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### Introduction

Tetradentate ligands including pyridine and alcohol groups are very useful for preparation of metal coordination compounds. The ligands can be formed from interesting dimers, trimers, and tetramers through direct deprotonation of hydroxyl groups.<sup>1</sup> In particular, metal complexes containing an Fe(m) ion with tetradentate ligands could exhibit significant catalytic activity, magnetic properties, and coordination chemistry.<sup>2</sup> Of these, dinuclear Fe(III) complexes bridged with alkoxo moieties have been studied in order to demonstrate the mechanism of action of metalloenzymes (e.g., purple acid phosphatases and methane monooxygenase) and investigate the superexchange couplings between the iron centers.<sup>3</sup> Recently,

## Catalysis and molecular magnetism of dinuclear iron(iii) complexes with N-(2-pyridylmethyl)iminodiethanol/-ate\*

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The reaction of N-(2-pyridylmethyl)iminodiethanol (H<sub>2</sub>pmide) and Fe(NO<sub>3</sub>)<sub>3</sub>·9H<sub>2</sub>O in MeOH led to the formation of a dimeric iron(III) complex, [(Hpmide)Fe(NO<sub>3</sub>)]<sub>2</sub>(NO<sub>3</sub>)<sub>2</sub>·2CH<sub>3</sub>OH (1). Its anion-exchanged form,  $[(pmide)Fe(N_3)]_2$  (2), was prepared by the reaction of 1 and NaN<sub>3</sub> in MeOH, during which the Hpmide ligand of **1** was also deprotonated. These compounds were investigated by single crystal X-ray diffraction and magnetochemistry. In complex  $\mathbf{1}$ , one iron(iii) ion was bonded with a mono-deprotonated Hpmide ligand and a nitrate ion. The two iron(III) ions within the dinuclear unit were connected by two ethoxy groups with an inversion center. In 2, one iron(III) ion was coordinated with a deprotonated pmide ligand and an azide ion. The Fe(pmide)( $N_3$ ) unit was related by symmetry through an inversion center. Both 1 and 2 efficiently catalyzed the oxidation of a variety of alcohols under mild conditions. The oxidation mechanism was proposed to involve an Fe<sup>IV</sup>=O intermediate as the major reactive species and an  $Fe^{V}$  — O intermediate as a minor oxidant. Evidence for this proposal was derived from reactivity and Hammett studies, KIE ( $k_{\rm H}/k_{\rm D}$ ) values, and the use of MPPH (2-methyl-1-phenylprop-2-yl hydroperoxide) as a mechanistic probe. Both compounds had significant antiferromagnetic interactions between the iron(III) ions via the oxygen atoms. 1 showed a strong antiferromagnetic interaction within the Fe(III) dimer. while 2 had a weak antiferromagnetic coupling within the Fe(III) dimer.

> a dinuclear iron(m) complex with a tetradentate ligand N,Nbis(2-pyridylmethyl)-*N*-(2-hydroxyethyl)amine (Hbpha) was reported as a biomimetic model that displayed catechol intradiol-cleaving dioxygenase activity.4 Furthermore, we have reported the structures and magnetic properties of dinuclear iron(III) complexes bridged with methoxy groups, i.e., [Fe(2,3pyma)(N<sub>3</sub>)<sub>2</sub>(µ-OCH<sub>3</sub>)]<sub>2</sub>·CH<sub>3</sub>OH [Fe(2,3-pyma)(NCS)<sub>2</sub>and  $(\mu$ -OCH<sub>3</sub>)]<sub>2</sub> (2,3-pyma = (2-pyridylmethyl,3-pyridylmethyl) amine).<sup>5</sup> In this context, we explored the formation of discrete iron(m) dinuclear complexes bridged with ethoxide ions that displayed catalytic properties and magnetic couplings. In particular, we were interested in the oxidation of alcohols using iron(III) dinuclear complexes. Herein, we report the synthesis, crystal structure, catalytic activity, and magnetic properties of bis-ethoxy-bridged diiron(m) complexes, [(Hpmide)Fe(NO3)]2- $(NO_3)_2 \cdot 2CH_3OH$  (1) and  $[(pmide)Fe(N_3)]_2$  (2)  $(H_2pmide =$ N-(2-pyridylmethyl)iminodiethanol).

## **Experimental**

#### General

All chemicals used in the synthesis and oxidation reaction were of reagent grade and used without further purification.



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#### Paper

N-(2-Pyridylmethyl)iminodiethanol (H<sub>2</sub>pmide) was prepared according to the literature procedure.<sup>6</sup> UV/Vis absorption spectra were recorded with a SCINCO S-2100 spectrophotometer. Infrared spectra were recorded with a Thermo Fisher Scientific IR200 spectrophotometer (±1 cm<sup>-1</sup>) using a KBr disk. Elemental analyses were carried out using a Fissons/ Carlo Erba EA1108 instrument. Magnetic susceptibilities were measured in an applied field of 5000 Oe between 2 and 300 K on a Quantum Design MPMS superconducting quantum interference device (SQUID) magnetometer. Diamagnetic corrections were made [387.5 (1) and 296.6  $\times$  10<sup>-6</sup> (2) emu mol<sup>-1</sup>] using Pascal's constants. Susceptibility data of 1 and 2 were simulated with the julX program package for magnetic models.<sup>7</sup> Product analyses for the oxidation reaction were performed on either a Hewlett-Packard 5890 II Plus gas chromatograph interfaced with a Hewlett-Packard Model 5989B mass spectrometer or a Donam Systems 6200 gas chromatograph equipped with a FID detector using a 30 m capillary column (Hewlett-Packard, HP-1, HP-5, and Ultra 2).

