

# $\mu$ -Oxo bridged diiron(III) complexes and hydrogen peroxide: oxygenation and catalase-like activities

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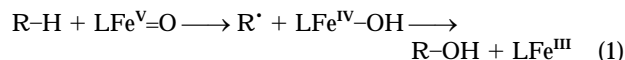
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The crystal structures of two dinuclear iron(III) compounds with a bent  $\mu$ -oxo bridge,  $[\text{Fe}_2\text{O}(\text{CH}_3\text{CO}_2)(\text{tpa})_2][\text{ClO}_4]_3 \cdot 2\text{H}_2\text{O}$  and  $[\text{Fe}_2\text{O}(\text{CH}_3\text{CO}_2)(\text{mep})_2][\text{ClO}_4]_3$ , were determined, where tpa and mep represent tris(2-pyridylmethyl)amine and *N,N'*-dimethyl-*N,N'*-bis(2-pyridylmethyl)ethane-1,2-diamine, respectively. Their structural features which include a ( $\mu$ -oxo)( $\mu$ -acetato)diiron(III) core are very similar. In spite of this, these two complexes exhibit very different reactivity towards hydrogen peroxide in solution; the tpa complex showed high catalase-like activity, whereas that of the mep complex was negligible. In the oxygenation of cyclohexane the mep complex- $\text{H}_2\text{O}_2$  system exhibited high activity giving cyclohexanol and cyclohexanone, but formation of oxygenated products was negligible with the tpa complex- $\text{H}_2\text{O}_2$ . The absorption spectrum of the tpa complex shows no change in the presence of  $\text{H}_2\text{O}_2$ ; however a drastic change was observed in the spectrum of the mep complex on addition of  $\text{H}_2\text{O}_2$ . Based on the structural and spectroscopic data, the structures of the active species for catalase- and oxygenase-like functions and the origin of the differences in reactivity observed for these two compounds are discussed.

The selective oxidation and functionalization of alkanes under mild conditions represent an exciting scientific and economic goal.<sup>1</sup> Although much research has focused on oxidations catalysed by metalloporphyrins (putative cytochrome P-450 mimics), there is a growing interest in catalysis by other types of metal complexes. Notably, Que and co-workers<sup>2</sup> have characterized some non-heme iron catalysts with tripodal tris(2-pyridylmethyl)amine (tpa) ligands,  $[\text{Fe}^{\text{III}}(\text{tpa})\text{X}_2]^+$ , and have employed these complexes together with *tert*-butyl hydroperoxide to oxidize cyclohexane or adamantane in acetonitrile at room temperature. However, these complexes are substantially poorer alkane-functionalization catalysts in the presence of hydrogen peroxide.<sup>3</sup>

Fontecave and co-workers<sup>4</sup> and Fish *et al.*<sup>5</sup> have observed that dinuclear oxo-bridged non-heme iron complexes with bipyridine or tetradentate ligands exhibit high activity for oxygenation of cyclohexane in the presence of hydrogen peroxide, and the former group<sup>4</sup> proposed that a high-valent oxoiron species derived from a metal-peroxide intermediate must participate in the alkane functionalization, *i.e.* equation (1). However, this mechanism has recently been questioned.<sup>6-8</sup>

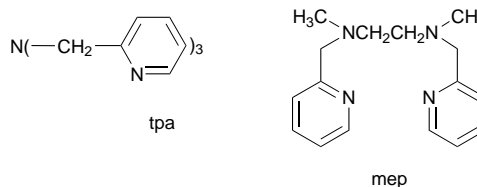


Recently we have found that the bent  $\mu$ -oxo dinuclear iron(III) complex,  $[\text{Fe}_2\text{O}(\text{CH}_3\text{CO}_2)(\text{mep})_2]^{3+}$  shows high oxygenation activity for cyclohexane in the presence of hydrogen peroxide, but its catalase activity is negligible compared with that of the corresponding tpa complex,  $[\text{Fe}_2\text{O}(\text{CH}_3\text{CO}_2)(\text{tpa})_2]^{3+}$ ,<sup>9</sup> where mep represents *N,N'*-dimethyl-*N,N'*-bis(2-pyridylmethyl)ethane-1,2-diamine. In this study we report the crystal structures of the mep and tpa complexes, show the origin of the difference in their reactivity towards hydrogen peroxide on the basis of structural and spectroscopic data, and propose a new chemical mechanism for oxygenation of alkanes by metal complex-hydrogen peroxide systems.

