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Synthesis, Characterization, and Activation of Thermally Stable *μ*-1,2-Peroxodiiron(III) Complex

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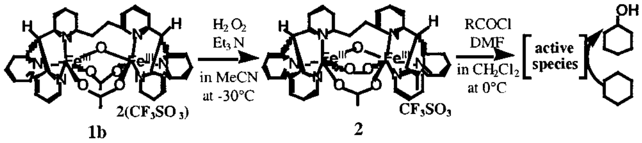
The mechanism of O_2-activation and oxygenation of CH_4 to CH_3OH by soluble methane monooxygenase hydroxylase (sMMOH) is of great current interest.[2] The diiron(II) center of sMMOH binds dioxygen to form a *μ*-peroxodiiron(III) intermediate **P**[3] via two transient intermediates **O** and **P***,[4] and **P** is converted to an active intermediate **Q**.[5] **P** and **Q** have been studied spectroscopically[3−5] and followed by model studies.[6,7] A radical-rebound mechanism of the C−H oxygenation by **Q** has been proposed on the basis of product analysis and the kinetic isotope effect.[8] These results have been supported by DFT calculations.[9] Now, the next target is to clarify the mechanism for the conversion of **P** to **Q**.[4a,6e]

Scheme 1



A thermally stable (*μ*-1,2-peroxo)diiron(III) complex which can be activated to oxygenate hydrocarbons is useful to study the O_2-activation.[7] Although a few thermally stable (*μ*-1,2-peroxo)diiron(III) complexes of sterically hindered ligands have been prepared,[6] their O_2-activation has not been clarified yet. The steric hindrance may inhibit the O_2-activation. We reported that diiron(III) complexes of a hexapyridine dinucleating ligand (L) $[Fe_2(O)(OAc)_2(L)]X_2$ {X = ClO_4 (**1a**) and CF_3SO_3 (**1b**)} catalyze alkane oxygenation by using *m*-CPBA as an oxidant where the turnover number (ca. 1000) is not affected by O_2 molecules, indicating that the oxygenation is not a radical chain reaction.[10] The high catalytic activity of **1** is due to the small steric hindrance of L. Here we report the synthesis, characterization, and activation of a thermally stable (*μ*-acetato)(*μ*-oxo)(*μ*-1,2-peroxo)diiron(III) complex $[Fe_2(O_2)(O)(OAc)(L)](CF_3SO_3)$ (**2**). The transformation of the diiron complexes in this study is shown in Scheme 1.

To a solution of **1b** (38 mg, 0.033 mmol) in MeCN (10 mL) were added 10 *μ*L of Et_3N (0.072 mmol) and 100 *μ*L of 20% H_2O_2/MeCN (0.50 mmol of H_2O_2) at −30 °C; then the solution turned dark purple. Upon addition of dry Et_2O to the mixture after concentration, **2** (36 mg, 95% yield) precipitated as a purple solid. In the solid state, **2** is stable at room temperature. The elemental analysis of **2** agrees with a formula $[Fe_2(O_2)(O)(OAc)(L)](CF_3SO_3)\cdot 5H_2O$.[11] A parent peak appears at *m*/*z* 739 ($[Fe_2(O_2)(O)(OAc)(L)]^+$) in the FAB MS spectrum of **2**. The electronic spectrum of **2** in MeCN shows two absorption bands at 510 (ϵ = 1300 M^{-1} cm^{-1}) and 605 nm (ϵ = 1310 M^{-1} cm^{-1}) (Figure 1), similar to that of $[Fe_2(O)(O_2)(6\text{-}Me_3\text{-}TPA)_2](ClO_4)_2$ (**3**).[7c] The resonance Raman spectrum obtained with 593 nm excitation of **2** shows strong bands at 816 and 472 cm^{-1}, which shift to 771 and 455 cm^{-1} by $^{18}O_2$-labeling with $H_2{}^{18}O_2$. These two ^{18}O-sensitive bands are respectively assigned to the ν_{O-O} and the ν_{Fe-O}

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(11) Elemental analysis data of **2**: Anal. Calcd for $C_{39}H_{41}F_3Fe_2N_6O_{13}S$: C, 46.72; H, 4.12; N, 8.38; Fe, 12.29. Found: C, 46.59; H, 3.80; N, 8.48; Fe, 12.14.