#### Syntheses of compounds

[(Hpmide)Fe(NO<sub>3</sub>)]<sub>2</sub>(NO<sub>3</sub>)<sub>2</sub>·2CH<sub>3</sub>OH (1). To a MeOH solution (5 mL) of Fe(NO<sub>3</sub>)<sub>3</sub>·9H<sub>2</sub>O (192 mg, 0.476 mmol) was added dropwise a MeOH solution (5 mL) of H<sub>2</sub>pmide (100 mg, 0.476 mmol); the color became dark red, and the solution was stirred for 30 min at room temperature. Greenish yellow crystals of 1 were obtained by diffusion of diethyl ether into the red solution for several days, collected by filtration, washed with diethyl ether and dried in air. Yield: 194 mg (50%). FT-IR (KBr, cm<sup>-1</sup>): 3471, 3084, 2926, 2884, 1608, 1384, 1066, 904, 763. Anal. Calcd for C<sub>20</sub>H<sub>34</sub>N<sub>8</sub>Fe<sub>2</sub>O<sub>18</sub>: C, 30.55; H, 4.36; N, 14.25. Found: C, 30.74; H, 4.22; N, 14.24.

[(pmide)Fe(N<sub>3</sub>)]<sub>2</sub> (2). To a MeOH solution (3 mL) of 1 (75 mg, 0.09 mmol) was added dropwise a MeOH solution (2 mL) of NaN<sub>3</sub> (13 mg, 0.2 mmol); the color became dark red, and the solution was stirred for 3 h at room temperature. Dark red crystals of 2 were obtained by diffusion of diethyl ether into the red solution for several days, collected by filtration, washed with MeOH and diethyl ether and dried in air. Yield: 78 mg (67%). FT-IR (KBr, cm<sup>-1</sup>): 3058, 2955, 2859, 2036, 1601, 1476, 1359, 1085, 904, 788, 606. Anal. Calcd for  $C_{20}H_{28}Fe_2N_{10}O_4$ : C, 41.12; H, 4.83; N, 23.98. Found: C, 40.72.74; H, 5.05; N, 24.12.

#### X-ray crystallographic data collection and refinement

Single crystals of **1** and **2** were coated with paratone-N oil and the diffraction data measured at 96(2) and 100(2) K, respectively, with synchrotron radiation ( $\lambda = 0.75000$  and 0.65000 Å for **1** and **2**) on an ADSC Quantum-210 detector at 2D SMC with a silicon (111) double crystal monochromator (DCM) at the Pohang Accelerator Laboratory, Korea. The ADSC Q210 ADX program<sup>8</sup> was used for data collection (detector distance is 63 mm, omega scan;  $\Delta \omega = 1^{\circ}$ , exposure time is 1 s per frame) and HKL3000sm (Ver. 703r)<sup>9</sup> was used for cell refinement, reduction and absorption correction. The crystal structures were solved by direct methods<sup>10</sup> and refined by full-matrix

Table 1 Summary of the crystallographic data for 1 and 2

Compound	1	2
Empirical formula	C <sub>22</sub> H <sub>38</sub> Fe <sub>2</sub> N <sub>8</sub> O <sub>18</sub>	C <sub>20</sub> H <sub>28</sub> Fe <sub>2</sub> N <sub>10</sub> O <sub>4</sub>
Formula weight	814.30	584.22
Crystal system	Monoclinic	Monoclinic
Space group	$P2_1/n$	$P2_1/c$
a (Å)	8.5580(17)	10.541(2)
b (Å)	18.487(4)	8.3690(17)
c (Å)	11.217(2)	13.436(3)
$\beta(\circ)$	108.06(3)	98.13(3)
$V(Å^3)$	1687.2(6)	1173.4(4)
Ζ	2	2
$d_{\rm calc} ({\rm g}{\rm cm}^{-3})$	1.603	1.654
$\lambda$ (Å)	0.75000	0.65000
$T(\mathbf{K})$	96(2)	100(2)
$\mu ({\rm mm}^{-1})$	1.091	1.007
<i>F</i> (000)	844	604
Reflections collected	14 596	15 079
Independent reflections	3919	4085
Reflections with $I > 2\sigma(I)$	3524	3779
Goodness-of-fit on $F^2$	1.093	1.145
Final <i>R</i> indices $[I > 2\sigma(I)]^a$	$R_1 = 0.0678$	$R_1 = 0.0299$
	$wR_2 = 0.1885$	$wR_2 = 0.0882$
Final <i>R</i> indices [all data] <sup><i>a</i></sup>	$R_1 = 0.0716$	$R_1 = 0.0325$
	$wR_2 = 0.1935$	$wR_2 = 0.0895$
CCDC no.	912273	955381
$^{a}R_{1} = \sum   F_{o}  -  F_{c}   / \sum  F_{o} , with the set of t$	$R_2 = \left[\sum w (F_0^2 - F_c^2)^2 / \sum \right]$	$w(F_0^2)^2]^{1/2}.$

least-squares refinement using the SHELXL-2013 computer program.<sup>11</sup> The positions of all non-hydrogen atoms were refined with anisotropic displacement factors, except C11 and O9 in **1** which have relatively large thermal ellipsoids. All hydrogen atoms were placed using a riding model, and their positions were constrained relative to their parent atoms using the appropriate HFIX command in SHELXL-2013, except the hydrogen of hydroxyl groups in **1**. The crystallographic data and the result of refinements of **1** and **2** are summarized in Table 1.

