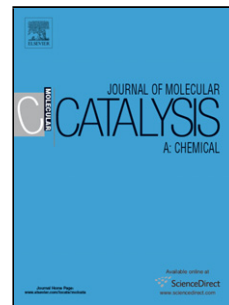


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Weakly distorted 8-quinolinolato iron(III) complexes as effective catalysts for oxygenation of organic compounds by hydrogen peroxide

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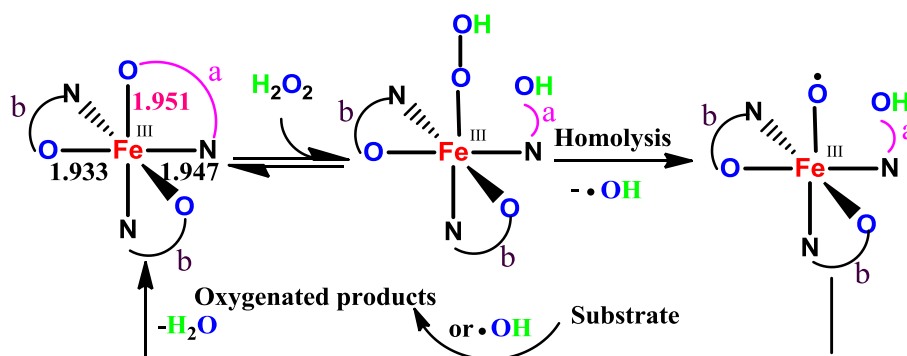
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Graphical abstract

Two heteroleptic 8-quinolinolato iron (III) ($\text{Qa}_1\text{Qb}_2\text{Fe}^{\text{III}}$, $\text{Qa}_2\text{Qb}_1\text{Fe}^{\text{III}}$) complexes designed by us were found to show a higher activity for the selective oxidation of organic compounds by hydrogen peroxide compared to the corresponding homoleptic ones, which should be due to their weakly distorted effect.



Highlights

- Two heteroleptic 8-quinolinolato iron(III) complexes were synthesized.
- The heteroleptic complexes showed a superiority for the catalyzed-oxygenation of hydrocarbons.
- This predominance was due to a structural distortion effect of both.
- A free radical mechanism for the catalytic system was proposed.

Abstract

This paper first discloses that two heteroleptic 8-quinolinolato iron(III) complexes ($\text{Qa}_1\text{Qb}_2\text{Fe}^{\text{III}}$, $\text{Qa}_2\text{Qb}_1\text{Fe}^{\text{III}}$) could be synthesized conveniently *via* the coordination of $\text{FeCl}_2 \cdot 6\text{H}_2\text{O}$ with 2 equivalents of 5,7-dichloro-8-hydroxyquinoline (Qb) or 5-chloro-8-hydroxyquinoline (Qa) under N_2 and then 1 equivalent of Qa or Qb under air. In comparison with the two homoleptic counterparts ($\text{Qa}_3\text{Fe}^{\text{III}}$ and $\text{Qb}_3\text{Fe}^{\text{III}}$), the proposed heteroleptic $\text{Q}_3\text{Fe}^{\text{III}}$ complexes possessed similar coordination features to the $\text{Qb}_3\text{Fe}^{\text{III}}$ one but showed similar catalysis performances to the $\text{Qa}_3\text{Fe}^{\text{III}}$ one in the oxygenation of cyclohexane to cyclohexanol and cyclohexanone by hydrogen peroxide (H_2O_2) in acetonitrile. More importantly, both heteroleptic $\text{Q}_3\text{Fe}^{\text{III}}$ complexes showed a better accelerating effect on this reaction and provided a slightly higher conversion than the $\text{Qa}_3\text{Fe}^{\text{III}}$ and especially $\text{Qb}_3\text{Fe}^{\text{III}}$ ones. Furthermore, this predominance in catalytic activity was more strikingly apparent upon both-catalyzed oxygenations of benzene, toluene, ethylbenzene or thioanisole by H_2O_2 . This should be due to a structurally distorted effect of the heteroleptic $\text{Q}_3\text{Fe}^{\text{III}}$ complexes the is induced by the different in ligand environment, as supported by DFT B3LYP/6-311G (d) calculation. Based the present reaction and UV-Vis spectral characterization results, a free radical mechanism for the present catalysis system was proposed.

Keywords: Heteroleptic 8-quinolinolato iron (III) complexes; Distorted effect; Catalytic oxygenation; Hydrogen peroxide; Organic compounds

1. Introduction

The selective oxygenation of inactivated hydrocarbons by hydrogen peroxide (H_2O_2) and especially dioxygen (O_2) or air constitutes an extremely important field of contemporary chemistry [1-5] due to the large demand for their oxidized products. And yet the well-known inertness of such hydrocarbons makes their transformation be a challenge from a basic science viewpoint. For example, the current industrial process for producing cyclohexanone and cyclohexanol (i.e. KA oil), important raw materials for the production of caprolactam and adipic acid, mainly relies on the cobalt-catalyzed oxidation of cyclohexane with air under harsh conditions (temperatures of 443~503 K and pressures of 10~15 bar), which should suppress cyclohexane conversion (lower than 10%) to obtain a relatively high selectivity for KA oil (*ca.*70%) [4, 6-9].

