

Research Note

# A highly efficient method of epoxidation of olefins with hydrogen peroxide catalyzed by changeable hexadentate 8-quinolinolato manganese(III) complexes

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## Abstract

Novel hexadentate binding 8-quinolinolato manganese(III) complexes were proposed and conveniently synthesized for the epoxidation of olefins with aqueous hydrogen peroxide in water–acetone media with ammonium acetate and acetic acid as additives. The catalytic efficiencies of the suggested catalysts were found to be obviously superior to the traditional tetradentate salen–Mn<sup>III</sup>Cl, due to their special hexadentate binding structures that could be easily converted to the corresponding pentadentate with pendant hydroxyl groups by opening an axial Mn–O bond in the reaction media, as supported by UV–vis spectra, *in situ* cyclic voltammetry, and quartz crystal microbalance characterizations.

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**Keywords:** Catalysis; Epoxidation; Hexadentate structure; Hydrogen peroxide; Olefins; 8-Quinolinolato Mn(III) complexes

## 1. Introduction

Epoxidation of olefins is one of the most important reactions in organic synthesis, because the reaction products—epoxides—can be easily converted to wide variety of compounds [1]. Consequently, there has been considerable interest in the development of highly efficient epoxidation catalysts [2–5]. In particular, nontoxic transition metals, such as Mn-mediated epoxidation with aqueous hydrogen peroxide (H<sub>2</sub>O<sub>2</sub>), have been appreciated as a green process [6]. But the efficient Mn-mediated epoxidation systems reported to date have used mainly tetradentate binding manganese complexes as catalysts [7] and have some disadvantages, including the use of toxic solvent, oxidative decomposition of organic ligands, opening by reaction of the desired epoxide product, unsatisfactory H<sub>2</sub>O<sub>2</sub> efficiency, and high cost.

We have been intrigued with the idea that 8-quinolinolato derivatives may be very promising candidates for developing novel Mn-based catalytic epoxidation with aqueous H<sub>2</sub>O<sub>2</sub>, based on the following considerations: (i) They could suppress the catalase feature of Mn ions, (ii) could chelate Mn<sup>3+</sup> ions to form hexadentate binding complexes different from planar tetradentate binding salen Mn ones, and (iii) could improve the epoxidative selectivity by lowering the Lewis acidity of Mn ions. Herein we report for the first time the valuable results obtained from using the hexadentate binding 8-quinolinolato manganese(III) complexes (Q<sub>3</sub>Mn<sup>III</sup> in Scheme 1) to catalyze the epoxidation of olefins with aqueous H<sub>2</sub>O<sub>2</sub> in water–acetone media containing ammonium acetate (NH<sub>4</sub>OAc) and acetic acid (HOAc), and *in situ* cyclic voltammetry (CV), quartz crystal microbalance (QCM), and UV–vis spectroscopy techniques are used to identify the structural transition of Q<sub>3</sub>Mn<sup>III</sup> from hexadentate to pentadentate mode in the catalytic process.

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## 2. Experimental

### 2.1. Preparation and characterizations of $Q_3Mn^{III}$ complexes

The general preparation procedure for the  $Q_3Mn^{III}$  complexes is as follows. First, 5 mL of  $Mn(OAc)_2$  aqueous solution ( $1\text{ mol L}^{-1}$ ) was added dropwise to 50 mL of stirred tetrahydrofuran (THF) containing 15 mmol of 8-hydroxyquinoline (8-HQ) or its derivative, followed by adding 30 wt% aq.  $H_2O_2$  (0.57 g, 5 mmol) into the solution and adjusting the solution pH to 6–7 with ammonia (measured using PHS-3C pH meter, China). Then, the reaction mixture was refluxed for 2 h, and the resulting precipitate was filtrated and washed with ethanol for at least three times. After air-drying, a deep-yellow solid (80–92% yield) was obtained and denoted as **1a** to **1e** (see Scheme 1). For the sake of comparison, a hexadentate binding 5-chloro-7-iodo-8-quinolinolato  $Fe^{III}$  ( $Q_3Fe^{III}$ ) and traditional salen- $Mn^{III}Cl$  complexes also was prepared.