## Experimental

### Materials

The  $\mu$ -oxo bridged iron(III) complexes with tpa and mep were prepared according to the general method.<sup>10</sup> The compound,



mep was obtained from the reaction of 2-pyridylmethyl chloride and *N,N'*-dimethylethane-1,2-diamine according to the method of Toftlund and Andersen<sup>11</sup> {Found: C, 42.60; H, 3.71; N, 10.62. Calc. for  $[\text{Fe}_2\text{O}(\text{CH}_3\text{CO}_2)(\text{tpa})_2][\text{ClO}_4]_3$  **1**: C, 42.19; H, 3.73; N, 10.63. Found: C, 39.64; H, 4.63; N, 10.81. Calc. for  $[\text{Fe}_2\text{O}(\text{CH}_3\text{CO}_2)(\text{mep})_2][\text{ClO}_4]_3$  **2**: C, 39.81; H, 4.62; N, 10.92%}.

### Crystallography

The tpa complex was recrystallized from a methanol-water solution, and the crystal used for structure determination is the dihydrate of the compound, **1**·2H<sub>2</sub>O. Crystal data for the two compounds are listed in Table 1. X-Ray diffraction intensities were measured up to  $2\theta = 55^\circ$  using Mo-K $\alpha$  radiation ( $\lambda = 0.71073 \text{ \AA}$ ) on a Rigaku four-circle diffractometer AFC-5 at 297 K. Absorption was corrected by a numerical integration method. Structure analyses were carried out using CRYSTAN-GM<sup>12a</sup> software on a SUN SPARK10 workstation at Keio University.

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### Catalase-like function

All reactions were performed at 20 °C in a reactor (10 cm<sup>3</sup>) containing a stirring bar under air. The flask containing an iron(III) complex (10 mmol) solution (5 cm<sup>3</sup>, acetonitrile) was closed with a rubber septum. Hydrogen peroxide solution (1 cm<sup>3</sup>, commercial 30% solution diluted to 1 M solution by acetonitrile) was injected through the septum with a syringe. The reactor was connected to a graduated burette filled with water and dioxygen evolved was measured at appropriate times by volumetry.

### Oxygenation of cyclohexane in the presence of iron(III) complex and hydrogen peroxide

In a typical run, an acetonitrile solution (20 cm<sup>3</sup>) containing iron(III) complex (0.05 mmol) and cyclohexane (840 mg) was

**Table 1** Crystal data for the compounds\*

	<b>1</b> ·2H <sub>2</sub> O	<b>2</b>
Formula	C <sub>38</sub> H <sub>45</sub> Cl <sub>3</sub> Fe <sub>2</sub> N <sub>8</sub> O <sub>15</sub> ·2H <sub>2</sub> O	C <sub>34</sub> H <sub>47</sub> Cl <sub>3</sub> Fe <sub>2</sub> N <sub>8</sub> O <sub>15</sub>
<i>M</i>	1 107.90	1 025.84
Crystal dimensions/mm	0.45 × 0.4 × 0.2	0.55 × 0.3 × 0.3
Space group	<i>P</i> 2 <sub>1</sub> / <i>n</i>	<i>C</i> 2/ <i>c</i>
<i>a</i> /Å	20.768(2)	21.010(9)
<i>b</i> /Å	22.523(2)	9.673(6)
<i>c</i> /Å	10.556(2)	21.888(5)
β/°	104.49(1)	102.56(2)
<i>V</i> /Å <sup>3</sup>	4 780.6(11)	4 341.8(34)
<i>D</i> /g cm <sup>-3</sup>	1.539	1.569
<i>F</i> (000)	2 288	2 120
μ(Mo-Kα)/mm <sup>-1</sup>	0.853	0.929
Scan type	θ-2θ	ω
Transmission factor range	0.769–0.855	0.667–0.818
Data collected	11 257	5 117
Observed data [ <i>F</i> > 3σ( <i>F</i> )]	5 560	3 319
No. variables	661	389
<i>R</i> ( <i>R</i> ')	0.0857(0.0739)	0.0695(0.0660)
(Δ/σ) <sub>max</sub>	0.14	0.13
Δρ <sub>max</sub> , Δρ <sub>min</sub> /e Å <sup>-3</sup>	0.77, -0.54	1.02, -0.90
Goodness of fit	1.70	1.78