In recent decades, the oxygenation of hydrocarbons through the action of metal complexes seems to be a very promising field, particularly when the complexes act as catalysts. This is mainly because the oxygenation of hydrocarbons by O_2 and especially H_2O_2 with metal complexes as catalysts occurs at relatively low temperatures and can be selective [9-24]. Among the transition metal complexes chiefly used as catalysts, metallo-porphyrin complexes are currently of considerable interest to promote these oxygenation reactions [10-14, 25-29]. The relatively high cost of this type of complexes, however, still hampers their commercialized applications.

Recently, our groups have reported that homoleptic 8-quinolinolato manganese(III) complexes ($\text{Q}_3\text{Mn}^{\text{III}}$) combined with H_2O_2 , constitute a valuable new family of heterogeneous systems for the epoxidation of olefins [30], the selective oxygenation of alcohols [31], thioanisole [32] and ethylbenzene [33]. This should be due to the distorted octahedral structure of these homoleptic $\text{Q}_3\text{Mn}^{\text{III}}$ complexes [30-32]. But more cost-effective homoleptic 8-quinolinolato iron(III)

complexes (Q_3Fe^{III}) show a poor activity for the epoxidation of olefins by H_2O_2 due to their symmetrically octahedral geometry [30]. More recently, our groups reported that visible light can obviously accelerate the homoleptic Q_3Fe^{III} complexes-catalyzed oxygenation of cyclohexane by H_2O_2 , which may originate from that the excited Q_3Fe^{III} complexes react with H_2O_2 more easily than the ground-state counterparts [34]. It is interesting to explore the preparation of heteroleptic Q_3Fe^{III} complexes with a distorted octahedral geometry and their potential advantages in catalysis oxygenations. To achieve this goal, for the first time the two heteroleptic Q_3Fe^{III} complexes were designed and synthesized *via* the centered iron ions successively coordinated 8-hydroxyquinoline ligands with different substituents and both catalytic performances were checked and compared with those of the homoleptic counterparts using the selective oxygenation of benzene, toluene, ethylbenzene, thioanisole and especially cyclohexane by H_2O_2 .

2. Experiment Section

2.1. Materials and apparatus

Materials and reagents used in this study were cyclohexane, benzene, toluene, ethylbenzene thioanisole, n-hexanol, acetonitrile (MeCN), anhydrous tetrahydrofuran (THF), ethanol, 30% aqueous hydrogen peroxide (H_2O_2), iron (III) trichloride ($FeCl_3 \cdot 6H_2O$), iron (II) dichloride ($FeCl_2 \cdot 4H_2O$), 5-chloro-8-hydroxyquinoline (Qa), 5, 7-dichloro-8-hydroxyquinoline (Qb), all of which were of analytical grade. Distilled water was used throughout this experiment.

Transmission FT-IR and UV-Vis diffuse reflectance spectra of samples were recorded from 400 to 4000 cm^{-1} on a Nicolet Nexus 510 P FT-IR spectroscopy as KBr disc and from 220 to 1000 nm on a DUV-370D spectrophotometer with $BaSO_4$ as a standard (Shimadzu, Japan), respectively.

Their liquid UV-Vis spectra in MeCN were recorded from 200 to 800 nm on UV-2450 spectrophotometer (Shimadzu, Japan). X-ray powder diffraction (XRD) analysis of the samples was carried out on a X'PERT³ powder diffractometer apparatus using Cu K α radiation ($\lambda=0.15406$ nm) and a graphite monochromator, operated at a voltage of 40 kV and a current of 40 mA. Diffraction patterns were recorded in the angular range of 5-50° with scanning rate 0.05°/s.

2.2. Preparation of 8-quinolinolato iron (III) complexes

The preparation procedure for two homoleptic 8-quinolinolato iron(III) complexes (Qa₃Fe^{III} and Qb₃Fe^{III}) could be found in our recent publication [34]. The preparation procedure for two heteroleptic Q₃Fe^{III} complexes is described as follows: the ligand Qb or Qa (4 mmol) was dissolved in 20 ml of anhydrous THF to obtain a solution, designated as “A”, and FeCl₂·4H₂O (2 mmol) was dissolved in 20 ml of THF to form the solution “B”, to which an excess amount of iron powder was added to prevent oxidation of ferrous ions to ferric ions. The solution “A” was added dropwise to the solution “B” under N₂ and then the reaction mixture was stirred at room temperature until the ligand Qb or Qa was consumed completely. After the iron powder was removed with a magnetic separation method, another ligand Qa or Qb (2 mmol) in anhydrous THF (10 mL) was added dropwise to the above reaction mixture under air, and then the reaction mixture was stirred at room temperature until the ligand Qa or Qb was consumed completely. Finally, the resulting precipitate was filtrated and washed with ethanol for three times. After air-drying, a black solid (denoted as Qa₁Qb₂Fe^{III} or Qa₂Qb₁Fe^{III}) was obtained in 90-95% yield. The Fe contents of four 8-quinolinolato Fe^{III} complexes were determined by conventional EDTA titration and the results are listed in Table 1. Herein, the found values for Qa₃Fe^{III} and Qb₃Fe^{III}

were in good agreement with those calculated from the corresponding formulae of the hexadentate structures. However, the found value for $Q_{a_1}Q_{b_2}Fe^{III}$ or $Q_{a_2}Q_{b_1}Fe^{III}$ was obviously higher than its calculated one, this is likely because a small amount of iron powder or tetradentate $Q_{a_2}Fe^{II}/Q_{b_2}Fe^{II}$ complexes still remains in the heteroleptic Q_3Fe^{III} complex with a hexadentate structure.