#### Synthesis of 2-methyl-1-phenyl-2-propyl hydroperoxide (MPPH)

MPPH was synthesized according to the literature method.<sup>12</sup> A mixture of 30% hydrogen peroxide (57.5 mL, 0.66 mol) and sulfuric acid (1.5 mL) was added to a flat-bottomed boiling flask by stirring for 10 min under an ice bath system. 2-Methyl-1-phenyl-2-propanol (17.2  $\mu$ L, 0.11 mol) was added slowly to the mixture by stirring over 10 min, and then stirred at 45 °C for 12 h. After distilled water (150 mL) was added to the reaction mixture, the resulting solution was extracted with pentane (75 mL) to obtain an oil layer. The solvent was removed by stirring with magnesium sulfate to afford an oil product. <sup>1</sup>H NMR (CDCl<sub>3</sub>, 400 MHz):  $\delta$  1.211 (s, 6H), 2.888 (s, 2H), 7.220 (m, 3H), 7.269 (m, 2H), 7.370 ppm (s, 1H).

# Catalytic alcohol oxidations by 1 and 2 with *tert*-butyl hydroperoxide (*t*-BuOOH)

To a mixture of substrate (0.3 mmol), **1** or **2** ( $1.2 \times 10^{-3}$  mmol), and solvent (CH<sub>3</sub>CN, 1 mL) was added *t*-BuOOH (0.03 mmol). The mixture was stirred at 50 °C (1 day for **1** and 3 days for **2**). Reaction products were monitored by GC/Mass analysis of

 $20~\mu$ L aliquots withdrawn periodically from the reaction mixture. All reactions were run at least three times and the average product yields are presented.

#### Competitive alcohol oxidations by 1 and 2 with t-BuOOH

To a mixture of benzyl alcohol (0.15 mmol), *sec*-phenethyl alcohol (0.15 mmol), **1** or **2** ( $1.2 \times 10^{-3}$  mmol), and solvent (CH<sub>3</sub>CN, 1 mL) was added *t*-BuOOH (0.03 mmol). The mixture was stirred for 1 day at 50 °C. Reaction products were monitored by GC/Mass analysis of 20 µL aliquots withdrawn periodically from the reaction mixture. The reaction was run at least three times and the average product ratio is presented.

# Kinetic isotope effect for the benzyl alcohol oxidation by 1 and 2 with *t*-BuOOH

In order to improve the accuracy for measuring the amount of the deuterated benzyl alcohol product, a 1:5 mixture of benzyl alcohol and deuterated benzyl alcohol was used. The reaction conditions are as follows: to a mixture of benzyl alcohol (0.05 mmol), deuterated benzyl alcohol (0.25 mmol), **1** or **2** ( $1.2 \times 10^{-3}$  mmol), and solvent (CH<sub>3</sub>CN, 1 mL) was added *t*-BuOOH (0.03 mmol). The mixture was stirred at 50 °C (1 day for **1** and 3 days for **2**), respectively. Reaction conversion was monitored by GC/Mass analysis of 20 µL aliquots withdrawn periodically from the reaction mixture. All reactions were run at least in triplicate and the average KIE value is presented.

# Competitive reactions of benzyl alcohol and *para*-substituted benzyl alcohols for the Hammett plot

To a mixture of benzyl alcohol (0.02 mmol), *para*(X)-substituted benzyl alcohol (0.02 mmol) (X =  $-\text{OCH}_3$ ,  $-\text{CH}_3$ , -Cl and  $-\text{CF}_3$ ), **1** or **2** ( $1.2 \times 10^{-3}$  mmol), and solvent (CH<sub>3</sub>CN, 1 mL) was added *t*-BuOOH (0.03 mmol). The mixture was stirred for 1 day at 50 °C. The amounts of benzyl alcohols before and after the reactions were monitored by GC/Mass analysis of 20 µL aliquots withdrawn periodically from the reaction mixture. The relative reactivities were determined using the following equation:  $k_x/k_y = \log(X_f/X_i)/\log(Y_f/Y_i)$  where  $X_i$  and  $X_f$  are each initial and final concentration of *para*-substituted styrenes and  $Y_i$  and  $Y_f$  are each initial and final concentration of styrene.<sup>13</sup>

# Analysis of the O–O bond cleavage products from cyclohexanol oxidation by MPPH in the presence of 1 and 2

To a mixture of cyclohexanol (0.3 mmol), **1** or **2**  $(1.2 \times 10^{-3} \text{ mmol})$ , and solvent (distilled CH<sub>3</sub>CN, 1 mL) was added MPPH (0.03 mmol). The mixture was stirred at 50 °C for 1 day (catalyst **1**) and 3 days (catalyst **2**), respectively. Reaction products were determined by GC/Mass analysis of 20 µL aliquots withdrawn periodically from the reaction mixture. All reactions were run at least in triplicate and the average product yields are presented.



Scheme 1 Synthesis of iron(III) dinuclear complexes 1 and 2.