\* Details in common: monoclinic; *Z* = 4; *w*<sup>-1</sup> = σ<sup>2</sup>(*F*<sub>o</sub>) + (0.02*F*<sub>o</sub>)<sup>2</sup>.

**Table 2** Selected bond lengths (Å) and angles (°) of complex **2**

Fe(1)···Fe(1')	3.253(1)	Fe(1)–O(5)	2.018(5)
Fe(1)–O(4)	1.804(3)	Fe(1)–N(15)	2.205(6)
Fe(1)–N(14)	2.156(6)	Fe(1)–N(17)	2.143(6)
Fe(1)–N(16)	2.260(6)		
O(4)–Fe(1)–O(5)	100.7(3)	O(4)–Fe(1)–N(14)	94.6(2)
O(4)–Fe(1)–N(15)	97.7(3)	O(4)–Fe(1)–N(16)	171.5(2)
O(4)–Fe(1)–N(17)	97.9(2)	O(4)–Fe(1)–O(5)	100.7(3)
O(4)–Fe(1)–N(14)	94.6(2)	O(4)–Fe(1)–N(15)	97.7(3)
O(4)–Fe(1)–N(16)	171.5(2)	O(4)–Fe(1)–N(17)	97.9(2)
O(5)–Fe(1)–N(14)	90.9(3)	O(5)–Fe(1)–N(15)	158.4(3)
O(5)–Fe(1)–N(16)	83.4(3)	O(5)–Fe(1)–N(17)	94.0(3)
N(14)–Fe(1)–N(15)	76.3(3)	N(14)–Fe(1)–N(16)	92.8(3)
N(14)–Fe(1)–N(17)	165.5(3)	N(15)–Fe(1)–N(16)	79.9(3)
N(15)–Fe(1)–N(17)	94.7(3)	N(16)–Fe(1)–N(17)	74.3(3)
Fe(1)–O(4)–Fe(1')	128.7(4)		

Symmetry code: *i* 2 - *x*, *y*, ½ - *z*.

added to an acetonitrile solution (10 cm<sup>3</sup>) containing hydrogen peroxide (1.13 g of commercial 30% solution), and after appropriate times the oxygenated products were determined by GC. Cyclopentanone was used as an internal standard. The turnover numbers of oxygenated products were also examined under a nitrogen atmosphere (by bubbling nitrogen gas passed once through an acetonitrile–cyclohexane solution).

### Other measurements

Absorption spectra were obtained with a Shimadzu model UV-2200 spectrophotometer at 25 °C.