2.3. General procedure for oxygenation of organic compounds

30 % Aqueous H_2O_2 solution (0.5-4 mmol) was added to a stirred mixture of acetonitrile (MeCN, 3mL), substrate (1 mmol) and catalyst Q_3Fe^{III} (0.01 mmol) and then the reaction mixture was stirred magnetically at 12-35 °C. After the desired reaction time had elapsed, the addition of MnO_2 decomposed the residual H_2O_2 and the solid residue was filtrated from the reaction solution, the resulting filtrate was subjected to an analysis of the oxygenated products. The content of various oxygenated products was measured on an Agilent 6890N gas chromatography with a DB-17 polysiloxane capillary column (30 m × 0.32 mm × 0.50 μm) and flame ionization detector (FID) using n-hexanol as an internal standard. Both the injector and detector temperature were 250°C, and the column temperature was 80-120°C. Each experiment was conducted in triplicate, the data deviation between three parallel experiments was lower than ca. 5%.

3. Results and discussion

3.1. Characterization of Q_3Fe^{III} complexes

The structure of Q_3Fe^{III} complexes was investigated by means of the density functional theory method (DFT B3LYP) with 6-311G(d) basis set and all the calculations were conducted on the Ganssinan-03 version C02 package with tight self-consistent field (SCF) convergence and ultrafine integration grids. Table 1 lists the Fe-O bond distances and the highest occupied and

lowest unoccupied molecular orbital (HOMO and LUMO) energies for the Q_3Fe^{III} complexes. It is seen from Table 1 that the three Fe–O bonds of Qa_3Fe^{III} or Qb_3Fe^{III} complex were exactly equal to each other in length, indicating that the two homoleptic Q_3Fe^{III} complexes possess a symmetrically octahedral geometry. On the contrary, the three Fe–O bonds of $Qa_1Qb_2Fe^{III}$ or $Qa_2Qb_1Fe^{III}$ complex were not equal to each other in length and there was one Fe–O bond to be the longest among them, indicating that both the heteroleptic Q_3Fe^{III} complexes have a distorted octahedral geometry. In comparison with the differences among the Mn–O bonds in the Q_3Mn^{III} complexes previously reported by us [31, 32], both heteroleptic Q_3Fe^{III} complexes exhibited much smaller differences among their Fe–O bonds (see Δ Fe–O value listed in Table 1), illustrating that such two complexes belong to a weakly distorted octahedral geometry. The HOMO or LUMO energy of these Q_3Fe^{III} complexes followed an ascending order: $Qa_3Fe^{III} > Qa_2Qb_1Fe^{III} > Qa_1Qb_2Fe^{III} > Qb_3Fe^{III}$, implying that the reactivity of Q_3Fe^{III} complexes with H_2O_2 should be the same sequence with their HOMO or LUMO energy.

Fig. 1 shows the FT-IR spectra of four Q_3Fe^{III} complexes and the corresponding ligands. It is seen from Fig. 1 that the FT-IR spectra of ligands (Qa and Qb) were similar to each other, consisting of one O–H stretching at 3192 cm^{-1} , three C=C stretching bands near $1400\text{--}1510\text{ cm}^{-1}$, one C=N stretching band at 1589 cm^{-1} and one C–O stretching band near $1045\text{--}1094\text{ cm}^{-1}$ [35–37]. Such characteristic IR bands in the corresponding Q_3Fe^{III} complexes all took place different degree of shift due to the coordinating effect. Moreover, disappearance of the fundamental stretching frequencies characteristic of OH group in the complexes suggests the occurrence of deprotonation process as the ligand reacts with iron ion [38].

Fig. 2 provides the UV-Vis diffuse reflectance spectra (DRS) of these samples in the 220-800 nm regions. The two ligands displayed a higher energy band near 328 nm, which should originate from the $\pi \rightarrow \pi^*$ transitions of ligands [39]. The Q_3Fe^{III} complexes exhibited two lower energy bands in the 450-640 nm region in addition to the $\pi \rightarrow \pi^*$ band assigned to the ligands. In that, one band in the region of 450-490 nm should be assigned to the ligand to metal charge-transfer transition (LMCT), as observed in an UV-Vis spectrum of the salen Fe(III) complex [40]. Another band in the region of 570-640 nm is responsible for the intense colors of the complex [41]. Notably, the two low energy bands for the Qb_3Fe^{III} was obviously stronger and shifted toward the longer wavelength region compared to both bands for the Qa_3Fe^{III} , illustrating that the Qb_3Fe^{III} generates the charge-transfer transition of ligand to Fe^{III} ion more easily than the Qa_3Fe^{III} . The complexes $Qa_1Qb_2Fe^{III}$ and $Qa_2Qb_1Fe^{III}$ displayed very similar UV-Vis spectral features to the Qb_3Fe^{III} , implying that the ligand Qb plays a dominant role in the coordination features of both heteroleptic Q_3Fe^{III} complexes.