### Results and discussion

#### Synthesis and characterization

The reaction of 1 equiv.  $H_2$  pmide and 1 equiv.  $Fe(NO_3)_3 \cdot 9H_2O$ in methanol under aerobic conditions afforded the iron(m) dinuclear complex 1 in moderate yield (Scheme 1). As expected, a bis-ethoxy-bridged diiron(m) compound was obtained. That is, both iron(III) ions in 1 were connected by the oxygen atoms of the two ethoxy groups supplied by the Hpmide ligand. The composition of 1 was determined by elemental analysis, infrared spectroscopy, and X-ray diffraction. The IR spectrum (KBr pellet) of 1 showed  $\nu_{\rm NO}$  of the nitrate ions at 1384  ${
m cm}^{-1}$  and  $u_{
m OH}$  of the Hpmide at 3471 cm<sup>-1</sup>.<sup>14</sup> The compound displayed CH peaks corresponding to the pyridine and ethoxy groups at 3084, 2926, and 2884 cm<sup>-1</sup>. Compound 2 was obtained by the reaction of 1 and NaN<sub>3</sub> in MeOH (Scheme 1). Interestingly, the reaction was accompanied by anion exchange of the nitrate to azide ions, as well as deprotonation of the Hpmide ligand of 1. The composition of 2 was also identified by elemental analysis, infrared spectroscopy, and X-ray diffraction. The IR spectrum (KBr pellet) of 2 exhibited the  $\nu_{\rm NN}$  of the azide ions at 2036 cm<sup>-1</sup>; however, no  $\nu_{OH}$  for the Hpmide near 3471 cm<sup>-1</sup> was observed.<sup>14</sup> Complex 2 exhibited CH peaks corresponding to the pyridine and ethoxy groups at 3058, 2955, and 2859  $\text{cm}^{-1}$ .

#### Description of crystal structures

**Structure of 1.** Compound **1** crystallized in the monoclinic  $P2_1/n$  space group, and the unit cell included two dinuclear complex molecules. The ORTEP drawing of **1** is shown in Fig. 1, and selected bond lengths and angles are listed in Table 2. In the asymmetric unit of **1**, one iron(III) ion was bonded with a mono-deprotonated Hpmide ligand and a nitrate ion. That is, an Fe(Hpmide)(NO<sub>3</sub>) unit resulted from the bridging of the two iron(III) ions through the terminal  $O_{alkoxo}$  of the tetradentate Hpmide ligand. The two Fe(Hpmide)(NO<sub>3</sub>) units were related by symmetry through an inversion center situated at the barycenter of the complex.



**Fig. 1** ORTEP (40% probable thermal ellipsoid) view of **1**. H atoms, MeOH molecules, and non-coordinated  $NO_3^-$  anions are omitted for clarity, except for the hydrogen atom of O1 (' = 2 - x, -y, -z).

Table 2 Selected bond distances (Å	Å) and	angles	(°)	for 1	L
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Fe1-O1	2.001(2)	Fe1-O3	2.061(2)
Fe1-O2	1.999(2)	Fe1–N1	2.080(3)
Fe1–O2 <sup>i</sup>	1.970(2)	Fe1–N2	2.229(3)
Fe1–Fe1 <sup>i</sup>	3.212(1)		
O2-Fe1-O2	71.95(10)	O1-Fe1-N1	151.77(11)
O1-Fe1-O2 <sup>1</sup>	103.40(10)	O3-Fe1-N1	90.68(11)
O1-Fe1-O2	102.17(10)	O2 <sup>i</sup> -Fe1-N2	150.39(9)
O2 <sup>i</sup> -Fe1-O3	81.18(9)	O2-Fe1-N2	78.72(9)
O2-Fe1-O3	151.92(9)	O1-Fe1-N2	78.61(10)
O1-Fe1-O3	91.64(10)	O3-Fe1-N2	128.43(9)
O2 <sup>i</sup> -Fe1-N1	104.76(10)	N1-Fe1-N2	77.97(11)
O2-Fe1-N1	88.47(10)	Fe1 <sup>i</sup> –O2–Fe1	108.05(10)

Symmetry transformations used to generate equivalent atoms: (i) 2 - x, -y, -z.

Interestingly, both iron(III) ions were coordinated by two different oxygen atoms which were supplied by the same Hpmide ligand, *i.e.*, one was protonated and the other deprotonated. Each iron(III) ion adopted a six-coordinate distorted octahedral configuration with an N2O4 donor set. The amine nitrogen and the bridging ethoxy oxygen atom were situated in the plane of the Fe<sub>2</sub>O<sub>2</sub> core.<sup>4,15</sup> The pyridine nitrogen atom and protonated ethoxy oxygen atom occupied the two axial positions in the octahedron. The oxygen atoms of the coordinated nitrate ions were trans to the deprotonated ethoxy oxygen from the other Hpmide ligand. The Fe-N<sub>Hpmide</sub> and Fe-O<sub>Hpmide</sub> bond distances were in the ranges of 2.080(3)-2.229(3) and 1.970(2)-2.001(2) Å, respectively. The Fe-O<sub>nitrato</sub> bond distance was 2.061(2) Å. The bite distance and angle of the five-membered chelate rings were in the ranges of 2.685(4)-2.713(4) Å and 77.97(11)-78.72(9)°, respectively. The two



**Fig. 2** ORTEP (50% probable thermal ellipsoid) view of **2**. H atoms are omitted for clarity (' = 2 - x, 1 - y, -z).

iron(m) ions within the dinuclear unit were connected by two deprotonated ethoxy groups with an inversion center. The Fe1-O2-Fe1(2 – x, -y, -z) angle was 108.05(10)°. The shortest Fe…Fe contact within the dimer was 3.212(1) Å and the shortest Fe…Fe distance between the dimers was 8.472(2) Å. Furthermore, the hydroxyl oxygen atom of the Hpmide formed a strong hydrogen bond with the uncoordinated oxygen atom of the free nitrate ion (O1…O6 2.569(4) Å, ∠O1-H11-O6 171.46°).<sup>16</sup>

