SYNTHESIS, CHARACTERIZATION AND CATALYTIC ACTIVITY OF MONONUCLEAR IRON(III) COMPLEXES TOWARDS HYDROCARBON OXIDATION AT ROOM TEMPERATURE

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ABSTRACT

Non-heme mononuclear iron(III) complexes $[\text{Fe}(\text{L}^1)\text{Cl}_2]\text{Cl}$ (1) and $[\text{Fe}(\text{L}^2)\text{Cl}_2]\text{Cl}$ (2), where $\text{L}^1 = \text{N,N}'\text{-bis(2-pyridylmethyl)-1,2-cyclohexanediamine}$ and $\text{L}^2 = \text{N,N}'\text{-bis(2-pyridylmethyl)ethane-1,2-diamine}$, have been synthesized and characterized by means of elemental analysis and spectral methods. The catalytic properties of the complexes for the oxidation of saturated hydrocarbons have been investigated at room temperature using hydrogen peroxide (H_2O_2) and *m*-chloroperbenzoic acid (*m*-CPBA) as oxidants. Catalytic oxidation by environmentally benign H_2O_2 suggested a radical-based reaction pathway in the oxidation reaction. Further, total quenching of the oxidation process in the presence of "radical scavenger" 2,4,6-tri-*t*-butylphenol (TTBP) confirmed the involvement of radicals during the catalytic cycles. Significant enhancement in the selectivity towards alkane oxidation and regioselectivity in the oxidation of adamantane by replacement of H_2O_2 with *m*-CPBA as oxidant indicated the involvement of metal-based intermediate during catalytic oxidation reaction.

Keywords: Catalysis, Non-heme, Iron Complex, Hydrogen Peroxide, *m*-Chloroperbenzoic Acid, Hydrocarbon Oxidation.

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INTRODUCTION

Selective transformation of saturated hydrocarbons under mild conditions is a subject of great interest in chemical science because of their great abundance in nature makes them a convenient chemical feedstock. Therefore, the development in this area is a key objective for the transformation of hydrocarbons to more valuable oxygen-containing products. However, the oxyfunctionalization of saturated hydrocarbons is a challenging issue due to their inertness toward chemical conversion. Hence, functionalization of an sp^3 C-H bond in a selective fashion under mild conditions remains a challenge of major interest in chemistry.¹⁻³ The high exothermicity of hydrocarbon oxidation using molecular oxygen makes oxidation reactions a thermodynamically allowed process. However, this same exothermicity usually makes these processes uncontrollable, because the initial oxygenates are vulnerable to complete combustion to produce thermodynamically stable products such as water and carbon dioxide. Thus, the selective oxidation and functionalization of hydrocarbons is an important and exciting issue in synthetic chemistry. Despite the inherent difficulty to accomplish selective oxidation of C-H bonds of hydrocarbons, nature has evolved several iron-containing metalloenzymes to carry out such transformations selectively under very mild conditions.^{4,5} In this context, heme iron-proteins such as haemoglobin, myoglobin and cytochromes oxygenase and non-heme enzymes such as methane monooxygenase and rieske dioxygenases have received much attention.⁶⁻¹¹ Inspired by these enzymes, development of model catalytic systems for hydrocarbon oxidation has evoked keen interest.¹²⁻¹⁹ Mononuclear iron(II) complexes of multidentate N-donor ligands have been extensively studied for modeling the active site of iron enzymes exhibiting a catalytic function.²⁰⁻²² However, synthesis and storage of the iron(II) catalysts invariably require moisture and air-free conditions and are generally performed in inert gas-filled glove boxes.^{23,24} Therefore, straightway use of iron(III) catalysts for oxidation of hydrocarbons with green H_2O_2 ²⁵⁻²⁷ as oxidant provides a useful alternative in terms of the development of the inexpensive catalytic system.

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Herein, we wish to describe the synthesis and characterization of non-heme mononuclear iron(III) complexes $[\text{Fe}(\text{L}^1)\text{Cl}_2]\text{Cl}$ **1** and $[\text{Fe}(\text{L}^2)\text{Cl}_2]\text{Cl}$ **2**, with N_4 -donor ligands, where $\text{L}^1 = \text{N,N}'\text{-bis}(2\text{-pyridylmethyl})\text{-1,2-cyclohexanediamine}$ and $\text{L}^2 = \text{N,N}'\text{-bis}(2\text{-pyridylmethyl})\text{ethane-1,2-diamine}$. The catalytic properties of the complexes **1** and **2** have been studied in the oxidation of hydrocarbons at room temperature with hydrogen peroxide (H_2O_2) and *m*-chloroperbenzoic acid (*m*-CPBA) as oxidants under mild conditions.

