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Synthesis and Characterization of Bis(μ-hydroxo)diiron(III) Complex of *N*-(4-Nitro-2-hydroxy)phenylmethyl-*N*-(2-pyridylethyl)-*N*-(2-pyridylmethyl)amine and Hydroxylation Reaction of Alkane

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Abstract—Bis(μ-hydroxo)diiron(III) complex, $[Fe_2^{III}(\mu\text{-}OH)_2(NE)_2](NO_3)_2 \cdot 3H_2O$ (**3**) (*N*-(4-nitro-2-hydroxy)phenylmethyl-*N*-(2-pyridylethyl)-*N*-(2-pyridylmethyl)amine = HNE, where H denotes a dissociable proton of the *p*-nitrophenol group), has been prepared and characterized by X-ray crystallography, electronic and magnetic spectroscopies. © 2001 Elsevier Science Ltd. All rights reserved.

Introduction

Binuclear iron(II) or iron(III) complexes bridged by bis-μ-hydroxo $(Fe_2(\mu\text{-}OH)_2)$ or bis-μ-oxo $(Fe_2(\mu\text{-}O)_2)$ have been found to be present in the active sites of various non-heme proteins such as ribonucleotide reductase (RNR)[1] and methane monooxygenase (MMO).[2] In the past decades many artificial model compounds for the active centers of metallo-proteins have been synthesized to understand the relationship between structure and reactivity of metallo-proteins.[3] Que et al., for example, have reported that bis(μ-oxo)diiron(III), **1**, and (μ-oxo)(μ-hydroxo)diiron(III), **2**, with tripodal ligands, TPA or 6-Me$_3$-TPA act as synthetic models of MMO and RNR (see Chart 1), and structurally characterized them.[3b] These complexes are related by an acid–base equilibrium as shown in Scheme 1.[4]

We have isolated a bis(μ-hydroxo)iron(III) complex, **3**, with a tripodal ligand, {HNE = *N*-(4-nitro-2-hydroxy)-phenylmethyl-*N*-(2-pyridylethyl)-*N*-(2-pyridylmethyl)-amine, where H denotes a dissociable proton of the *p*-nitrophenol group}, of rare structural motif. We report here the synthesis of the bis(μ-hydroxo)iron(III) complex of HNE, $[Fe_2^{III}(\mu\text{-}OH)_2(NE)_2](NO_3)_2 \cdot 3H_2O$, **3**, its X-ray crystal structure, spectroscopic properties and alkane hydroxylation by **3**–hydrogen peroxide system.

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Results and Discussion

Syntheses

The tripodal ligand, HNE, was prepared according to the literature procedure.[4] The bis(μ-hydroxo)iron(III) complex, $[Fe_2^{III}(\mu\text{-}OH)_2(NE)_2](NO_3)_2 \cdot 3H_2O$, **3**, was synthesized as shown in Scheme 2. To a solution of 500 mg
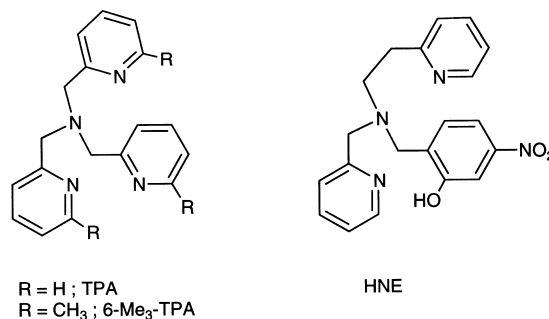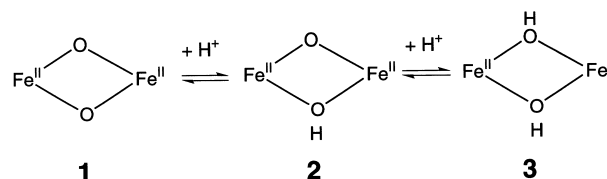

R = H ; TPA
R = CH$_3$; 6-Me$_3$-TPA

HNE

Chart 1.