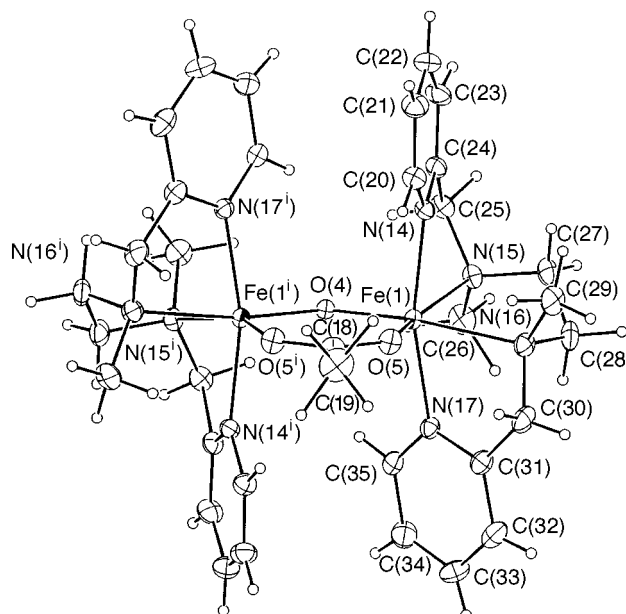
## Results and Discussion

### Crystal structure

The structural properties of complex **1**·2H<sub>2</sub>O are essentially the same as those with of **1**·H<sub>2</sub>O·CH<sub>3</sub>COCH<sub>3</sub>.<sup>9</sup> An ORTEP<sup>12b</sup> representation of the mep complex, **2** is shown in Fig. 1, and selected bond distances and angles are listed in Table 2. The mep complex has a crystallographic two-fold axis through the O(4), C(18) and C(19) atoms. The (μ-oxo)(μ-acetato)diiron(III) core is essentially the same as that of **1** and of the corresponding complex with *N,N'*-bis(2-pyridylmethyl)ethane-1,2-diamine.<sup>13</sup> The Fe–μ-O bond distances in **2** are 1.804(3) Å, which are within the range reported for (μ-oxo)diiron(III) complexes.<sup>14</sup> The Fe–N (pyridine, average 2.148 Å) and Fe–N

**Table 3** Turnover numbers of the products (turnover number = mol of product/mol of iron(III) complex)

Complex	Cyclohexanol		Cyclohexanone	
	30	60 min	30	60 min
tpa	0.2	0.1	0.1	0.1
mep	2.2	2.5	2.8	2.8

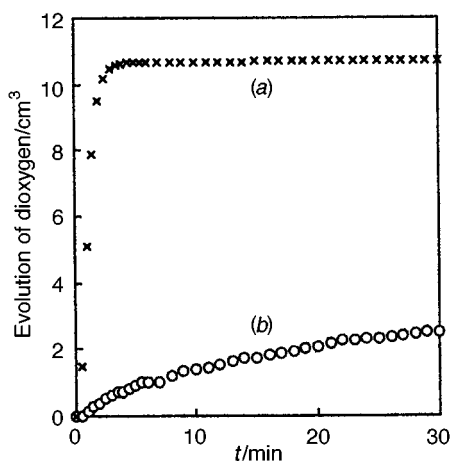


**Fig. 1** An ORTEP drawing of [Fe<sub>2</sub>O(CH<sub>3</sub>CO<sub>2</sub>)(mep)<sub>2</sub>]<sup>3+</sup> (ellipsoids at 20% probability level; disorder was found for the methyl group of the acetate)

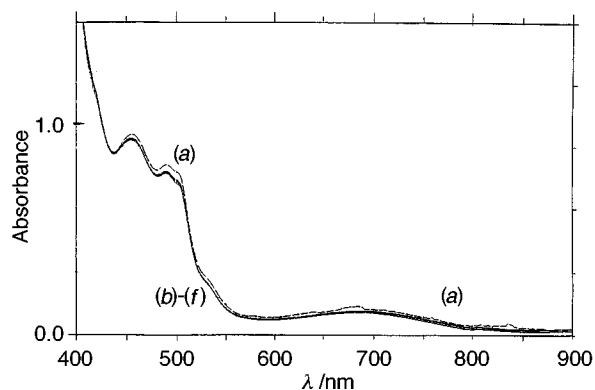
(amine nitrogen, average 2.235 Å) distances and Fe–O–Fe angle of 128.7(4)° are also typical for analogous compounds. The atoms *trans* to the μ-oxo atom are both aliphatic nitrogen atoms in the mep complex, but in the case of the tpa complex one is a pyridine nitrogen and the other an aliphatic nitrogen atom.<sup>9</sup>

### Oxygenation of cyclohexane

In Table 3 the turnover numbers of the products, cyclohexanol and cyclohexanone, are listed; under our experimental condi-