CHN and metal elemental analyses of these complexes indicate that **1a–1e** and  $Q_3Fe$  complexes are hexadentate, whereas 5-nitryl-8-quinolinolato  $Mn^{III}$  (denoted as **1\*f**) is tetradentate (see Supporting Information). The diffusion reflection UV–vis spectra of the solid  $Q_3Mn^{III}$  complexes were recorded from 200 to 800 nm on an UV-3310 spectrophotometer ( $BaSO_4$  as a standard, Hitachi). The CV and QCM techniques used to characterize these complexes are described in detail in the Supporting Information.

### 2.2. Epoxidation procedure

The general procedure for epoxidation is as follows. To a cooled ( $10\text{ }^\circ\text{C}$ ) and stirred water–acetone (v/v 1:3, 3 mL) mixture of olefin (1 mmol), catalyst  $Q_3Mn^{III}$  (0.02 mmol),  $NH_4OAc$  (0.2 mmol), and  $HOAc$  (0.1 mmol), 10%  $H_2O_2$  (1.5 mmol) was added dropwise over a specified period (generally within a half of the total reaction time length) to improve the utilization efficiency of  $H_2O_2$ . After  $H_2O_2$  was consumed, the catalyst was separated from the reaction mixture by filtration, and the filtrate was analyzed on an Agilent 6890N gas chromatography (GC) with a HP-5 quartz capillary column ( $30\text{ m} \times 0.32\text{ mm} \times 0.25\text{ }\mu\text{m}$ ) and flame ionization detector (FID) using ultra-pure nitrogen as a carrier gas (rate  $1.0\text{ mL/min}$ ). Both the injector and detector temperature were  $250\text{ }^\circ\text{C}$ , and the column temperature was between  $90$  and  $170\text{ }^\circ\text{C}$ . The isolated epoxides were determined by  $^1H$  NMR and also satisfactorily identified by comparing their MS spectra with those of the authentic samples.

## 3. Results and discussion

### 3.1. Characterization of $Q_3Mn^{III}$ complexes

The diffusion reflection UV–vis spectra of the solid  $Q_3Mn^{III}$  complexes (**1b**, **1d**, and **1e**) were very similar (Fig. 1), consisting of two bands in the 269–346 nm region that can be assigned to the  $\pi \rightarrow \pi^*$  transitions of ligands. The complexes also exhibited a strong band at ca. 400–428 nm, probably as a result of

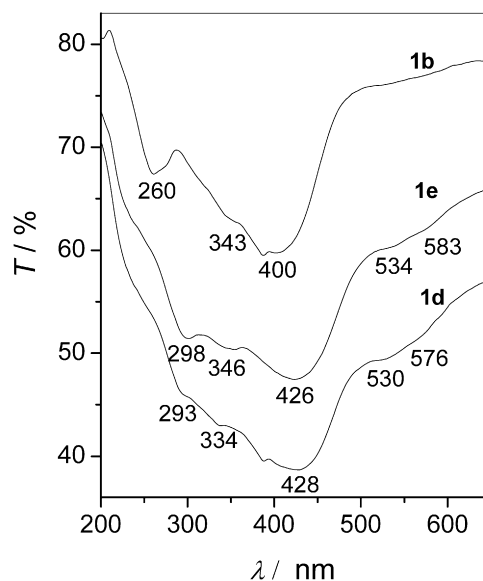


Fig. 1. The diffusion reflection UV–vis spectra of some typical solid  $Q_3Mn^{III}$  complexes.

the metal-to-ligand charge transfer (MLCT) reported for other  $Mn(III)$  complexes [8]. In addition, the two very weak bands in the 530–583 nm region may be attributed to the spin-allowed d–d transitions of the centered  $Mn$  ions, supporting the supposition that the  $Q_3Mn^{III}$  complexes have a distorted octahedral geometry [9].