1   **2**   **3**

Scheme 1.

$$2HNE + 2Fe^{III}(NO_3)_3 + 4piperidine + 2H_2O \longrightarrow [Fe^{III}_2(\mu\text{-}OH)_2(NE)_2](NO_3)_2 + 4(piperidineH^+)(NO_3^-)$$

Scheme 2.

(1.37 mmol) of HNE and 544 mg (1.37 mmol) of $Fe(NO_3)_2 \cdot 9H_2O$ in degassed methanol were added dropwise with stirring a solution of 214 mg (2.74 mmol) of piperidine in 5 mL of methanol at 50 °C. The initial violet solution turned to a dark red solution and a brown precipitate appeared immediately, which was collected by suction and washed with methanol. Drying in vacuo yielded 455 mg (32%) of the title compound as a reddish brown powder. Recrystallization from acetonitrile/water (1:1 v/v) provided dark red crystals suitable for crystallographic analysis. Elemental analysis supports chemical formula $[Fe_2^{III}(\mu\text{-}OH)_2(NE)_2](NO_3)_2 \cdot 3H_2O$.[5]

X-ray crystal structure

The crystal structure of complex **3** was determined by X-ray crystallography.[6] The asymmetric unit contains two halves of complex **3**, which are related to the other halves through crystallographical inversion center forming two dimers, $[Fe_2^{III}(\mu\text{-}OH)_2(NE)_2]^{2+}$ (denoted as A and B), two nitrate ions, and three water molecules. ORTEP drawings of the cations (A and B) are shown in Figure 1. Each Fe^{III} center forms an octahedral geometry with the tripodal ligand, HNE, and two oxygen atoms in hydroxo moieties acting as bridging atoms
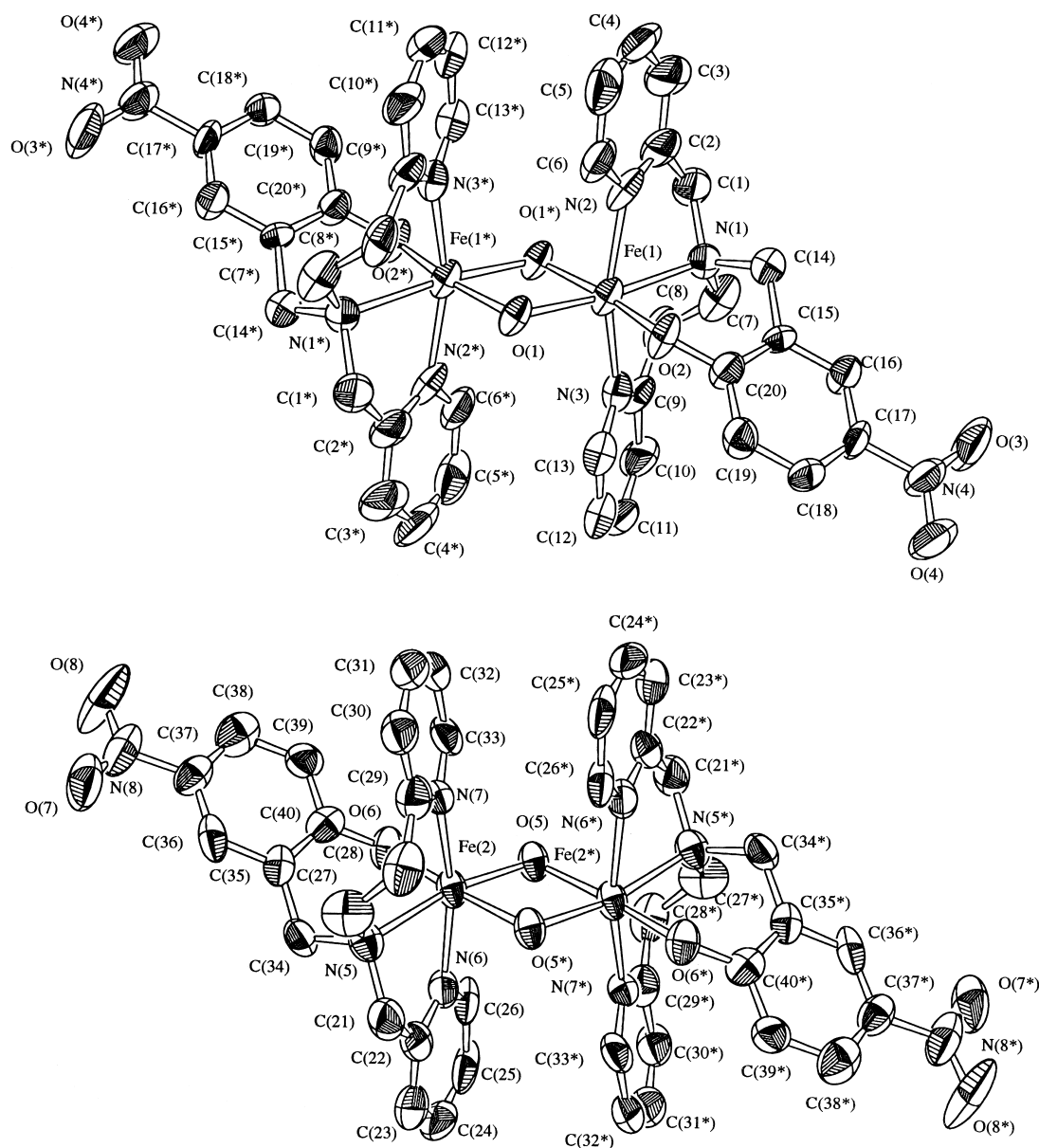