**Fig. 2** Evolution of dioxygen catalysed by the iron(III) complex: (a) tpa complex, (b) mep complex



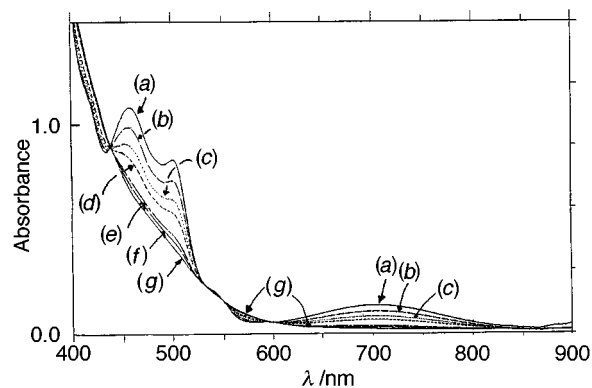
**Fig. 3** Spectra of the tpa compound (concentrations of complex and hydrogen peroxide are  $10^{-3}$  and  $10^{-1}$  mol dm $^{-3}$ , respectively, in acetonitrile, 298 K): (a) 0 min after addition of hydrogen peroxide; (b)–(f) 15, 30, 60, 90 and 150 min after addition

tions the molar ratio of iron complex:hydrogen peroxide:substrate is 1:200:100. It should be noted here that the mep complex shows high activity for the oxygenation of cyclohexane under the experimental conditions where the dinuclear iron(III) complex with tpa exhibits negligible activity.

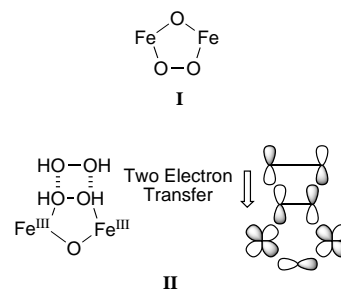
#### Catalase-like function

The  $H_2O_2$  dismutation activity was tested by measuring the dioxygen evolution over 60 min in acetonitrile with a complex:  $H_2O_2$  ratio of 1:100. As shown in Fig. 2, the iron(III) compound with tpa exhibited rather high activity for decomposition of hydrogen peroxide, but the activity of the mep complex is much lower. These results on the oxygenation reaction of cyclohexane and catalase-like function clearly demonstrate that there are two different kinds of iron(III)–peroxide adduct in solution,<sup>15</sup> and that the structure of the active species for decomposition of hydrogen peroxide is different from that for oxygenation of cyclohexane.

**Spectroscopic data for the solution containing hydrogen peroxide.** In Fig. 3 the absorption spectra of the tpa compound are illustrated. The spectra in acetonitrile solutions are typical for bent ( $\mu$ -oxo)diiron(III) compounds.<sup>14</sup> When hydrogen peroxide was added no change occurred in the solution of the tpa complex. However, drastic changes were observed for the mep complex, as shown in Fig. 4; the final spectrum, (g) is essentially the same as that of a linear  $\mu$ -oxo bridged diiron(III) complex.<sup>14</sup> This may indicate that the original bent  $\mu$ -oxo structure decomposes to form a linear  $\mu$ -oxo type or mononuclear complex in the reaction with hydrogen peroxide. The appearance of



**Fig. 4** Spectra of the mep complex (concentrations of iron(III) complex and hydrogen peroxide are  $10^{-3}$  and  $10^{-1}$  mol dm $^{-3}$ , respectively, in acetonitrile, 298 K): (a) 0 min after addition of hydrogen peroxide; (b)–(g) 15, 30, 60, 90, 150 and 180 min after addition



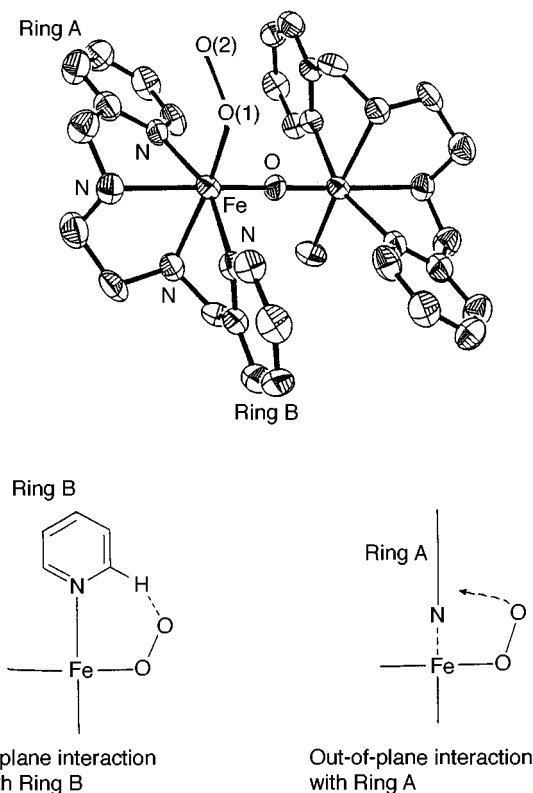
shoulders around 400 nm and presence of an intense feature near 350 nm in (g) support the former possibility,<sup>16</sup> that is there should be a linear ( $\mu$ -oxo) diiron(III) species in the solution of the mep complex. Higher concentrations of  $H_2O_2$  greatly enhance the rate of change in the absorption spectrum of the mep complex.

