2O_2$, and 1.0 M substrate. For adamantane, due to its low solubility the final concentration of the substrate is 20 mM. The solution was stirred for an additional 30 min upon completion of $H_2O_2$ addition, after that pentafluoroiodobenzene was added as internal standard and the mixture was filtered

over a short plug of silica followed by elution of ethyl acetate (2 mL). Finally the solution was subjected to GC analysis. The products were identified by comparison of their GC retention times with those of authentic compounds.

**VI.4.3.2. Substrate Limiting Reaction Conditions**

In a typical reaction, $H_2O_2$ (diluted from 30% $H_2O_2$ solution with $CH_3CN$ resulting in a 150 mM solution) was delivered by syringe pump at rate 0.8 mL/hr at room temperature in air to a vigorously stirred $CH_3CN$ solution containing iron complex, olefin substrate. The final concentration of iron complex was 1.0 mM. The solution was stirred for an additional 30 min after syringe pump addition, after that internal standard was added and the same treatment was followed as in the case for oxidant limiting condition.

**VI.4.3.3. General procedure for iterative addition protocol**

A 15 mL vial was charged with the following: catalyst (1.0 mL, 1 mM), substrate (100 mM), $CH_3CN$ (0.5 mL), and a magnetic stirring bar. The vial was placed on a stir plate and stirred vigorously at room temperature. A solution of $H_2O_2$ (1.5 equiv *w.r.t* substrate, 300µL) was added drop wise via a syringe pump over a period of 30 mins. After the addition was complete, the solution was further stirred for 10 mins. A second addition was performed in the same manner for a total of 2 mol% and 3 equiv of $H_2O_2$. In this way a third, fourth and fifth additions were performed giving a total of 5 mol% of **1**, and 7.5 equiv. of $H_2O_2$. Each addition was allowed to stir for 10 min, for a total of reaction of 50 min.

**VI.4.4. Crystallographic data collection and structure refinement**

Single crystals of **1** suitable for X-ray diffraction study were immersed in paratone-N oil and mounted on the tip of a glass fibre. Details about data collection and structure refinements have already been discussed in the Experimental Section of Chapter II.

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