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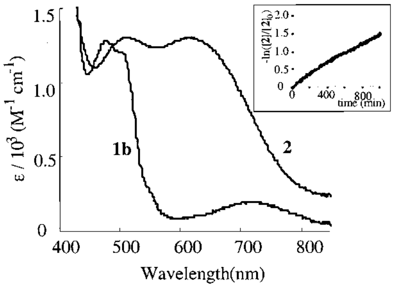

Figure 1. UV−vis absorption spectra of **1b** and **2** in MeCN. The first-order plots of the spontaneous decomposition of **2** in MeCN at 300 K (inset).

of a bound peroxide.[12] The ν_{O-O} value of **2** is notably below the range of 848−900 cm^{-1} reported for a lot of (μ-1,2-peroxo)diiron(III) complexes.[6,7,13] It is reported that ν_{O-O} value mainly depends on the Fe−O−O angle of the peroxodiiron complex.[6e] **2** may have smaller Fe−O−O angles than the known complexes because the Fe−Fe distance is decreased by L and by an μ-oxo bridge. The Mössbauer spectrum of **2** at 4.2 K displays only a quadrupole doublet with $\Delta E_Q = 1.67(8)$ mm/s and $\delta = 0.53(8)$ mm/s,[14] indicating that the high-spin diiron(III) unit is symmetrically bridged by the peroxide. These values are very close to $\Delta E_Q = 1.68$ mm/s and $\delta = 0.54$ mm/s of **3**,[7c] and $\Delta E_Q = 1.79$ mm/s and $\delta = 0.52$ mm/s of $[Fe_2(O_2)(OBz)_2\{HB(pz')_3\}_2]$ (**4**).[6d,15] On the basis of the Heisenberg model [$H = -2J\mathbf{S}_1\cdot\mathbf{S}_2$], the exchange-coupling constant (J) of **2** is estimated to be -55 cm^{-1},[16] showing that the magnetic interaction in a pair of Fe(III) ions of **2** is stronger than that of **4** ($J = -33$ cm^{-1}) because of the μ-oxo bridge in **2**.[6e] All these data demonstrate that **2** has the (μ-acetato)(μ-oxo)(μ-1,2-peroxo)diiron(III) core structure which is quite unique in the peroxodiiron(III) complexes reported so far.

The spontaneous decomposition of **2** in MeCN monitored at 605 nm obeys good first-order kinetics with $k = 2.5 \times 10^{-5}$ s^{-1} at 300 K (the half-life time $\tau_{1/2} = 7.7$ h) (Figure 1). The $\tau_{1/2}$ value of **2** is much larger than 10 min of $[Fe_2(O_2)(O)(OAc)(tripy)_2](ClO_4)$ at 263 K (tripy = 2-(bis(2-pyridyl)methyl)-6-methylpyridine; a half part of L) and 7.2 min of **3**[3] at 243 K. L specifically stabilizes the peroxodiiron core probably because L encapsulates the $Fe_2(O)(O_2)(OAc)$ core.

Table 1. Oxygenation of Hydrocarbons via Activation of **2**

substrate	reagents	product [yield (%)]
cyclohexane	m-ClC$_6$H$_4$COCl/DMF[a]	cyclohexanol [11][b]
cyclohexane	m-ClC$_6$H$_4$COCl/DMA[a]	cyclohexanol [6][b]
cyclohexane	CH$_3$COCl/DMF[a]	cyclohexanol [8][b]
cyclohexane	CCl$_3$COCl/DMF[a]	cyclohexanol [29][b]
cyclohexane	m-ClC$_6$H$_4$CO$_3$H/**1a**	cyclohexanol [41][c]
cyclohexene	m-ClC$_6$H$_4$COCl/DMF[a]	cyclohexenol [24],[b] [28][b,d] cyclohexenone [5],[b] [7][b,d]

[a] To a solution of **2** (0.05 mmol) in CH$_2$Cl$_2$/DMF (or DMA)/substrate (2 mL/0.5 mL/2 mL) was added 5 equiv of RCOCl at 0 °C under Ar. [b] Yield based on **2** used. [c] Yield based on m-ClC$_6$H$_4$CO$_3$H used. [d] The reaction was carried out under O$_2$.