### 3.2. Catalytic epoxidations

The epoxidation of styrene with aqueous  $H_2O_2$  was used to check the catalytic performances of  $Q_3Mn^{III}$ ,  $Q_3Fe^{III}$ , 5-nitryl-8-quinolinolato  $Mn^{III}Cl$  (**1\*f**), and salen- $Mn^{III}Cl$  complexes, and the obtained results are listed in Table 1. To our delight, the hexadentate  $Q_3Mn^{III}$  complexes (**1a–1e**), with the help of  $NH_4OAc$ – $HOAc$ , exhibited modest to high activity and excellent epoxidative selectivity in water–acetone media, whereas the tetradentate **1\*f** and salen- $Mn^{III}Cl$ , as well as the hexadentate  $Q_3Fe^{III}$ , all gave very poor epoxide yields under the same reaction conditions (entries 6–8). These findings suggest that the ligand, metal ion, and chelate mode had a significant affect on the catalytic efficiency of these catalysts. Entries 2–5 further show that the substituents of 8-hydroxyquinoline (8-HQ) had a large influence on the catalytic performances of  $Q_3Mn^{III}$  complexes. Compared with 8-HQ-based  $Q_3Mn^{III}$  (**1a**), the 5- and 7-halogenated  $Q_3Mn^{III}$  catalysts (**1b–1e**) significantly improved the epoxide yield (80–98%). The activity followed an increasing sequence of **1e** > **1d** > **1c** > **1b**, most likely due to the increase of electron-donating effect of halogen substituents from Cl, Br to I on the ligand's aryl ring and the high resistance of halogenated 8-HQ ligands against oxidative degradation of the  $Q_3Mn^{III}$ , as reported for chlorinated porphyrin- $Mn^{III}$  [10].

The effects of additives were further studied with catalyst **1e** as an example (entries 9–12). In the absence of additives, **1e** demonstrated relatively low catalytic efficiency (entry 9). Among the additives examined, the  $NH_4OAc$ – $HOAc$  mixture

Table 1  
The epoxidation of olefins with aqueous H<sub>2</sub>O<sub>2</sub> catalyzed by Q<sub>3</sub>Mn<sup>III</sup> complexes<sup>a</sup>

Entry	Catalyst	Substrate	Additive (mmol)	Time (h)	Conversion (%)	Selectivity for epoxide (%)
1	<b>1a</b>			2	60	98
2	<b>1b</b>			2	82	98
3	<b>1c</b>			4	85	98
4	<b>1d</b>	Styrene	NH <sub>4</sub> OAc (0.2)	2	90	98
5	<b>1e</b>		+ HOAc (0.1)	2	100	98
6 <sup>b</sup>	<b>1*f</b>			2	30	95
7 <sup>c</sup>	Salen–Mn <sup>III</sup>			2	8	90
8	Q <sub>3</sub> Fe <sup>III</sup>			48	21	25
9	<b>1e</b>		No additive	5	27	96
10	<b>1e</b>		NH <sub>4</sub> OAc (0.2)	2	84	98
11	<b>1e</b>	Styrene	HOAc (0.1)	14	88	95
12	<b>1e</b>		NH <sub>4</sub> OAc (0.2) + NH <sub>3</sub> ·H <sub>2</sub> O (0.1)	2	25	96
13 <sup>d,e</sup>	<b>1e</b>	1-Hexene		20	62	83
14 <sup>d,e</sup>	<b>1e</b>	1-Octene		24	50	95
15	<b>1e</b>	β-Pinene		2	100	99
16 <sup>f</sup>	<b>1e</b>	α-Methyl styrene	HOAc (0.1)	3	98	98
17 <sup>d,g</sup>	<b>1e</b>		+ NH <sub>4</sub> OAc (0.2)	4	95	85
18 <sup>d,g</sup>	<b>1e</b>	Cyclohexene		4	95	85
19 <sup>d,g</sup>	<b>1e</b>			4	93	85
20	<b>1e</b>	<i>trans</i> -2-hexene-1-ol		4	73	80

<sup>a</sup> Unless otherwise specified, the reactions were performed using substrate (1 mmol), catalyst Q<sub>3</sub>Mn<sup>III</sup> (2% molar percentage), 10% H<sub>2</sub>O<sub>2</sub> (1.5 mmol) and water/acetone (1/3, 3 mL) at 10 °C; H<sub>2</sub>O<sub>2</sub> was added dropwise to the solution. Conversion and selectivity for olefins were determined by GC using an internal standard technique.