Crystal phase of these samples was measured by X-ray diffraction (XRD) techniques. As shown in Fig. S1, the homoleptic Qa_3Fe^{III} complex exhibited some strong and sharp XRD peaks in the angular range of 8-30° in its XRD pattern, indicating that this complex has a good crystallinity. On the contrary, the XRD pattern of another homoleptic Qb_3Fe^{III} complex only showed several very weak and broad XRD peaks in 5-30°, illustrating that this complex has a poor crystalline quality. Notably, the $Qa_2Qb_1Fe^{III}$ and especially $Qa_1Qb_2Fe^{III}$ complexes exhibited very similar XRD peaks to the Qb_3Fe^{III} , indicating that the crystalline behavior of both heteroleptic Q_3Fe^{III} complexes is mainly dominated by the ligand Qb, which is consistent with the results from UV-Vis characterization. We have tried our best to improve the crystalline quality of heteroleptic

Q_3Fe^{III} complexes, but did not succeed. Therefore, the crystallographic structure information for these complexes can not be given at present.

3.2. Catalytic oxygenation

Table 2 lists the data for the Q_3Fe^{III} complexes-catalyzed oxygenation of cyclohexane by aqueous hydrogen peroxide (H_2O_2) in acetonitrile (MeCN) at 12 °C. As predicted above, the Qa_3Fe^{III} complex presented a good activity for cyclohexane oxygenation, achieving ca. 13.0 % cyclohexane conversion at 8 h with cyclohexanol and cyclohexanone as mainly oxygenated products (Entry 1). But the Qb_3Fe^{III} complex showed a poor activity for this oxygenation under the same conditions (Entry 2). Interestingly, the $Qa_1Qb_2Fe^{III}$ and $Qa_2Qb_1Fe^{III}$ complexes possessed a better activity for this oxygenation compared to the Qa_3Fe^{III} and especially Qb_3Fe^{III} complexes, respectively providing ca. 19.8 and 20.3 % conversion under the same conditions (Entries 3 and 4). If a mechanical mixture consisting of Qa_3Fe^{III} and Qb_3Fe^{III} with 1:2 molar ratio (its composition was similar to that of $Qa_1Qb_2Fe^{III}$) was used to catalyze this reaction, the conversion is ca. 8.6% under the same conditions (entry 5). These findings support that the catalytic activity of homoleptic Q_3Fe^{III} complex is directly proportional to its HOMO or LUMO energy and the outstanding catalytic activity of heteroleptic complex is likely due to its distorted octahedral geometry that is induced by the difference in the coordination capacity of ligands Qa and Qb to the centered Fe^{III} ions, as supported by the foregoing DFT calculation results.

In the following experiments, the effect of temperature on the oxygenation of cyclohexane by H_2O_2 was checked using $Qa_1Qb_2Fe^{III}$ as a catalyst and the results obtained are listed in table 2. As expected, the accelerated effect of temperature on this reaction was evident. Cyclohexane

conversion gradually increased from 7.8 to 22.0 % with increasing temperature from 0 to 25 °C (Entries 6, 3 and 7). when the temperature was further increased to 35°C, the catalytic reaction was accelerated drastically and the time to achieve ca. 23.7 % conversion was shortened to 2 h (see entry 8).

The effect of reaction time on the oxygenation of cyclohexane by H₂O₂ was examined using the Qa₃Fe^{III} and Qa₁Qb₂Fe^{III} as catalysts, respectively. As shown in Fig. 3, when reaction time was

The effect of reaction time on cyclohexane oxidation was examined using the Qa₃Fe^{III} and Qa₁Qb₂Fe^{III} as catalysts, respectively. As shown in Fig. 3, when reaction time was between 2 and 12 h, the conversion of cyclohexane over Qa₃Fe^{III} increased slowly with the time, and then, it ascended rapidly in 12-24 h and finally achieved ca. 23.2 % at 24 h. After that, the conversion hardly increased with the time (Curve 1) likely due to the oxidative degradation of Qa₃Fe^{III}, which can be confirmed from the facts that the dissolved and decolorized phenomena of Qa₃Fe^{III} were observed clearly during the period of 24-33 h. The selectivity for cyclohexanol continuously and slowly descended with the time (Curve 3), with a concomitant increase in cyclohexanone selectivity (Curve 6). The effect of reaction time on the Qa₁Qb₂Fe^{III}-catalyzed this reaction was very similar to the Qa₃Fe^{III} catalytic system described above, but its conversion went up faster than that of Qa₃Fe^{III} in 2-12 h and achieved ca.22.2 % at 12 h (Curves 2 vs 1 in Fig.3). When the time was further prolonged to 33 h, the conversion was ca. 25.6 %. These findings further indicate that the heteroleptic Qa₁Qb₂Fe^{III} complex has a faster catalysis rate and achieves a slightly higher conversion for this reaction than the homoleptic Qa₃Fe^{III} one.