**Active species for decomposition of  $H_2O_2$ .** In a previous paper we have investigated the catalase-like function of the dinuclear iron(III) complexes with a  $\mu$ -alkoxo bridge, and concluded that an active species for the decomposition of hydrogen peroxide should be of the ( $\mu$ - $\eta^1$ : $\eta^1$ -peroxo)diiron(III) structure<sup>17</sup> **I**. This was supported by the recent work of Fontecave and co-workers<sup>4</sup> who observed the formation of a colored species when hydrogen peroxide was added to the dinuclear iron(III) complex, which may be due to adduct **I**. Thus it seems quite reasonable to assume that  $[Fe_2O(CH_3CO_2)(tpa)_2]^{3+}$  reacts with hydrogen peroxide, yielding a peroxide adduct with  $\mu$ - $\eta^1$ : $\eta^1$  co-ordination, and this should be an intrinsic active species for decomposition of hydrogen peroxide. This may be supported by the spectroscopic data, *i.e.* a bent structure is present in the solution containing the tpa complex and hydrogen peroxide, and also by recent crystal structure determinations on analogous peroxodiiron(III) compounds.<sup>18</sup>

In the decomposition of hydrogen peroxide catalysed by the tpa complex a two-electron-transfer reaction from hydrogen peroxide to the peroxide adduct **I** is allowed because the phases of the orbitals of the two reactants are coincident<sup>19</sup> as illustrated in **II**, and the peroxide adduct with  $\mu$ - $\eta^1$ : $\eta^1$  co-ordination mode is of an electrophilic nature.<sup>17,20</sup>

#### Chemical mechanism of oxygenation of alkanes

According to the above discussion and also that previously reported,<sup>15</sup> we can conclude that there is little formation of a peroxide adduct with  $\mu$ - $\eta^1$ : $\eta^1$  co-ordination in the solution of the mep complex and hydrogen peroxide. The spectra in Fig. 4 suggest that a peroxide adduct with  $\eta^1$  co-ordination (see Fig. 5; this structure is based on the crystal structure determination<sup>15</sup>) may exist in this solution.

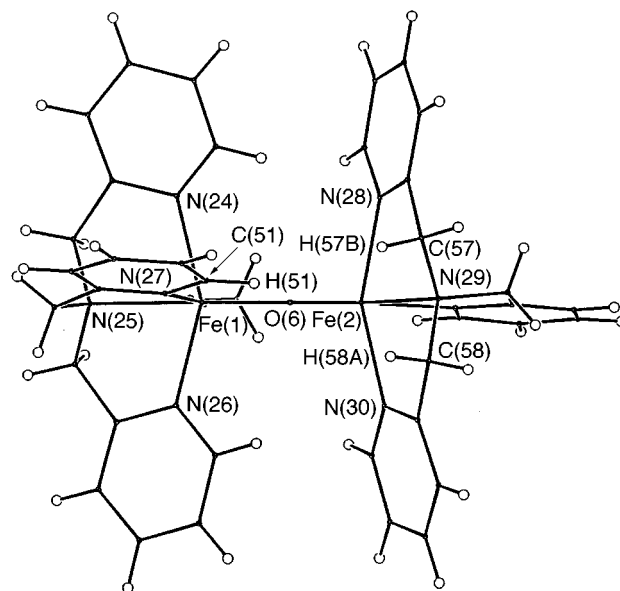


**Fig. 5** Assumed structure for a peroxide adduct in a solution of the mep complex and hydrogen peroxide. The conformation of the chelate ring is based on the crystal structure determination of an analogous compound.<sup>13</sup> A peroxide ion with  $\eta^1$  co-ordination mode can interact with pyridine rings A and B in both in- and out-of-plane modes, respectively