<sup>b</sup> Using MnCl<sub>2</sub> as a Mn source.

<sup>c</sup> Salen–Mn<sup>III</sup>Cl was prepared from *N,N'*-bis(salicylidene) ethylenediamine and MnCl<sub>2</sub> following reported procedures [2].

<sup>d</sup> 0.05 mmol NH<sub>4</sub>OAc and 0.05 mmol HOAc were added.

<sup>e</sup> 1.5 mmol H<sub>2</sub>O<sub>2</sub> (30%) and water/acetone (v/v 1/4, 3 mL) were added.

<sup>f</sup> **1e** of 3.5% molar percentage was used.

<sup>g</sup> Entry 17 used the fresh **1e**, 18 and 19 employed the recovered **1e** once and twice, respectively.

(pH 7.13 in the water–acetone medium) gave the highest epoxide yield (entry 5), although NH<sub>4</sub>OAc (pH 8.09 in its water–acetone solution) was very effective in increasing the epoxidative efficiency (entry 10), and HOAc (pH 5.23 in its water–acetone solution) also exhibited good results, provided that reaction time was prolonged (entry 11). However, the weak basic additives NH<sub>4</sub>OAc–NH<sub>3</sub>·H<sub>2</sub>O (pH 9.24 here) gave very disappointing results (entry 12). These findings indicate that the pH value of reaction medium plays a key role in the catalytic performance of the Q<sub>3</sub>Mn<sup>III</sup> complexes.

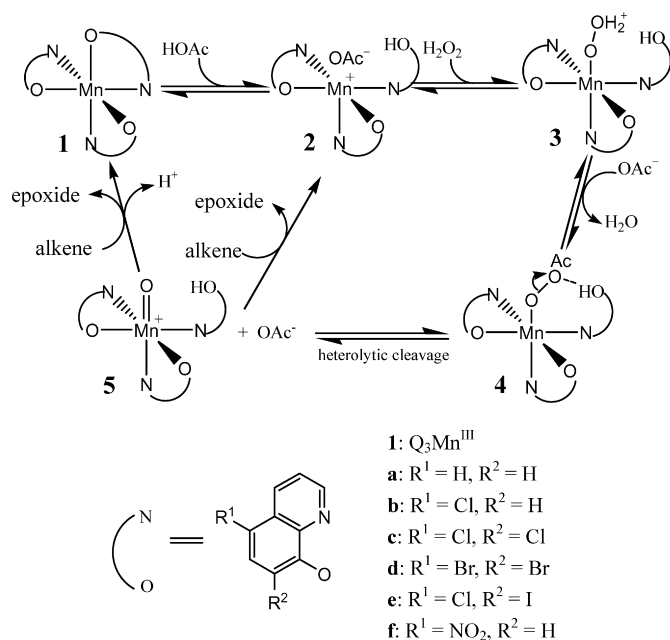
Entries 13–19 further illustrate that the Q<sub>3</sub>Mn<sup>III</sup> catalyst **1e** also was very efficient for the epoxidation of other unfunctionalized alkenes. 1-Hexene and 1-octene as nonactivated terminal olefins could give >50% conversion and modest to excellent selectivity using a relatively low terminal oxidant excess (1.5 equivalents of H<sub>2</sub>O<sub>2</sub>; see entries 13 and 14). β-Pinene was nearly quantitatively oxidized to its epoxide without cyclobutane rupture (entry 15). Entry 16, for the epoxidation of α-methyl styrene, illustrates that even extremely acid-sensitive epoxide can be formed with 98% selectivity, indicating that the ligand's basicity of the Q<sub>3</sub>Mn<sup>III</sup> can suppress the opening side reactions of the desired epoxide by decreasing the Lewis acidity of Mn<sup>3+</sup> ions. The reuse of the catalyst **1e** was checked by the epoxidation of cyclohexene; the catalyst could be filtered from the reaction media and reused twice without loss of activity

(entries 17–19). Finally, entry 20 illustrates that the *trans*-2-hexene-1-ol as a functionalized alkene also could be selectively oxidized to form the corresponding epoxide with modest yield, but the hydroxyl of allylic alcohol was partly oxidized to form the corresponding aldehyde as byproduct.