Figure 1. ORTEP drawings of the cations of **3A** (top) and **3B** (bottom), showing 50% probability thermal ellipsoids. Relevant bond lengths (Å) and angles (°) are as follows. For **3A**: Fe(1)–Fe(1*), 3.113(3); Fe(1)–O(1), 1.975(6); Fe(1)–O(1*), 2.023(6); Fe(1)–O(2), 1.924(6); Fe–N(1), 2.249(8); Fe(1)–N(2), 2.126(10); Fe(1)–N(3), 2.134(9), Fe(1)–O(1)–Fe(1*), 102.4(3). For **3B**: Fe(2)–Fe(2*), 3.105(3); Fe(2)–O(5), 1.952(6); Fe(2)–O(5*), 2.049(6); Fe(2)–O(6), 1.917(6); Fe(2)–N(5), 2.219(8); Fe(2)–N(6), 2.116(9); Fe(2)–N(7), 2.124(8); Fe(2)–O(5)–Fe(2*), 101.9(3).

linking the two halves of the dimer. The tertiary amine (Fe(1)–N(1) 2.249(8) and Fe(2)–N(5) 2.219(8) Å) and one phenolate oxygen atom (Fe(1)–O(2) 1.924(6) and Fe(2)–O(6) 1.917(6) Å) are in equatorial positions with respect to the bridging hydroxos and form an FeNO$_3$ plane. The two pyridyl nitrogen atoms (Fe(1)–N(2) and –N(3) 2.126(10) and 2.134(9) Å for A and Fe(2)–N(6) and –N(7) 2.116(9) and 2.124(8) Å) are *trans* to each other and coordinate axially to the iron(III) atom. The Fe–μ-OH bond lengths of 1.975(6) for A and 1.952(6) Å for B *trans* to the tertiary amine are shorter than those of 2.023(6) and 2.049(6) Å *trans* to the phenolate oxygen atom, giving rise to a slightly asymmetric diamond core ($\Delta r = 0.048$–0.097 Å). The Fe–μ-OH distances are within the normal range as compared to those found for Fe$_2^{III}$(μ-OH)$_2$ complexes (1.937–2.055 Å).[3a,7] The Fe–Fe distances are 3.113(3) and 3.105(3) Å for A and B, respectively, while the Fe–μ-OH–Fe angles are 102.4(3) and 101.9(3)° for A and B, respectively. These Fe–Fe distances and Fe–μ-O–Fe angles are comparable with those distances known for Fe$_2^{III}$(μ-OH)$_2$ complexes (3.08–3.16 Å and 102.8–105.3°).[7a–g] Moreover, complex **3** is probably stabilized by stacking between the pyridine rings with an intramolecular distance of ca. 3.8 Å.