Structure of 2. Compound 2 crystallized in the monoclinic  $P2_1/c$  space group, and the unit cell included two dinuclear complex molecules. The ORTEP drawing of 2 is shown in Fig. 2, and the selected bond lengths and angles are listed in Table 3. In the asymmetric unit of 2, one iron(III) ion was coordinated with a deprotonated pmide ligand and an azide ion, *i.e.*, Fe(pmide)(N<sub>3</sub>). In addition, the two Fe(pmide)(N<sub>3</sub>) units were connected through two Oalkoxo of the pmide ligands belonging to each unit in which the dimeric iron(III) complex was formed. As shown in Fig. 2, each iron(m) ion adopted a six-coordinate distorted octahedral configuration with an N2O4 donor set. The amine nitrogen and the bridged ethoxy oxygen atom were situated in the plane of the Fe<sub>2</sub>O<sub>2</sub> core.<sup>4,15</sup> The pyridine nitrogen atom and the non-bridged ethoxy oxygen atom occupied two axial positions in the octahedron. The nitrogen atoms of the coordinated azide ions were trans to the ethoxy oxygen from the other pmide ligand. Thus, the structure of 2 was isomorphous to that of 1. Remarkably, the coordinated pmide ligands in 2 were deprotonated fully, in contrast to 1 with mono-deprotonated Hpmides.15 The Fe-N<sub>pmide</sub> and Fe-O<sub>pmide</sub> bond distances were in the ranges of 2.1891(12)-2.2427(10) and 1.8629(10)-2.0723(8) Å, respectively.

Table 3 Selected bond distances (Å) and angles (°) for 2

Fe1–O1	1.8629(10)	Fe1–O2 <sup>i</sup>	1.9395(9)
Fe1-O2	2.0723(8)	Fe1-N2	2.2427(10)
Fe1-N1	2.1891(12)	Fe1-N3	2.0628(10)
Fe1–Fe1 <sup>i</sup>	3.1987(8)		
O1-Fe1-O2 <sup>i</sup>	108.21(4)	N3-Fe1-N1	84.33(4)
O1-Fe1-N3	93.32(4)	O2-Fe1-N1	84.09(3)
O2 <sup>i</sup> -Fe1-N3	99.12(4)	O1-Fe1-N2	81.23(4)
O1-Fe1-O2	100.63(4)	O2 <sup>i</sup> -Fe1-N2	151.99(3)
O2 <sup>i</sup> -Fe1-O2	74.30(4)	N3-Fe1-N2	106.73(4)
N3-Fe1-O2	165.84(4)	O2-Fe1-N2	78.08(4)
O1-Fe1-N1	154.62(4)	N1-Fe1-N2	75.34(4)
O2 <sup>i</sup> –Fe1–N1	97.10(4)	Fe1 <sup>i</sup> -O2-Fe1	105.70(4)
Symmetry trans -x + 2, -y + 1, -y +	sformations used -z.	to generate equivale	ent atoms: (i)

The Fe-N<sub>azido</sub> bond distance was 2.0628(10) Å. The bite distance and angle of the five-membered chelate rings were in the ranges of 2.688(1)–2.721(1) Å and 75.34(4)–81.23(4)°, respectively. The two iron(m) ions within the dinuclear unit were linked by two deprotonated ethoxy groups. The angle of Fe1–O2–Fe1(2 - x, 1 - y, -z) was 105.70(4)°. The shortest Fe…Fe contact within the dimer was 3.199(1) Å and the shortest Fe…Fe distance between the dimers was 6.739(1) Å.

**Magnetic properties.** Variable-temperature (2–300 K) magnetic susceptibility,  $\chi$ , measurements on solid samples of 1 and 2 were performed on a SQUID magnetometer (external field 5000 Oe). For 1, at room temperature, the effective magnetic moment,  $\mu_{\text{eff}} [= (8\chi_M T)^{1/2}]$ , was 5.70  $\mu_{\text{B}}/\text{Fe}_2$ . This value was less than the spin-only value of 8.37  $\mu_{\text{B}}/\text{Fe}_2$  expected for two independent Fe<sup>III</sup> spins (g = 2, S = 5/2), indicative of significant antiferromagnetic coupling. As shown in Fig. 3,  $\mu_{\text{eff}}(T)$  decreased with decreasing temperature, consistent with the presence of an antiferromagnetic interaction between the iron(m) ions. The  $\mu_{\text{eff}}(T)$  data were fitted to an analytical expression for  $\chi(T)$  for a coupled S = 5/2 dinuclear spin model (eqn (1)) based on the Hamiltonian  $H = -2JS_1 \cdot S_2$  ( $S_1 = S_2 = 5/2$ ).<sup>7</sup> The best fit to eqn (1) had J = -23.5 cm<sup>-1</sup>, g = 2.0, and spin impurities,  $\rho = 0.024$  (TIP = 400 × 10<sup>-6</sup> emu mol<sup>-1</sup>).



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Fig. 3 Temperature dependence of  $\mu_{eff}$  for 1 (x) and 2 (O) at 5000 Oe. The solid lines are the best-fit curves, as discussed in the text.

This value was less than the spin-only value of 8.37  $\mu_{\rm B}/{\rm Fe_2}$ expected for two independent  $Fe^{III}$  spins (g = 2, S = 5/2), indicative of significant antiferromagnetic coupling.  $\mu_{\text{eff}}(T)$ decreased with decreasing temperature, consistent with the presence of an antiferromagnetic interaction between the iron(m) ions (Fig. 3). The  $\mu_{\text{eff}}(T)$  data were fitted to an analytical expression for  $\chi(T)$  for a coupled S = 5/2 dinuclear spin model based on the Hamiltonian  $H = -2JS_1 \cdot S_2$   $(S_1 = S_2 = 5/2)$ .<sup>7</sup> The best fit had  $J = -11.6 \text{ cm}^{-1}$ , g = 2.0, and spin impurities,  $\rho =$ 0.013 (TIP =  $400 \times 10^{-6}$  emu mol<sup>-1</sup>). The experimentally determined J value  $(-11.6 \text{ cm}^{-1})$  for 2 was almost half that of 1  $(-23.5 \text{ cm}^{-1})$ . This means that the magnetic interaction within the dimeric unit for 1 was much stronger in antiferromagnetic terms than that for 2. The difference in coupling constants was attributed to the different environments around the iron(m) ions (i.e., nitrate and azide ions, protonated and deprotonated