### 3.3. Catalytic mechanism

To investigate the catalytic mechanism of the Q<sub>3</sub>Mn<sup>III</sup> epoxidation system, *in situ* CV and QCM methods were used to study the Q<sub>3</sub>Mn<sup>III</sup>, Q<sub>3</sub>Fe<sup>III</sup>, 5-nitryl-8-quinolinolato Mn<sup>III</sup>Cl (**1\*f**), and salen–Mn<sup>III</sup>Cl complexes, as detailed in the Supporting Information. Therein, the main results and conclusions are summarized as follows:

1. Cyclic voltammography for **1e** and its ligand (**e**, 5-Cl-7-I-8-HQ) in water–acetone medium showed high quantitative similarity, even at different potential-scan rates and different solution-pH values. Ligand-redox peaks were also found for **1b** and **1d** under identical conditions. These findings suggest that these pristine hexadentate Q<sub>3</sub>Mn<sup>III</sup> catalysts with Mn<sup>3+</sup>(d<sup>4</sup>) ions could cleave at the axial Mn<sup>III</sup>–O coordination site in the water–acetone medium to give pentadentate structures with pendant electroactive hydroxyl groups, as depicted in Scheme 1.



Scheme 1. Proposed catalytic cycle.

- Obvious Mn-redox peaks for the effective hexadentate  $Q_3Mn^{III}$  catalysts were not seen in the water–acetone medium, but their Mn-redox peaks were evident in the *N,N*-dimethylformamide (DMF) medium, likely due to the limited solubility values, the enhanced steric hindrance of the ligands (hexadentate) to the interfacial electron transfer of Mn, and the possible masking of the ligand-redox peaks against Mn-redox peaks in the water–acetone medium.
- In contrast, the Mn-redox peaks of **1\*f** became obvious in both water–acetone and DMF media, suggesting that this complex has a different coordination structure, supporting the elemental analysis results demonstrating that this complex is tetradentate. In addition, the tetradentate salen– $Mn^{III}Cl$  gave its obvious Mn-redox peaks in water–acetone medium.
- No redox waves of ligand and Fe ions were recorded for  $Q_3Fe^{III}$ , supporting that this complex with  $Fe^{3+}(d^5)$  ions owns a stable hexadentate structure (elemental analysis), and it could not be converted to the pentadentate structure with pendant electroactive hydroxyl groups.
- The QCM experiments showed that the dissolution of the **1e** coated on a QCM Au electrode became faster soon after the HOAc was added to an aqueous  $NH_4OAc$ , but such a phenomenon was not observed for the  $Q_3Fe^{III}$  under the same experimental conditions, also demonstrating in the coexistence of HOAc and  $NH_4OAc$  that the hexadentate **1e** was able to open to give a more soluble pentadentate structure, but the  $Q_3Fe^{III}$  with a stable hexadentate structure could not.

The **1e** epoxidation system was further examined by UV–vis spectroscopy; the results are illustrated in Fig. 2, in which **A** is the spectrum of **1e** in acetone where an absorption band