Spectroscopic and magnetic properties

The absorption spectrum of complex **3** in methanol (Fig. 2) showed the intense bands at 490 nm (ε = 2060 M^{-1} cm^{-1}/Fe), 400 nm (5400 M^{-1} cm^{-1}/Fe), 350 nm (10,380 M^{-1} cm^{-1}/Fe), and 250 nm (10,500 M^{-1} cm^{-1}/Fe). The 400 nm band is assignable to a charge transfer band from *p*-nitrophenolate to the nitro group, while the band at 490 nm results from *p*-nitrophenolate to iron(III) LMCT transition. The intense bands at <350 nm are dominated by π–π* and n–π* transitions of both *p*-nitrophenolate and pyridine.

The magnetic susceptibility was measured on powdered sample using the SQUID method under 1 T applied magnetic field at the temperature between 2–300 K.[8] The temperature dependence of magnetic behavior of complex **3** is shown in Figure 3, where χ_A and μ_{eff} are the magnetic susceptibility and magnetic moment per iron, respectively. When the temperature is lowered, the μ_{eff} value decreases gradually from 4.75 μ_B at 300 K to ca. 0.36 μ_B at 2 K. The room temperature μ_{eff} value of 4.75 μ_B for complex **3** is slightly lower than the spin-only moment of 5.92 μ_B per ion for $S = 5/2$ system but consistent with those found in other iron(III) complexes with the Fe^{III}(μ-OH)$_2$ core (4.94–5.24 μ_B).[7] The decrease of μ_{eff} at low temperature indicates that two high-spin iron(III) centers are antiferromagnetically coupled.

Alkane hydroxylation by complex 3 with hydrogen peroxide

In order to determine whether complex **3** catalyzes hydroxylation of alkane such as cyclohexane in the presence of hydrogen peroxide as oxidant, oxidation reactions were carried out in acetonitrile at 25 °C using syringe-pump techniques.[9,10] Cyclohexane (1 mmol) in acetonitrile was reacted with hydrogen peroxide (1 mmol) in the presence of 0.01 mmol of complex **3** at 25 °C. The products were analyzed by GLC to be cyclohexanol (0.08 mmol) and cyclohexanone (0.117 mmol).[11] The product ratio for the cyclohexanol formation from competitive oxidation of cyclohexane (C$_6$H$_{12}$ and C$_6$D$_{12}$) by complex **3**–hydrogen peroxide system was determined to be 1.3 and the value of k_H/k_D is within in the range reported for alkane hydroxylations by hydroxyl radical.[12,13] Moreover, addition of a small amount of CCl$_3$Br to a cyclohexane reaction mixture afforded 25 turnovers of cyclohexyl bromide and trace amounts of cyclohexanol and cyclohexanone. These results demonstrated that complex **3** catalyzes the hydroxylation of cyclohexane by hydrogen peroxide via free radical pathways such as the Harber–Weiss process.