The effects of the amount of catalyst, oxidant and substrate on cyclohexane oxygenation were checked at 12°C using $Qa_1Qb_2Fe^{III}$ as a catalyst and the results are presented in Fig. S2, S3 and S4, respectively. As shown in Fig. S2, S3 and S4, the increasing catalyst or oxidant amount or the decreasing substrate amount was conducive to improve cyclohexane conversion. For example, when the amount of catalyst was raised from 0.025 to 0.01 mmol, the conversion increased 3.5-fold. When the amount of cyclohexane was reduced 8-fold (from 4.0 to 0.5 mmol), the conversion increased by 23 %. Also, the distribution of oxygenated products was influenced by the variables above-described. The selectivity for cyclohexanol continuously decreased with increasing the amount of catalyst, oxidant or substrate, along with an increase in cyclohexanone selectivity. The optimized amounts of catalyst, substrate and oxidant were 0.01, 1.0 and 4.0 mmol, respectively.

Finally, the Q_3Fe^{III} complexes-catalyzed oxygenation of other substrates, such as benzene, toluene, ethylbenzene and thioanisole by H_2O_2 , was examined in MeCN at 18 °C. As shown in Table 3, the catalyst Qa_3Fe^{III} was still active for the selective oxidation of benzene, toluene and especially ethylbenzene,, respectively providing phenol for benzene, benzaldehyde for toluene and acetophenone for ethylbenzene as their main oxygenated products (Entries 1, 5 and 9). The reactivity of three substrates over Qa_3Fe^{III} complex followed an increasing sequence of ethylbenzene>benzene>toluene. And yet the Qb_3Fe^{III} did not show any activity for these oxygenations (Entries 2, 6 and 10). It is noteworthy that the catalytic activity of both heteroleptic Q_3Fe^{III} complexes for these oxygenations was obviously superior to that of the Qa_3Fe^{III} complex at a predetermined reaction time 8h (Entries 3 and 4 vs 1, 7 and 8 vs 5, 11 and 12 vs 9). For example, the conversions of benzene, toluene and ethylbenzene over the $Qa_1Qb_2Fe^{III}$ complex were ca. 10.1, 9.7 and 24.3 %, being 2-, 3- and 1.0-fold higher than those over the Qa_3Fe^{III} complex, respectively.

Entries 13-16 illustrate that thioanisole oxygenation easily proceeded upon catalysis with these Q_3Fe^{III} complexes, providing methyl phenyl sulfoxide as a main oxidation product. Thioanisole conversion over both heteroleptic Q_3Fe^{III} complexes was ca. 100 %, being higher than those over the Qa_3Fe^{III} (95.5 %) and especially Qb_3Fe^{III} (23.5 %). This further supports that the distorted effect of heteroleptic Q_3Fe^{III} complex can help to improve its activity for the oxygenation of these substrates by H_2O_2 .

3.3. Catalytic mechanism

In order to explore the possible reaction pathway, a stepwise overlay of UV-Vis spectra for $Qa_1Qb_2Fe^{III}$ catalysis system in MeCN at 20°C are illustrated in Fig. 4. As described above in Fig.2, the complex $Qa_1Qb_2Fe^{III}$ displayed two weak and broad coordination bands in 450-600 nm in the presence of cyclohexane (curve **A** in Fig. 4). When H_2O_2 was added to the **A** solution, such two bands decreased immediately (see curve **B0**), which is likely due to the rapid reaction of $Qa_1Qb_2Fe^{III}$ with H_2O_2 . With prolonging the interaction time of H_2O_2 with the complex, both the bands further decayed and were nearly disappeared after 22 min (curve **B1-B4**). Meanwhile the absorbance near 350-380 nm grew gradually (see inset in Fig. 4), which is indicative of the formation of phenoxy radical [40]. Notably, the spectral changes above-described could be noticed in the UV-Vis spectra of Qa_3Fe^{III} catalysis system previously reported by us [34], but both coordinated bands of $Qa_1Qb_2Fe^{III}$ showed a much faster decay with increasing the time than those of Qa_3Fe^{III} (Fig. 5 A vs B). This further confirms that the heteroleptic $Qa_1Qb_2Fe^{III}$ reacts with H_2O_2 more easily than the homoleptic Qa_3Fe^{III} .

Based on the above findings, as well as those in previous studies [42-45], we propose that heteroleptic $Qa_1Qb_2Fe^{III}$ complex (**1** in Scheme 1) easily reacts with H_2O_2 to form a pentadente

Qa₁Qb₂Fe^{III}-OOH with a pendant hydroxyl group (**2**) through opening its longest Fe-O bond. Then, the **2** may undergo a homolytic cleavage of its O-OH bond to generate a Qa₁Qb₂Fe^{III}O (**3**) and OH radicals in solution, which leads to spurious reactions that can degrade the catalyst [46], as supported by the above results of catalytic reactions and UV-vis spectral characterizations. Finally, organic substrates can be oxidized to the corresponding oxygenated products by the **3** or OH radicals, along with the regeneration of catalyst **1**. Probably, the catalytic rate of Q₃Fe^{III} complex depends on its reactivity with H₂O₂. A fast catalytic rate of the homoleptic Qa₃Fe^{III} should originate from its higher HOMO or LUMO orbital energy. While the heteroleptic Q₃Fe^{III} with a distorted octahedral structure, should easily open the longest Fe-O bond to form the intermediate **2** in the participation of H₂O₂, so that its catalysis rate is much faster than that of the homoleptic counterpart with a symmetrically octahedral structure, as supported by the present reaction and UV-vis spectral characterization results.