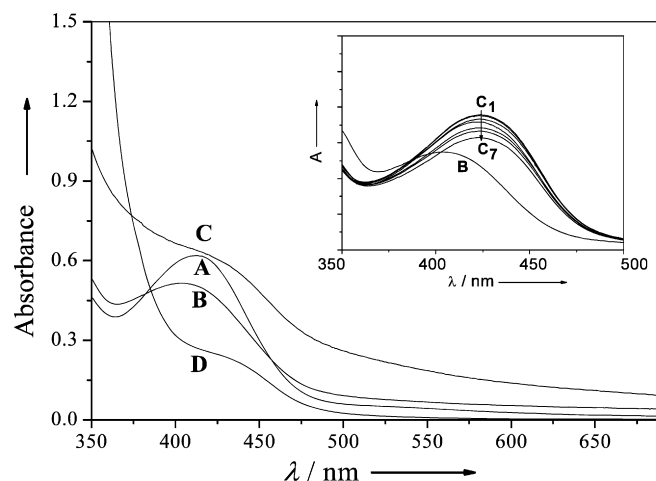


Fig. 2. UV–vis spectra of (A) an acetone solution of catalyst **1e** ( $6 \times 10^{-5}$  M, 4 mL); (B) a water–acetone (v/v 1/3, 4 mL) solution of **1e** ( $6 \times 10^{-5}$  M) and  $NH_4OAc$ –HOAc; (C) adding 3  $\mu$ L 30%  $H_2O_2$  to the solution **B**; (D) adding 0.2 mmol styrene to the solution **C**. Inset shows visible absorption spectral changes observed upon adding 1  $\mu$ L 30%  $H_2O_2$  to a acetone–water (v/v 3/1) solution of catalyst **1e** and  $NH_4OAc$ –HOAc (**B**), spectral scanning was taken at average 3 min intervals (**C**<sub>1</sub>–**C**<sub>7</sub>).

with  $\lambda_{max} \sim 412$  nm is assigned to the metal to ligand charge transfer (MLCT) [8]. When **1e** was dissolved in water–acetone containing  $NH_4OAc$ –HOAc, this MLCT absorbance decreased significantly and exhibit some blue shifting ( $\lambda_{max} \sim 402$  nm, see **B** in Fig. 1), possibly due to the cleavage of axial Mn–O bond of **1e** to form intermediate **2** (see Scheme 1). After aqueous  $H_2O_2$  was added to this solution, repeated scanning revealed a successive change in the MLCT absorbance (inset in Fig. 2); specifically, the MLCT band immediately became shifted to  $\lambda_{max} \sim 424$  nm and its intensity increased significantly after the addition of  $H_2O_2$  (**B** vs **C**<sub>1</sub> in the inset), indicating that  $H_2O_2$  interacted with **2** to form a new intermediate. Subsequently, the MLCT absorbance gradually decreased with time (**C**<sub>1</sub> to **C**<sub>7</sub>), implying the further change in such a new intermediate. After several hours, a new absorption band centered around 500 nm was developed, the maximum of which was obscured by the tailing of strongly absorbing species at  $\lambda_{max} > 500$  nm (**C** in Fig. 2), as reported by Kochi et al. using salen–Mn mediated epoxidations with iodobenzene [11]. This spectral change should be assigned to the formation of  $Q_3Mn^V=O$  (**5** in Scheme 1) through a heterolytic cleavage of O–O bond. After the addition of the substrate (styrene), it gave a spectrum **D** that illustrates that the  $Q_3Mn^V=O$  species is involved in oxygen atom transfer stage. But if the salen– $Mn^{III}Cl$  was treated with aqueous  $H_2O_2$  under the aforementioned experimental conditions, its MLCT absorbance continuously decreased, and a slight blue shift of the salen’s  $\pi \rightarrow \pi^*$  band ( $\lambda_{max} \sim 337$  nm) occurred simultaneously with time (Fig. 3). This spectral change likely implies that the salen– $Mn^{III}Cl$  induces homolytic cleavage of the O–O bond of  $H_2O_2$  to generate free radicals in solution, which leads to spurious reactions that can degrade the catalyst [7], as supported by the foregoing catalytic experiment (see entry 7).