EXPERIMENTAL

Materials and Methods

All chemical reagents were purchased from Sigma Aldrich and were used as received. The active oxygen contents of the oxidants (H_2O_2 and *m*-CPBA) were determined iodometrically before use. Acetonitrile and dichloromethane were distilled under argon and stored over molecular sieves (4 Å). Electronic spectra were recorded on a JASCO V-530 spectrophotometer. The infrared spectra were performed on KBr disc in a JASCO 5300 FT-IR spectrophotometer. The ^1H NMR analyses were undertaken on a Bruker 400 MHz NMR spectrometer. Magnetic susceptibility measurements were carried out using MSB mk1-Sherwood magnetic susceptibility balance. Elemental analyses were performed on a Heraeus Carlo Erba 1108 elemental analyzer. The products were analyzed by using Perkin Elmer Clarus-500 Gas Chromatograph equipped with an FID detector (Elite-I, Polysiloxane, 15-meter column).

Synthesis of the Ligands

Synthesis of $\text{N,N}'\text{-bis}(2\text{-pyridylmethyl})\text{-1,2-cyclohexanediamine}$ (L^1)

The ligand was synthesized according to the literature procedure.²⁸

Yield: 86%. ^1H NMR (400 MHz, CDCl_3): δ 8.49 (d, 2H, Py, $J = 4$ Hz), 7.61 (m, 2H, Py), 7.37 (d, 2H, Py, $J = 8$ Hz), 7.2 (m, 2H, Py), 4.04 and 3.84 (d, 2 x 2H, $J = 16$ Hz), 3.03 (s, 2H, NH), 2.35 (m, 2H, CyH), 2.12 (m, 2H, CyH), 1.7 (m, 2H, CyH), 1.2 (m, 4H, CyH).

Synthesis of $\text{N,N}'\text{-bis}(2\text{-pyridylmethyl})\text{ethane-1,2-diamine}$ (L^2)

L^2 was prepared by the same procedure employed for L^1 , using ethylenediamine in place of *trans*-1,2-diaminocyclohexane.

Yield: 88%. ^1H NMR (400 MHz, CDCl_3): δ 8.51 (d, 2H, Py, $J = 4$ Hz), 7.7 (m, 2H, Py), 7.41 (d, 2H, Py, $J = 8$ Hz), 7.23 (m, 2H, Py), 4.12 (s, 4H), 3.36 (s, 2H, NH), 3.13 (s, 4H).

Synthesis of the Catalysts

Synthesis of $[\text{Fe}(\text{L}^1)\text{Cl}_2]\text{Cl}$ (**1**)

A 5 mL methanol solution of anhydrous FeCl_3 (0.1624 g, 1 mmol) was added to a stirred methanolic solution (10 mL) of L^1 (0.296 g, 1 mmol) at room temperature. After stirring for 1 h, the yellow precipitate obtained was collected by filtration, washed with diethyl ether and then dried. The complex was obtained as shining crystals upon recrystallization from acetonitrile.

Yield: 70%. Anal. Calc. for $\text{C}_{18}\text{H}_{24}\text{Cl}_3\text{FeN}_4\cdot 2\text{H}_2\text{O}$: C, 43.71; H, 5.71; N, 11.33. Found: C, 43.38; H, 5.41; N, 11.15%.

Synthesis of $[\text{Fe}(\text{L}^2)\text{Cl}_2]\text{Cl}$ (**2**)

This compound was prepared according to the literature procedure.²⁹

$\text{FeCl}_3\cdot 6\text{H}_2\text{O}$ (0.270 g, 1 mmol) was added to a stirred solution of $\text{L}^2\cdot 4\text{HCl}$ (0.388 g, 1 mmol) in water (8 mL) and the solution was stirred at room temperature for 10 min. The yellow solid that precipitated after the addition of sodium acetate (0.408 g, 3 mmol) was filtered off and dried. The complex was recrystallized from acetonitrile as yellow needles.

Yield: 74%. Anal. Calc. for $\text{C}_{14}\text{H}_{18}\text{Cl}_3\text{FeN}_4$: C, 41.57; H, 4.49; N, 13.85. Found: C, 41.14; H, 4.48; N 13.65%.