4. Conclusion

In summary, for the first time we have designed and synthesized two heteroleptic 8-quinolinolato iron (III) (Q₃Fe^{III}) complexes with a weakly distorted octahedral geometry. The proposed two Q₃Fe^{III} complexes show faster catalysis rates and provide higher conversions for the oxygenation of some organic compounds by H₂O₂ compared to the homoleptic counterparts. Having found this kind of the heteroleptic Q₃Fe^{III} complexes with a superior catalysis oxidation performance, we are interested in exploiting the synthesis of other heteroleptic metal complexes and their potential applications for the selective oxygenation of organic compounds by H₂O₂ and more especially dioxygen or air.

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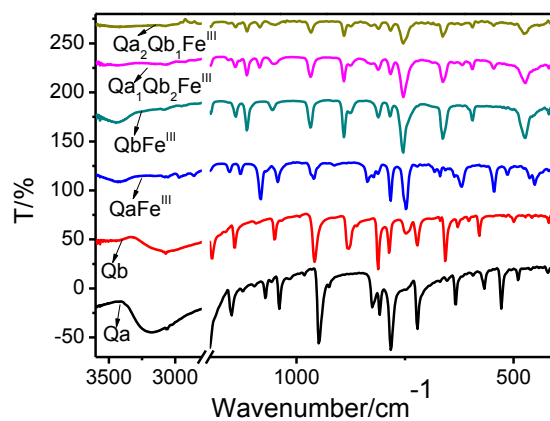


Fig. 1. FT-IR spectra of four Q_3Fe^{III} complexes and their ligands

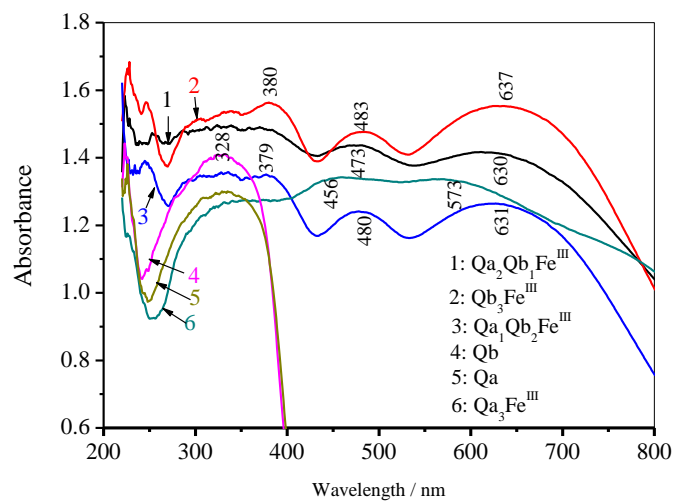


Fig. 2. UV-Vis diffuse reflectance spectra of four Q_3Fe^{III} complexes and their ligands

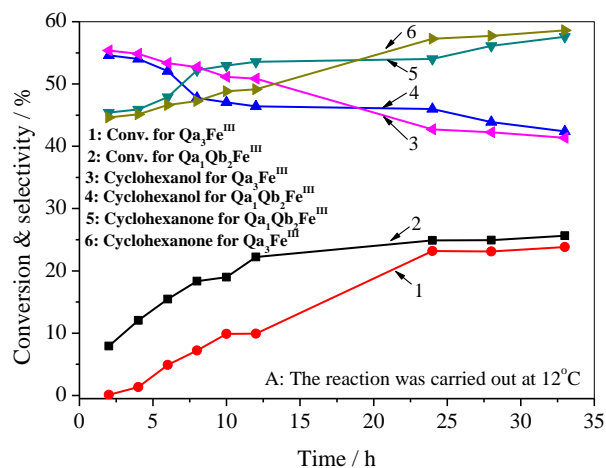


Fig. 3. Reaction time-dependence of conversion and selectivity for the Q_3Fe^{III} -catalyzed cyclohexane oxygenation by H_2O_2 at 12°C in MeCN