$$\chi_{\rm M} = \frac{N\beta^2 g^2}{3kT} \left[ \frac{6\exp(2J/T) + 30\exp(6J/T) + 84\exp(12J/T) + 180\exp(20J/T) + 330\exp(30J/T)}{1 + 3\exp(2J/T) + 5\exp(6J/T) + 7\exp(12J/T) + 9\exp(20J/T) + 11\exp(30J/T)} \right] (1-\rho) + 2\rho \left[ \frac{N\beta^2 g^2}{3kT} S(S+1) \right]$$
(1)

It should be noted that the *J* value of **1** indicates that the ethoxo groups mediate the antiferromagnetic couplings between the two iron(III) ions separated by *ca*. 3.212 Å. The coupling constant of **1** was comparable to -20.5 and -24.6 cm<sup>-1</sup> for [Fe<sub>2</sub>(dbe)<sub>2</sub>(bz)<sub>2</sub>][(ClO<sub>4</sub>)<sub>2</sub>] and [PH(*t*-Bu)<sub>3</sub>]<sub>2</sub>[Fe<sub>2</sub>-( $\mu$ -OEt)<sub>2</sub>Cl<sub>6</sub>] (dbe = 2-[bis(2-benzimidazolylmethyl)amino]-ethanolato; bz = benzoate), respectively.<sup>15,17</sup> For **2**, the effective magnetic moment  $\mu_{eff}$  at room temperature was 6.91  $\mu_{\rm B}$ /Fe<sub>2</sub>.

ethoxy groups), as well as the Fe–O–Fe' angle (108.05° for 1 and 105.70° for 2).<sup>7a</sup>

**Catalytic properties.** Currently, there is strong interest in the biomimetic oxidation chemistry of non-heme iron complexes, as they have been identified or implicated in a number of non-heme iron enzymes which activate dioxygen.<sup>18</sup> As part of our efforts to model the non-heme iron enzymes,<sup>19</sup> we examined the reactivity of **1** and **2** in the epoxidation and alcohol

lysts 1 and 2 with t-BuOOH in CH<sub>3</sub>CN<sup>a</sup> Yield  $(\%)^b$ Substrate Product 1 2 Entry 98 ± 5  $84 \pm 5$ 1 HC 2 92 ± 7  $81 \pm 1$ 3  $69 \pm 1$  $35 \pm 4$  $96 \pm 3$ 4  $95 \pm 3$ 5  $65 \pm 1$  $27 \pm 0$  $\cap$  $62 \pm 1$  $55 \pm 4$ 6 OH 7  $90 \pm 5$  $88 \pm 0$  $5 \pm 1$  $3 \pm 1$ kH/kD $4.4 \pm 0.2$  $5.0 \pm 0.0$ 8 100  $88 \pm 2$ 9  $90 \pm 6$  $87 \pm 5$ 9 ± 1  $8 \pm 0$ 

Table 4 Oxidation reaction of various alcohols catalyzed by iron cata-

<sup>*a*</sup> Reaction condition: catalyst; 1 mg, alcohol; 0.3 mmol, *t*-BuOOH; 0.03 mmol, dodecane; 0.01 mmol, solvent;  $CH_3CN$  (1 mL) at 50 °C. <sup>*b*</sup> Yields are based on the oxidant.

oxidation of a wide range of olefin and alcohol substrates with environmentally friendly oxidants such as  $H_2O_2$  and *tert*-butyl hydroperoxide (*t*-BuOOH).<sup>20</sup> The combination of catalyst 1 or 2 with *t*-BuOOH was effective for alcohol oxidation, and CH<sub>3</sub>CN was the best solvent for the reactions. To a mixture of substrate (0.3 mmol) and catalyst (1 or 2;  $1.2 \times 10^{-3}$  mmol) in CH<sub>3</sub>CN was added *t*-BuOOH (0.03 mmol), and the mixture was stirred at 50 °C (1 day for 1 and 3 days for 2). We confirmed that the direct alcohol oxidation by *t*-BuOOH was negligible (see Fig. S1†),<sup>21</sup> and catalysts 1 and 2 were sufficiently robust during the catalytic reactions, as shown in Fig. S2.† Table 4

reveals the high catalytic activities for the oxidation of a variety of alcohols by catalysts 1 and 2 under mild conditions.<sup>13,22</sup> With catalyst 1, cyclohexanol, cis-2-methylcyclohexanol, and endo-norborneol were almost quantitatively oxidized to the corresponding ketones (92-98%, entries 1, 2, and 4), whereas sterically hindered alcohols such as trans-2-methylcyclohexanol and exo-norborneol were less efficiently oxidized to ketones (compare entries 2 and 3, and entries 4 and 5).<sup>13</sup> The linear aliphatic secondary alcohol 2-hexanol was converted to the corresponding 2-hexanone in moderate yield (62%, entry 6). Primary and secondary benzylic alcohols also showed high reactivity for the oxidative dehydrogenation (entries 7 and 8). It was notable that benzyl alcohol was smoothly oxidized to afford benzaldehyde, with only a very small amount of the further oxidation product of the aldehyde, benzoic acid.<sup>13</sup> In competition experiments of benzylic alcohols, the primary benzyl alcohol was about twice as reactive as sec-phenethyl alcohol, perhaps because of steric hindrance. The catalytic system was also applicable in the oxidation of aliphatic allylic alcohols (entry 9).<sup>23</sup> The secondary allylic alcohol 3-buten-2-ol afforded the corresponding enone (90%) with a small amount of epoxide (9%). Catalyst 2 also yielded similar results, albeit with longer reaction times (3 days). Two exceptions were the substrates trans-2-methylcyclohexanol and exo-norborneol, which afforded yields of the corresponding products reduced by ca. 50%. Presumably, the fast catalytic reaction with 1 might be due to an effect of the protonated oxygen of the ethanol moiety in **1**. The protons  $(pK_{a1} = 3.03)$ and  $pK_{a2} = 7.03$ , Fig. S3 in the ESI<sup>†</sup>) might promote the fast O-O bond cleavage of the initially formed intermediate (t-BuOO-Fe(III)).