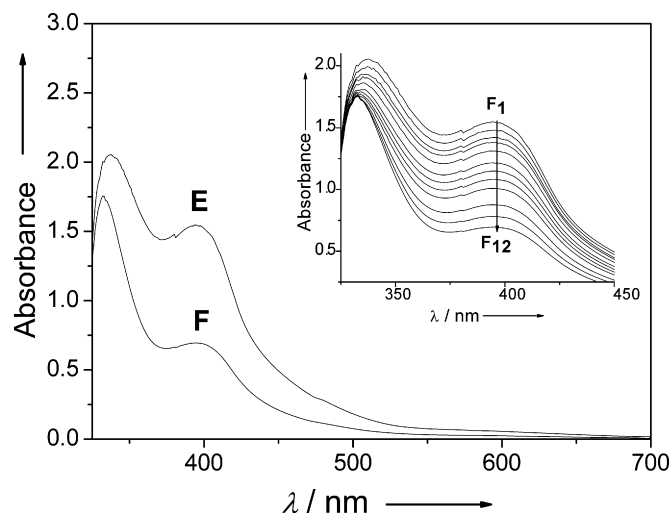


Fig. 3. UV-vis spectra of (E) a solution of salen-Mn<sup>III</sup>Cl ( $1 \times 10^{-4}$  M) in acetone–water (v/v 3/1, 4 mL) containing NH<sub>4</sub>OAc–HOAc; (F) adding 2  $\mu$ L 30% H<sub>2</sub>O<sub>2</sub> to the solution E. Inset shows the successive changes of UV-vis absorption spectra observed upon adding 2  $\mu$ L 30% H<sub>2</sub>O<sub>2</sub> to the solution E, spectral scanning was taken at average 5 min intervals (F<sub>1</sub>–F<sub>12</sub>).

Based on our findings, a mechanism for Q<sub>3</sub>Mn<sup>III</sup> system is proposed (Scheme 1). Theoretically, because of the Jahn–Teller effect of Mn<sup>3+</sup> ions with d<sup>4</sup> [12], it is anticipated that the Q<sub>3</sub>Mn<sup>III</sup> (1) has a distorted octahedral structure with an axial Mn–O bond longer than its equatorial Mn–O bond. The axial Mn–O bond may be more easily cleaved to form a more soluble pentadentate structure with pendant hydroxyl groups (2) in the presence of NH<sub>4</sub>OAc–HOAc due to competitive O–H bonding. Then the 2, which has a basic structure similar to that of porphyrin- or salen-Mn<sup>III</sup> with imidazole as its axial ligand [13,14], may activate H<sub>2</sub>O<sub>2</sub> to form an intermediate 3. The 3 eventually may be converted to form an intermediate Q<sub>3</sub>Mn<sup>V</sup>=O (5) after undergoing a pathway of forming an intermediate 4 with the help of OAc<sup>−</sup> ions, as reported for the porphyrin-Mn<sup>III</sup> catalyzed epoxidation of alkenes [15]. Notably, the pendant O–H group near the Mn<sup>3+</sup> ions in intermediate 2 likely acts as a highly active and competitive coordination group to prevent the catalyst from forming the  $\mu$ -oxomanganese dimers [7]. On the other hand, it easily forms intramolecular hydrogen bond with Mn<sup>III</sup>–O–OAc group in intermediate 4 (Scheme 1), which can activate the O–O bond toward heterolytic cleavage to form Mn<sup>V</sup>=O active species. These two effects can explain why the Q<sub>3</sub>Mn<sup>III</sup> has much better stability and higher efficiency of H<sub>2</sub>O<sub>2</sub> utilization compared with salen-Mn<sup>III</sup>Cl in water–acetone medium containing NH<sub>4</sub>OAc–HOAc.

#### 4. Conclusion

In summary, for the first time we have developed hexadentate Q<sub>3</sub>Mn<sup>III</sup> complexes as very efficient catalysts for epoxi-

dation of olefins with aqueous H<sub>2</sub>O<sub>2</sub>, and have introduced *in situ* CV and QCM methods for studying the catalytic mechanisms of the Q<sub>3</sub>Mn<sup>III</sup> complexes. This system has the following advantages: (i) utilization of more cost-effective and green water–acetone solvent, (ii) facile operation, and (iii) very high catalytic efficiency and stability. The system also may be exploited in the future for industrial applications and asymmetric epoxidation. Moreover, the CV and QCM tests provide much useful information on catalytic mechanism, and they can be expected to find wider applications in catalytic science and technology, including electrochemistry-assisted redox catalysis.

#### Acknowledgments

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#### Supplementary material

The online version of this article contains additional supplementary material (preparation of Q<sub>3</sub>Fe<sup>III</sup> complex; elemental analyses; CV and QCM tests of the catalysts).

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