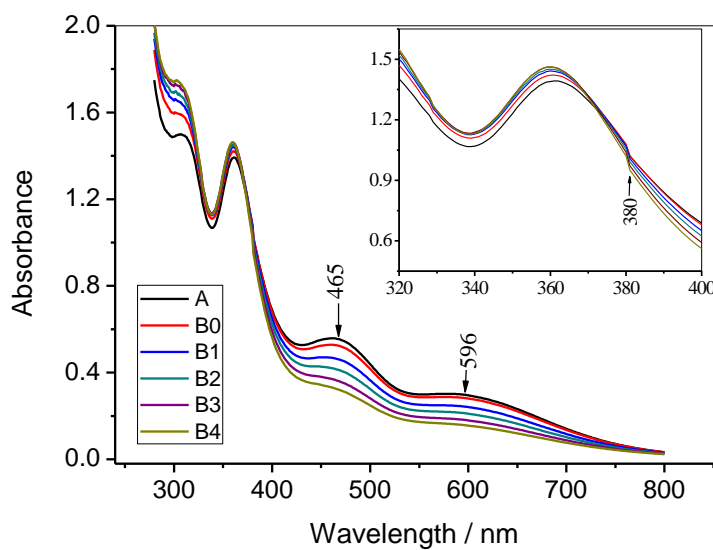


Fig. 4. UV-Vis spectra of (A) a saturated solution of $Q_1Q_2Fe^{III}$ in MeCN (10 ml) and cyclohexane (27 μ mol); **B0**: Adding 13 μ mol 30 % H_2O_2 to the solution **A**; **B1**: 1 min later; **B2**: 2 min later; **B3**: 12 min later; **B4**: 22 min later. Inset is the amplified traces in 350-400 nm.

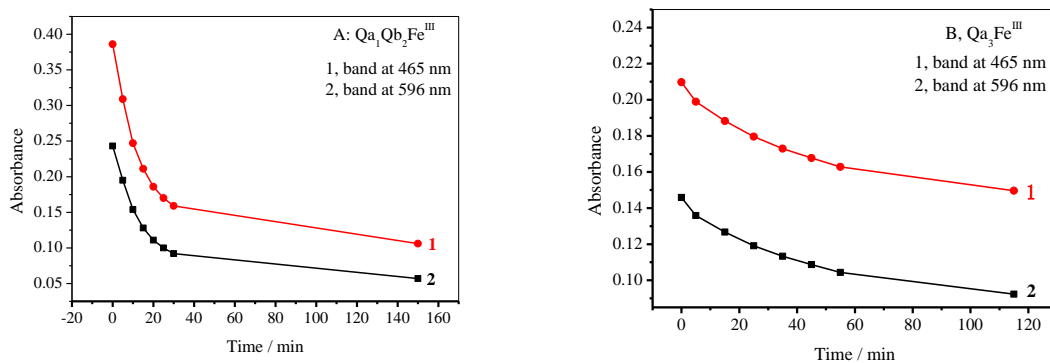
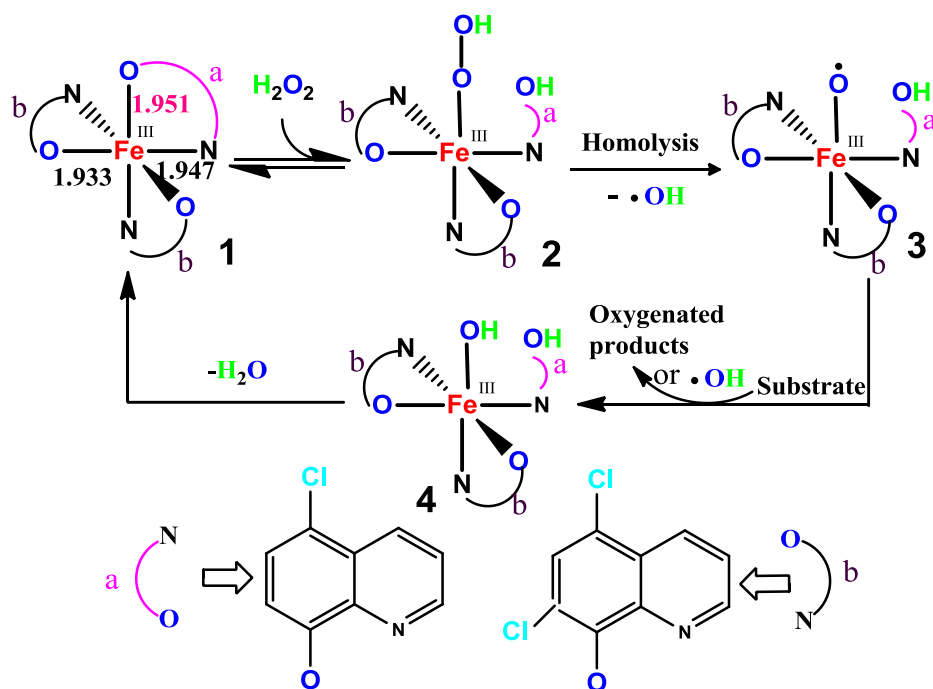


Fig. 5. Decay curves for both the bands at 465 and 596 nm of $Qa_1Qb_2Fe^{III}$ (A) and Qa_3Fe^{III} (B)

complexes with interaction time of H_2O_2



Scheme 1. Proposed reaction *pathway* for the $Qa_1Qb_2Fe^{III}$ -catalyzed oxygenation