As kinetic isotope effects (KIE) have been used extensively as a mechanistic probe to understand the nature of the oxidizing species in alkane hydroxylation reactions catalyzed by both iron-containing enzymes and model complexes,<sup>13,24</sup> we carried out a competitive intermolecular alcohol oxidation with benzyl alcohol and deuterated benzyl alcohol. The KIEs for benzaldehyde formation by 1 and 2 with t-BuOOH as the oxidant were determined to be 4.4 and 5.0, respectively (entry 7, Table 4), which indicated that C-H bond cleavage by the oxidizing species was the rate-determining step for alcohol oxidation. These values were higher than those of a corresponding hydrogen abstraction reaction by the tert-butoxy radical (3.6) and by the combination of an iron(m) porphyrin complex ([F20TPP]FeCl) (F20TPP = tetrakis(pentafluorophenyl)porphyrin) and m-chloroperoxybenzoic acid (3.3). However, the results were lower than those of oxoiron(IV) porphyrin  $\pi$ -cation radicals (21 for [(TDCPP)Fe<sup>IV</sup>=O]<sup>++</sup> at -100 °C and 20 for [(TMP)Fe<sup>IV</sup>=O]<sup>++</sup> at -60 °C) and mononuclear non-heme oxoiron(w) complexes (48 for [(N4Py)- $Fe^{IV} = O$ ] at 0 °C and 58 for [(tpa)Fe<sup>IV</sup> = O] at -40 °C). These results led us to propose that the major reactive species responsible for alcohol oxidation in our catalytic systems may be a high-valent iron oxo species that is produced by the O-O bond cleavage in the iron(m)-peroxide intermediate (t-BuOO-Fe<sup>III</sup>).

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Fig. 4 Hammett plots for relative reactivities depending on *para*-substituent constants  $\sigma_p$  of benzyl alcohol; (a) for catalyst 1 and (b) for catalyst 2.

To gain further information about the nature of the reactive intermediates responsible for these alcohol oxidation systems, we conducted the competitive oxidation of benzyl alcohol and para-substituted benzyl alcohols (see the Experimental section for details). As shown in Fig. 4, a significant electronic effect on the reaction rate was observed, showing that more electronrich alcohols reacted faster than electron-deficient alcohols. Hammett plots afforded negative  $\rho$  values of -0.52 for 1 and -0.40 for 2, suggesting that the reactive intermediates responsible for alcohol oxidation were electrophilic. These  $\rho$  values were higher than those determined from the alcohol oxidation reactions by mononuclear non-heme oxoiron(IV) complexes,  $[(tpa)Fe^{IV}=O]$  (-0.06) and  $[(N4Py)Fe^{IV}=O]$  (-0.07),<sup>25</sup> and similar to those investigated in cytochrome P450 enzymes  $(around -0.4)^{26}$  and heme model compounds such as oxoiron(IV) porphyrin  $\pi$ -cation radicals, [(TDCPP)Fe<sup>IV</sup>=O]<sup>++</sup> (-0.39) and [(TMP)Fe<sup>IV</sup>=O]<sup>•+</sup> (-0.43).<sup>25</sup>

Based on these results and KIE values, we propose the most plausible mechanism for alcohol oxidation by catalysts **1** and **2** as shown in Scheme 2. *t*-BuOOH reacts with an iron(m) complex to form an initial iron(m)-peroxide species (*t*-BuOO– Fe<sup>III</sup> (3)). The O–O bond of the coordinated anion of *t*-BuOOH can then cleave heterolytically to form a high-valent iron(v)– oxo complex (**4**) and *t*-BuOH (pathway (a)), or homolytically to form a high-valent iron(v)–oxo complex (**5**) and *t*-BuO<sup>•</sup> radical (pathway (b)).

To determine whether the iron(m)-peroxide species *t*-BuOO-Fe<sup>III</sup> (3) decomposes by heterolysis or homolysis, we used MPPH (2-methyl-1-phenyl-2-propyl hydroperoxide) as a mechanistic probe, given the well-established use of MPPH in distinguishing the heterolytic versus homolytic cleavage of the alkyl peroxide O-O bond.27 If the O-O bond of the t-BuOO-Fe<sup>III</sup> is cleaved heterolytically, then *t*-BuOO-Fe<sup>III</sup> would yield 2-methyl-1-phenyl-2-propanol (MPPOH (6)) (Scheme 3). In contrast, the homolytic cleavage of the O-O bond in t-BuOO-Fe<sup>III</sup> would generate an alkoxy radical (MPPO'), which would undergo an extremely fast  $\beta$ -scission (2.2 × 10<sup>8</sup> s<sup>-1</sup>) to produce benzyl alcohol (7), benzaldehyde (8), and toluene (9). Therefore, the mechanism of the O-O bond cleavage of alkyl hydroperoxides can be determined by analyzing the products derived from the decomposition of MPPH by iron complexes.