General Catalytic Oxidation Procedure

In a typical oxidation experiment, 7 mM of H_2O_2 (2 mM in case of *m*-CPBA) was added at room temperature to an acetonitrile solution (2 mL) containing 0.7 mM of catalyst and 700 mM of alkane

(cyclohexane or cyclooctane) in small screw-capped vials fitted with PTFE septa with a final catalyst:oxidant:substrate ratio 1:10:1000. The mixture was magnetically stirred at room temperature for 3 h (or 1 h in case of oxidation reaction with *m*-CPBA). The products were identified and quantified from the response factors of standard product samples by GC with pentafluoroiodobenzene (PFIB) as an internal standard. Due to the poor solubility of adamantane in acetonitrile, 1:1 mixture (v/v) of acetonitrile and dichloromethane was used as a solvent in the oxidation of adamantane. In the case of alcohol oxidation, the reaction was initiated by adding 2 mM of H₂O₂ to an acetonitrile solution containing 0.7 mM of catalyst and 100 mM of the substrate.

RESULTS AND DISCUSSION

Synthesis

The ligands L¹ and L² were prepared according to the reported two-step procedure involving condensation of pyridine-2-carboxaldehyde and diamine followed by reduction with NaBH₄.²⁸ Complex **1** was readily synthesized by the reaction of equimolar amounts of L¹ and anhydrous FeCl₃ in methanol medium (Scheme-1) at room temperature. Iron(III) complex of L², **2**, was prepared according to the literature procedure.²⁹

Scheme-1: Synthesis of Complex, **1**

Characterization

IR and ¹H NMR Spectral Data

The synthesized ligands were characterized by IR and ¹H NMR spectral techniques. The IR spectrum of N,N'-bis(2-pyridylmethylene)-diamine moiety exhibits absorption at 1644 cm⁻¹, characteristic of N=C bond,³⁰ which is absent in the IR spectrum of N,N'-bis(2-pyridylmethyl)-1,2-cyclohexanediamine (L¹) and N,N'-bis(2-pyridylmethyl)ethane-1,2-diamine (L²). Both the ligands show absorption around 3300 cm⁻¹ corresponds to N-H stretch¹¹. The ¹H NMR spectral data of L¹ and L² are provided in the experimental section and are in good agreement with the reported data.³¹

Electronic Spectra

The electronic spectra of iron(III) complexes were recorded in acetonitrile. Complexes **1** and **2** exhibit absorption bands in the region of 250-400 nm (Table-1, Fig.-1). Both the complexes exhibit an intense band near 255 nm which is due to the pyridyl π→π* transitions.^{32,33} The two other broad bands at 293 (sh) and 358 nm for complex **1** and 287 (sh) and 353 nm for complex **2** are assigned to the chloro-to-iron(III) charge transfer transition.^{32,34}

Table-1: Electronic Spectral Data for Complexes **1** and **2** in Acetonitrile

Complex	λ_{max} (nm)	ϵ (M ⁻¹ cm ⁻¹)
1	252	22,100
	293(sh)	10,200
	358	6,000
2	253	9,300
	287(sh)	5,100
	353	2,700

Fig.-1: Electronic Spectra of Complexes **1** and **2** in Acetonitrile

Magnetic Property

The magnetic susceptibility of complexes **1** and **2** was determined in the solid-state at 298 K. Complex **1** exhibits a magnetic moment of 5.9 μ_B , which suggests the high spin configuration in mononuclear iron(III).²⁹ Complex **2** shows effective magnetic moment of 5.4 μ_B , consistent with high spin mononuclear iron(III).

Catalytic Oxidation of Hydrocarbons

The catalytic activities of the synthesized non-heme iron(III) complexes **1** and **2** have been examined in the oxidation of saturated hydrocarbons (cyclohexane, cyclooctane and adamantane) with H₂O₂ and *m*-CPBA as oxidants under the aerobic condition at room temperature. The results of catalytic oxidation are summarized in Table-2. Both the complexes catalyzed the oxidation of cyclohexane to cyclohexanol (CyOH) and cyclohexanone (CyO). Complex **1** in presence of H₂O₂ catalyzed cyclohexane oxidation with an A/K ratio of 0.7. The total yield of the oxygenates for a 3 h reaction time was 17% based on H₂O₂ (Table-2, entry 1). Under similar reaction conditions, complex **2** exhibited a catalytic activity of 10% with the same A/K ratio (Table-2, entry 2).