In summary, we have prepared the bis(μ-hydroxo)iron-(III) complex, **3**, and characterized it by X-ray crystallography. Complex **3** catalyzes the hydroxylation of cyclohexane with hydrogen peroxide.
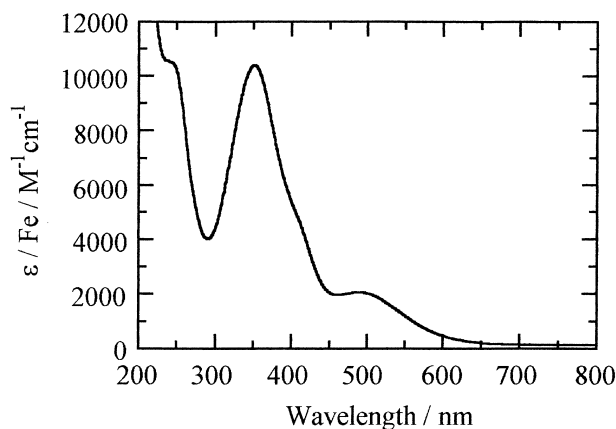

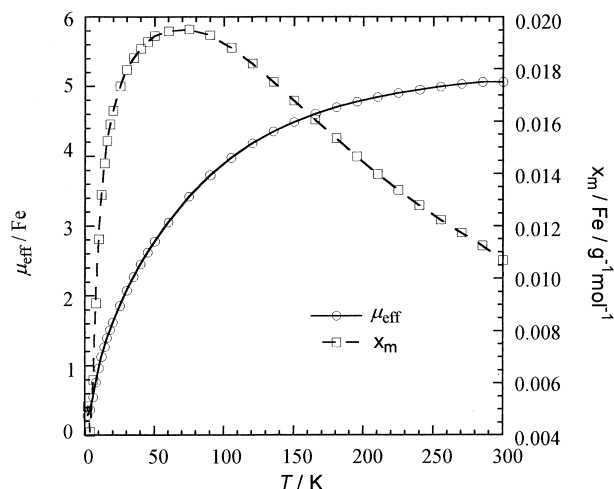**Figure 2.** UV–visible spectrum of complex **3** in methanol at 25 °C.

Figure 3. Molar susceptibility (χ_A) and effective magnetic moment (μ_{eff}) per Fe^{III} ion of complex **3** as a function of the temperature.

Acknowledgements

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6. X-ray crystal data for [Fe^{III}(μ-OH)$_2$(NE)$_2$](NO$_3$)$_2$·3H$_2$O: $M = 1050.55$ (Fe$_2$C$_{40}$H$_{46}$N$_{10}$O$_{17}$), triclinic, space group $P\bar{1}$, $a = 12.723(7)$, $b = 16.327(5)$, $c = 12.014(7)$ Å, $\alpha = 93.75(4)$, $\beta = 109.29(5)$, $\gamma = 102.75(4)°$, $D_c = 1.536$ g cm^{-1}, $Z = 2$, $\mu = 7.23$ cm^{-1}, 8851 measured reflections, 2659 with $I > 3\sigma(I)$, $R = 0.057$, and $R_w = 0.040$. Intensity measurement: Rigaku AFC-7R diffractometer, Mo-K_α radiation, graphite monochromater, $2\theta_{max} = 55°$, ω–2θ scan and $T = 20 \pm 1 °C$. The structure was solved by direct methods. Non-hydrogen atoms

were refined anisotropically and the hydrogen atoms were included in models at their calculated but not refined. Atomic coordinates, bond angles, and bond lengths and thermal parameters have been deposited at the Cambridge Crystallographic Data Center in .cif format. CCDC number: 158024.

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8. Magnetic susceptibilities were measured with an MPMS5 SQUID susceptometer (Quantum Design Inc.). The calibrations were made with palladium. Effective magnetic moments were calculated with the equation $\mu_{eff} = 2.828(\chi_A T)^{1/2}$, where χ_A is the magnetic susceptibility per iron ion.

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12. Reaction conditions: 0.01 mmol of complex **3** was reacted with 1 mmol hydrogen peroxide, 0.05 mmol cyclohexane, and 0.05 mmol cyclohexane-d_{12} in 10 mL acetonitrile for 6 h at 25 °C. The product ratio from competitive oxidation of cyclohexane for the cyclohexanol formation is determined according to: product ratio for cyclohexane oxidation = ([cyclohexanol] + [cyclohexanone])/([deuterium cyclohexanol] + [deuterium cyclohexanone]).

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