The catalytic oxidation of cyclohexanol by MPPH was carried out in the presence of 1 and 2 in CH<sub>3</sub>CN, and the product distribution results are shown in Table 5. In the cyclohexanol oxidation catalyzed by 1 and MPPH, the homolytic cleavage products benzaldehyde (69.2%) and benzyl alcohol (16.7%) were the predominant degradants of the oxidant, with a small amount of the heterolytic cleavage product, MPPOH (5.3% based on MPPH) (entry 1). These results demonstrate that the MPPOO-Fe<sup>III</sup> species 3 generated from the reaction of 1 and MPPH underwent partitioning between 94% homolysis and 6% heterolysis. Before we were confident of the 94:6 ratio, we carried out another control experiment to determine whether MPPH was completely consumed by catalyst 1 during the reaction period (1 day). Therefore, we added triphenylphosphine (PPh<sub>3</sub>) into the reaction solution to trap any possibly remaining MPPH after 1 day; it is well known that alkyl hydroperoxides react quickly with PPh<sub>3</sub> to give the corresponding alcohols. Nearly identical product distributions were obtained with and without PPh3 (entries 1 and 2, Table 5), suggesting that MPPH decomposed completely during the alcohol oxidation reactions. Therefore, these results indicate that homolytic cleavage (94%) of the *t*-BuOO–Fe<sup>III</sup> intermediate (3) is the major pathway, with a small portion (6%) of heterolytic cleavage. These results led us to conclude that most of the alcohol was oxidized to ketone by the  $Fe^{IV} = O$  intermediate (4) and the tert-butoxy radical, and that a small amount of the alcohol was oxidized to the ketone by the Fe<sup>V</sup>=O intermediate. Nearly identical results were also obtained for 2 (entries 3 and 4, Table 5), indicating that both catalysts 1 and 2 catalyzed alcohol oxidation by the same reaction mechanism. Moreover, the nearly identical product distribution from MPPH by



Scheme 2 Plausible mechanism on the formation of reactive species responsible for alcohol oxidation by iron complexes with t-BuOOH.



Scheme 3 Possible O–O bond cleavage mechanism of MPPH by iron complexes.

Table 5 Yield of products derived from 2-methyl-1-phenylprop-2-yl hydroperoxide (MPPH) mediated by catalysts 1 and 2 in the presence of cyclohexanol<sup>a</sup>

Entry	Catalyst	Triphenyl phosphine (mM)	Heterolysis <sup>b</sup> MPPOH ( <b>6</b> )	Homolysis <sup>b</sup>				
				Benzaldehyde (7)	Benzyl alcohol (8)	Toluene (9)	Hetero (6)/Homo (7 + <b>8</b> + <b>9</b> )	Cyclohexanone <sup>b</sup>
1	1	0	$5.3 \pm 0.1$	$69.2 \pm 0.7$	$16.7 \pm 0.0$	0	5.8/94.2	$62.9 \pm 0.4$
2	1	$100^{c}$	$6.3 \pm 0.4$	$65.6 \pm 0.7$	$15.9 \pm 1.8$	0	7.2/92.8	$64.1 \pm 2.6$
3	2	0	$5.1 \pm 0.8$	$74.0\pm6.7$	$12.1 \pm 2.2$	0	5.6/94.4	$58.4 \pm 4.8$
4	2	$100^{c}$	$6.2\pm0.3$	$72.2\pm4.5$	$12.2\pm1.1$	0	6.8/93.2	$\textbf{58.4} \pm \textbf{5.1}$

<sup>*a*</sup> Reaction conditions: catalyst; 1 mg, cyclohexanol; 0.3 mmol, MPPH; 0.03 mmol, dodecane; 0.01 mmol, solvent; CH<sub>3</sub>CN (1 mL), reaction time; 1 day for 1 and 3 days for 2 at 50 °C. MPPOH indicates 2-methyl-1-phenyl-2-propanol. <sup>*b*</sup> Based on MPPH. <sup>*c*</sup> Triphenyl phosphine was added into the reaction solution 1 day (for 1) and 3 days (for 2), respectively, after the oxidation reaction ended.

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catalysts **1** and **2** supported our prior assumption that the proton on the oxygen of the ethanol moiety in **1** does not affect the partition between homolytic and heterolytic O–O bond cleavage; rather, it may accelerate only the O–O bond cleavage rate, in contrast to the known action of protons in driving the heterolytic cleavage of the O–O bonds of alkyl hydroperoxides.<sup>28</sup>

### Conclusions

We prepared two new bis-ethoxy-bridged iron(III) dinuclear complexes 1 and 2 which showed significant antiferromagnetic couplings through the bridging ethoxy groups between the iron(III) ions. Complex 1 showed much stronger antiferromagnetic interactions than 2 due to geometric effects. 2 was obtained from 1 through an anion exchange process using azide ions. Surprisingly, the coordinated Hpmide ligand of 1 was deprotonated during the formation of 2. The dimers 1 and 2 efficiently catalyzed the oxidation of a variety of alcohols under mild conditions. Reactivity and Hammett studies, KIE  $(k_{\rm H}/k_{\rm D})$  values, and the use of MPPH as a mechanistic probe suggested that an Fe<sup>IV</sup>=O intermediate might be the major reactive species responsible for the alcohol oxidation, with an Fe<sup>V</sup>=O intermediate as a minor oxidant. This reaction provides a new, environmentally friendly, and economical route for the conversion of alcohols to carbonyl groups.

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