Table-2: Catalytic Oxidation of Hydrocarbons with mild H₂O₂ at Room Temperature

Entry	Substrate	Catalyst	Yield (%) ^a	Product Selectivity (%) ^b			Remarks ^c
				Cyclohexanol	Cyclohexanone		
1	Cyclohexane	1	17	41	59		A/K
2		2	10	40	60		0.7
				Cyclooctanol	Cyclooctanone		A/K
3	Cyclooctane	1	14	36	64		0.6
4		2	9	33	67		0.5
				1-adamantanol	2-adamantanol	2-adamantanone	3°/2°
5	Adamantane	1	22	73	18	9	8.0
6		2	14	72	14	14	7.5

^aYields are based on oxidant concentration; ^bSelectivity is percentage expressed with respect to total yield;

^cA/K = alcohol/ketone, 3°/2° = (1-ol x 3)/(2-ol + 2-one).

It is interesting to observe that the selectivity towards alcohol formation decreases with an increase in reaction time. After 6 h reaction time, with complex **1** as a catalyst, A/K ratio decreases to 0.3 (CyOH 24%, CyO 76%), after 8 hours it becomes 0.2 (CyOH 18%, CyO 82%) and interestingly A/K ratio does not change on further increasing the reaction time. The total yield of the oxidation products remains the same (17%). This illustrates that the product cyclohexanol is subsequently oxidized to cyclohexanone under catalytic conditions with an increase in reaction time (Fig.-2).

Fig.-2: Time-dependent Oxidation of Cyclohexane by Catalyst **1** using H₂O₂ as Oxidant

Cyclooctane was oxidized to the corresponding alcohol and ketone in a ratio (A/K) of 0.6 with 14% conversion by complex **1** and 0.5 with a low conversion of 9% by complex **2** (Table-2, entries 3, 4). The catalytic activities of the complexes **1** and **2** were further explored for the oxidation of adamantane. Oxidation of adamantane afforded 1-adamantanol along with 2-adamantanol and 2-adamantanone as minor products by the present catalytic system. The overall conversion of 22% based on H₂O₂ with 3°/2° ratio of 8.0 has been achieved by complex **1**. Under the same conditions, the conversion diminished to 14% with 3°/2° ratio of 7.5 using complex **2** as catalyst (Table-2, entries 5, 6).

Oxidation of saturated hydrocarbons has also been studied at room temperature using *m*-CPBA as an oxidant with high selectivity, but to a lower extent by the present catalytic system. The results are compiled in Table-3. A conversion of 8-9% with an improved A/K ratio of 1.7-2.0 was obtained for the oxidation of cyclohexane by both the complexes (Table-3, entries 1, 2). Similar results were obtained in the cyclooctane oxidation also (Table-3, entries 3, 4). In the case of adamantane oxidation, replacement of H₂O₂ with *m*-CPBA led to the promotion of the regioselectivity with 3°/2° ratio of 11.3-13.6, with a final conversion of 17% for catalyst **1** and 14% for catalyst **2** (Table-3, entries 5, 6). For comparison, 3°/2° ratios of 2.7 found for Gif-type oxidations, about 2 for the oxidation of alkanes by hydroxyl radicals³⁵ and values of 3.1-3.3 for [Fe(N4Py)(CH₃CN)](ClO₄)₂.³⁶ A 3°/2° ratio of 9.5-10.0 has been observed for [Fe₂O(bpy)₄(H₂O)₂](ClO₄)₄ or [Fe(tpa)Cl₂](ClO₄)₃³⁷⁻³⁹ and 11-48 for oxidation with PhIO catalyzed by P450 mimics.^{40,41} In all the cases, the use of *m*-CPBA leads to an enhanced selectivity and regioselectivity but with a lower yield of oxygenates, in contrast to H₂O₂.