Table 1 The iron contents and Fe-O bond distances of Q₃Fe^{III} complexes

Sample	Fe content ^a / wt%		Fe-O bond distances ^b (Å)			HOMO ^b (kcal.mol ⁻¹)	LUMO ^b (kcal.mol ⁻¹)
	found	theoretical	Fe-O1	Fe-O2	Fe-O3		
Qa ₃ Fe ^{III}	9.46	9.49	1.942	1.942	1.942	-133.46	-49.45
			ΔFe-O bond ^c		=0	Δ ^d	84.01
Qb ₃ Fe ^{III}	8.01	8.06	1.944	1.944	1.944	-138.94	-56.26
			ΔFe-O bond ^c		=0	Δ ^d	82.68
Qa ₁ Qb ₂ Fe ^{III}	10.01	8.42	1.933	1.947	1.951	-137.09	-54.67
			ΔFe-O bond ^c		0.011	Δ ^d	82.42
Qa ₂ Qb ₁ Fe ^{III}	10.55	8.95	1.954	1.936	1.940	-135.36	-52.62
			ΔFe-O bond ^c		0.016	Δ ^d	82.74

^aThe iron content of Q₃Fe^{III} complexes was measured by EDTA complexometric titration, their theoretical iron content was calculated based on Q₃Fe^{III} complexes; ^b Their Fe-O bond distances and HOMO LUMO energy were calculated by the B3LYP/6-311+G (d) basis set; ^cΔFe-O bond value for Q₃Fe^{III} = the longest Fe-O bond –(additive value of other two Fe-O bond)/2; ^d Δ value = LUMO energy – HOMO energy.

Table 2 Various Q₃Fe^{III} complexes-catalyzed oxygenation of cyclohexane by H₂O₂ in MeCN ^a

Entry	Catalyst	Temp. / °C	Time / h	Conv. / %	Yield of oxygenated products (%)	
					Cyclohexanol	cyclohexanone
1	Qa ₃ Fe ^{III}	12	8	13.0	6.5	6.5
2	Qb ₃ Fe ^{III}	12	8	0.5	0.3	0.2
3	Qa ₁ Qb ₂ Fe ^{III}	12	8	19.8	10.2	9.6
4	Qa ₂ Qb ₁ Fe ^{III}	12	8	20.3	10.1	10.2
5	Mixture ^b	12	8	8.6	4.3	4.3
6	Qa ₁ Qb ₂ Fe ^{III}	0	8	7.8	3.8	4.0
7	Qa ₁ Qb ₂ Fe ^{III}	25	8	22.0	10.5	11.5
8	Qa ₁ Qb ₂ Fe ^{III}	35	2	22.7	9.9	12.8

^a Reaction conditions: substrate (1 mmol), catalyst (0.02 mmol), 30 % H₂O₂ (4 mmol), MeCN (3 ml). Conversion and yield for products were determined by GC; ^bUsing a mechanical mixture of Qa₃Fe^{III} and Qb₃Fe^{III} with 1: 2 molar ratio

Table 3 Q₃Fe^{III} complexes-catalyzed oxidation of other organic compounds by H₂O₂ in MeCN ^a

Entry	Catalyst	Substrate	Conv./ %	Main oxygenated products (yield / %)
1 ^b	Qa ₃ Fe ^{III}	Benzene	3.3	Phenol (3.2)
2	Qb ₃ Fe ^{III}		0	----
3 ^b	Qa ₁ Qb ₂ Fe ^{III}		10.1	Phenol (9.6)
4 ^b	Qa ₂ Qb ₁ Fe ^{III}		9.8	Phenol (9.5)
5	Qa ₃ Fe ^{III}	Toluene	2.3	Benzaldehyde (2.3)
6	Qb ₃ Fe ^{III}		0	----
7 ^c	Qa ₁ Qb ₂ Fe ^{III}		9.7	Benzaldehyde (6.5)
8 ^c	Qa ₂ Qb ₁ Fe ^{III}		10.8	Benzaldehyde (6.7)
9 ^d	Qa ₃ Fe ^{III}	Ethylbenzene	12.0	Acetophenone (7.3)
10	Qb ₃ Fe ^{III}		0	----
11 ^d	Qa ₁ Qb ₂ Fe ^{III}		24.3	Acetophenone (17.2)
12 ^d	Qa ₂ Qb ₁ Fe ^{III}		26.4	Acetophenone (16.5)
13 ^e	Qa ₃ Fe ^{III}	Thioanisole	95.5	Methylphenyl sulfoxide (91.7)
14	Qb ₃ Fe ^{III}		23.5	Methylphenyl sulfoxide (23.5)
15 ^e	Qa ₁ Qb ₂ Fe ^{III}		100	Methylphenyl sulfoxide (92.1)
16 ^e	Qa ₂ Qb ₁ Fe ^{III}		100	Methylphenyl sulfoxide (93.6)

^a Reaction conditions: substrate (1 mmol), catalyst (0.02 mmol), 30 % H₂O₂ (4 mmol), MeCN (3 ml), the reaction temperature, 18°C, the reaction time, 8h. The oxygenation products were identified by GC-MS and the conversion and product yield were determined by GC; ^bA trace amount of benzoquinone was detected; ^cA small amount of hydroxylated products (o- and m-cresols) was detected; ^dA small amount of benzaldehyde, phenylacetaldehyde and phenethyl alcohol was detected; ^eA small amount of methylphenyl sulfone was detected.