Recently, we have observed that an iron(III)–peroxide adduct with  $\eta^1$  co-ordination is highly electrophilic, forming chemical bonding with the organic moiety nearby through electronic interaction,<sup>6,21</sup> and this interaction plays an important role in activation of peroxide ion bound to a metal ion, leading to facile oxygenation of alkanes, such as cyclohexane.<sup>16</sup> This suggestion is consistent with that proposed for heme oxygenase.<sup>22</sup> In the case of the peroxide adduct shown in Fig. 5 the peroxide may interact with both pyridine rings A and B electronically.<sup>6,15,21</sup> In the present case we consider the out-of-plane interaction<sup>22</sup> (see Fig. 5) may play an important role in the formation of a peroxide adduct and activation of the peroxide ion bonded to the iron(III).<sup>16,21</sup> The reason is as follows: Fish and co-workers<sup>23</sup> have reported a high activity of their compound for alkane functionalization in the presence of hydrogen peroxide, in spite of the negligible activity of the linear  $[\text{Fe}_2\text{OCl}_2(\text{tpa})_2]^{3+}$  complex. In these cases, an out-of-plane interaction between the peroxide ion and an aromatic ring (in this case an imidazole ring) is possible only in Fish's compound, but an in-plane interaction is possible for both the tpa and Fish compounds. We have found that the turnover numbers of the oxygenated products in the solution with nitrogen bubbling are comparable to those in the solution with oxygen bubbling, suggesting that radical reaction does not play an important role in the oxygenation of cyclohexane observed in this study. Our results seem to be consistent with those reported by Fontecave and co-workers.<sup>4</sup> These all support that the intrinsic species for oxygenation of cyclohexane is the peroxide adduct shown in Fig. 5.

#### Structural origin for low oxygenation activity of the tpa complex

As shown in our previous paper,<sup>15</sup> it seems likely that bent ( $\mu$ -oxo)diiron(III) complexes tend to change to a linear  $\mu$ -oxo bridged ones on addition of hydrogen peroxide, if the steric



**Fig. 6** Short intramolecular H...H contacts in the tpa complex: H(51)···H(57B) 2.76, H(51)···H(58A) 3.16 Å. If the Fe(1)–O(6)–Fe(2) angle changed from 129.9(4) to 180°, three H...H distances would be in the range 1.4–1.5 Å

repulsion between the ligands is negligible. This may be due to some electronic stabilizing origin through the overlapping between  $d_{xz}$  orbitals ( $d_{xz}$ ,  $d_{yz}$ ) and orbitals of the oxo-oxygen atom.<sup>24</sup> However, in the tpa complex short H...H intramolecular contacts prevent the opening of the Fe–O–Fe angle as seen in Fig. 6.

Until now, two examples are known of linear  $\mu$ -oxo iron(III) with tpa:  $[\text{Fe}_2\text{OCl}_2(\text{tpa})_2]^{2+}$  and  $[\text{Fe}_2\text{O}(\text{H}_2\text{O})(\text{ClO}_4)(\text{tpa})_2]^{3+}$ .<sup>25</sup> In both cases, the atoms *trans* to the  $\mu$ -oxo oxygen are aliphatic nitrogen atoms. Thus, the conversion from the bent structure of  $[\text{Fe}_2\text{O}(\text{CH}_3\text{CO}_2)(\text{tpa})_2]^{3+}$ ,<sup>9</sup> where one of the atoms *trans* to the  $\mu$ -oxo oxygen is a pyridine nitrogen, into a linear one will require some rearrangement of the ligand atoms (this is not necessary for the mep complex). It seems that this conversion is energetically unfavorable and may explain why  $[\text{Fe}_2\text{O}(\text{CH}_3\text{CO}_2)(\text{tpa})_2]^{3+}$  exhibits high catalase-like activity but no oxygenation activity.

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