Table-3: Catalytic Oxidation of Hydrocarbons with *m*-CPBA at Room Temperature

Entry	Substrate	Catalyst	Yield (%) ^a	Product Selectivity (%) ^b			Remarks ^c
				Cyclohexanol	Cyclohexanone	A/K	
1	Cyclohexane	1	9	67	33	2.0	
2		2	8	63	37	1.7	
				Cyclooctanol	Cyclooctanone	A/K	
3	Cyclooctane	1	6	67	33	2.0	
4		2	5	60	40	1.5	
				1-adamantanol	2-adamantanol	2-adamantanone	3°/2°
5	Adamantane	1	17	82	12	6	13.6
6		2	14	79	14	7	11.3

^aYields are based on oxidant concentration; ^bSelectivity is percentage expressed with respect to total yield;

^cA/K = alcohol/ketone, 3°/2° = (1-ol x 3) / (2-ol + 2-one).

The low A/K ratio (0.5-0.7) in the oxidation of cyclohexane and cyclooctane and the poor regioselectivity with $3^\circ/2^\circ$ ratios in the range of 7.5-8.0 in adamantane oxidation with H_2O_2 as oxidant suggests the involvement of radical based reaction pathway.⁴²⁻⁴⁴ In contrast, enhanced selectivity in the oxyfunctionalization of alkanes with *m*-CPBA indicates the involvement of a metal-based intermediate.^{45,46} The radical character of the oxidation reactions with H_2O_2 has been confirmed by conducting the reactions in the presence of “radical scavenger” 2,4,6-tri-*t*-butylphenol (TTBP). In the case of cyclohexane oxidation, the addition of TTBP before H_2O_2 addition resulted in total quenching of the oxidation reaction. This observation suggests the possible involvement of a typical radical based reaction mechanism in the oxidation reactions with H_2O_2 as oxidant.

Oxidation of Alcohols

The time dependence catalytic oxidation of cyclohexane by H_2O_2 established that the product cyclohexanol is subsequently oxidized to cyclohexanone with an increase in reaction time. Over-oxidation of hydrocarbons to ketone has been further confirmed by performing the oxidation of alcohols under similar reaction conditions (Table-4).

Table-4: Catalytic Oxidation of Alcohols with mild H_2O_2 at Room Temperature

Entry	Substrate	Catalyst	Product	Yield (%) ^a
1	Benzyl alcohol	1	Benzaldehyde	77
2		2		70
3	4-Hydroxybenzyl alcohol	1	4-Hydroxybenzaldehyde	100
4		2		88
5	4-Methoxybenzyl alcohol	1	4-Methoxybenzaldehyde	99
6		2		84
7	4-Nitrobenzyl alcohol	1	4-Nitrobenzaldehyde	76
8		2		69
9	Cyclohexene-1-ol	1	Cyclohexene-1-one	100
10		2		97
11	Adamantane-2-ol	1	Adamantane-2-one	37
12		2		32

^aYields are based on oxidant concentration.

The oxidation of benzyl alcohol catalyzed by non-heme iron(III) complexes, **1** and **2**, afforded benzaldehyde with 70-77% yield based on H_2O_2 (Table-4, entries 1, 2). The substituted benzylic alcohols have also been converted to the corresponding carbonyl compounds by the present catalytic system in high yields (Table-4, entries 3-8). No over oxidation of the primary alcohols to the corresponding acids was observed. Both the complexes have also been found effective in oxidizing the secondary alcohols with H_2O_2 at room temperature (Table-4, entries 9-12). Cyclohexene-1-ol was converted to the corresponding ketone almost quantitatively, but the conversion decreases to 32-37% when adamantane-2-ol was used as a substrate. The results suggested that the distribution of the product obtained in the oxidation of alkanes by catalyst/ H_2O_2 system is partly derived from the in situ oxidation of alcohols.

CONCLUSION

Non-heme mononuclear iron(III) complexes with N_4 -donor ligands, **1** and **2**, have been synthesized and characterized. Both the complexes are found to be effective to carry out the oxidation of saturated hydrocarbons at room temperature using H_2O_2 and *m*-CPBA as oxidants. Oxidation of cyclohexane and cyclooctane with environmentally benign H_2O_2 provides a mixture of alcohol and ketone revealing poor selectivity towards alcohol formation whereas poor regioselectivity in the oxidation of adamantane suggests radical based reaction pathway in the oxidation reaction. Total quenching of the oxidation

process in the presence of “radical scavenger” 2,4,6-tri-*t*-butylphenol (TTBP) confirms the involvement of radicals during catalytic cycles. Replacement of H₂O₂ with *m*-CPBA as terminal oxidant led to significant enhancement in the selectivity towards alkane hydroxylation and the regioselectivity of adamantane oxidation indicating the involvement of metal-based intermediate during the catalytic oxidation.

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