Activation of **2** is examined under various conditions. Upon spontaneous decomposition of **2**[17] in the presence of alkane, alkane is not oxygenated at all. Upon addition of HClO$_4$ or m-ClC$_6$H$_4$COCl (m-CBC), **2** decomposes more rapidly [$k_{obs} = 8.0 \times 10^{-2}$ s^{-1} for **2** (1.0×10^{-3} M)/m-CBC (3.0×10^{-2} M) in CH$_2$Cl$_2$/MeCN (6:2, v/v) at 273 K], but oxygenation of alkane does not occur. In the presence of DMF, the decomposition of **2** is 20-fold accelerated [$k_{obs} = 1.6$ s^{-1} for **2** (1.0×10^{-3} M)/m-CBC (3.0×10^{-2} M) in CH$_2$Cl$_2$/MeCN/DMF (6:2:1, v/v) at 273 K], and cyclohexane is oxygenated to cyclohexanol and cyclohexanone.[18] Upon using cyclohexene, similar results were obtained as shown in Table 1. RCOCl may need activating with DMF (or DMA) to acylate the peroxide oxygen of **2**. The yields of the C−H oxygenation products with **2**/RCOCl/DMF are not affected under O$_2$, similarly to the **1a**/m-CPBA, indicating that the reaction is not autoxidation. It is concluded that the stable peroxodiiron(III) complex **2** is activated in the presence of acid chloride and DMF to oxygenate external hydrocarbons, and an acylperoxodiiron(III) complex[10a] $[Fe_2(RCO_3)(AcO)(O)(L)]^{2+}$ may be generated as an intermediate. The acylation of **2** may decrease the O−O bond energy to accelerate heterolytic O−O bond scission. It is postulated that the intermediate **P** of sMMOH is converted by protonation to a μ-1,1-Fe$^{III}_2$O$_2$H species and activated via heterolytic O−O bond scission.[6e] Therefore, the present results may support that the heterolytic O−O bond scission in the O$_2$-activation by sMMOH is accelerated by protonation (acylation in this study) to the peroxide moiety.

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Supporting Information Available: Experimental details for the synthesis, characterization, and activation of **2** and Figures S1−S4 containing the FAB mass, the resonance Raman, and the Mössbauer spectra of **2** and plots of the temperature dependence of magnetic susceptibility and the magnetic moment of **2**. This material is available free of charge via the Internet at http://pubs.acs.org.

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(12) The assignment of the two resonace Raman bands is consistent with the observed ^{18}O-shifts of 45 and 17 cm^{-1} for the ν_{O-O} and the ν_{Fe-O} bands, respectively.

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(14) The Mössbauer spectra were reproduced by repetition of the measurements with the same sample for several times, showing that **2** is not decomposed during the measurements. The relatively small isomer shift of **2** may be due to the back-donation to the π-amine ligands (pyridyl groups of L).

(15) HB(pz′)$_3$ represents hydrotris(3,5-diisopropyl-1-pyrazolyl)borate.

(16) Temperature dependences of magnetic susceptibility and magnetic moment of **2** are shown in the Supporting Information (Figure S4). The result indicates a strong antiferromagnetic spin-coupling between a pair of Fe(III) ions. An excellent fit of the $\chi_M - T$ data to a dinuclear model is obtained when $J = -55$ cm^{-1}, $g = 2.00$, and paramagnetic impurity (%) = 0.007 are assumed for **2**.

(17) See the Supporting Information.

(18) Cyclohexane is oxygenated to cyclohexanol as shown in Table 1 with a trace amount of cyclohexanone.