Important Role of Tetrahydrofuran Ring in Activation of Hydrogen Peroxide in the Presence of Binuclear Iron(III) Complexes with Linear μ-Oxo Bridge

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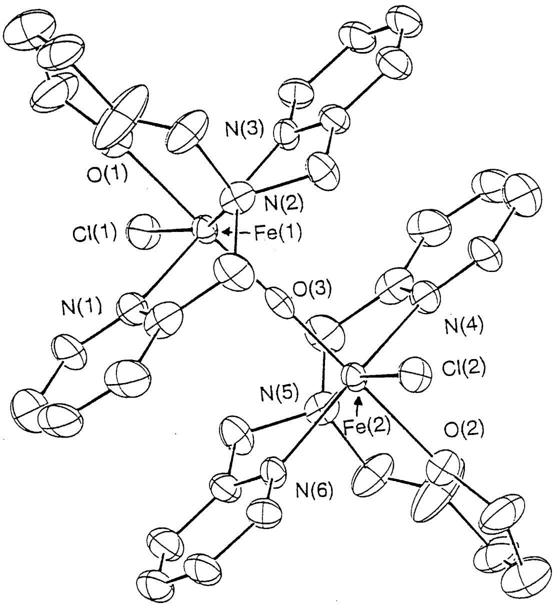
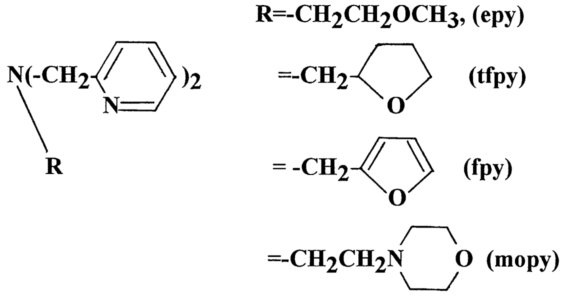
Binuclear μ-monooxo bridged iron(III) complex with tripodal-like ligand containing tetrahydrofuran ring exhibits much higher activity for alkane hydroxylation reaction in the presence of hydrogen peroxide than that of pyridine analogue; origin for high activity of the former complex was developed.

Structural and alkane functionalization studies of plausible biomimetic models of methane monooxygenase(MMO) have been an active area of research.[1] Recent spectroscopic studies including an X-ray crystallography[2] on MMO have shown that the active site has a diiron μ-hydroxo structure with both terminal and μ-carboxylato anions. Until now, many binuclear iron(III) compounds with μ-oxo bridge have been used as a model,[1] however detailed activation mechanism of dioxygen molecule in MMO remains unsolved at present. In this article we will show that tetrahydrofuran ring in the vicinity of an iron(III) atom exhibits very important role in activating hydrogen peroxide, leading to facile hydroxylation reaction of cyclohexane or adamantane.

Figure 1. ORTEP drawing of complex **1**.
Fe(1)-Cl(1), 2.279(5); Fe(1)-O(1), 2.227(13); Fe(1)-O(3), 1.780(3); Fe(1)-N(1), 2.128(13); Fe(1)-N(2), 2.212(14); Fe(1)-N(3), 2.154(14), Fe(2)-Cl(2), 2.272(4); Fe(2)-O(3), 1.778(3); Fe(2)-O(2), 2.225(12); Fe(2)-N(4), 2.144(12); Fe(2)-N(5), 2.224(11); Fe(2)-N(6), 2.118(12) Å.



The chemical structures of the ligand cited in this study are illustrated below;



Reaction of a methanol solution of the ligand, ferric chloride and triethylamine provided the binuclear iron(III) compounds with formula, $Fe_2OCl_2(L)_2^{2+}$, and the crystal structures of the three new compounds were determined; structure of complex with (tfpy), **1**[3] is illustrated in Figure 1. Complex **1** has a linear μ-oxo strucutre and an Fe-Fe separation of 3.558 Å. These features are completely the same as those of the corresponding (tpa) compound,[4] where (tpa) represents tris(2-pyridylmethyl)-amine. The structural properties of (epy) complex are essentially the same as those of **1**.[5] In the case of (mopy) compound,[6] a bent structure(Fe-O-Fe, 176.0°) is observed, while other structural features are very similar to those observed in **1** and other related complexes.

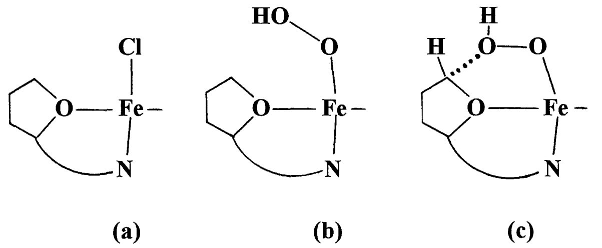
Table 1 shows the turn-over numbers of the products when cyclohexane was reacted with the binuclear iron(III) complex and hydrogen peroxide.[7] It should be noted here that formation of oxidized products is greatly dependent on the complex used, i.e., complexes **1** and that with (epy) exhibit high activity whereas those of (tpa), (fpy) and (mopy) show almost negligible activity. Since the spectral change is almost negligible on the addition of hydrogen peroxide to a solution of the iron(III) complex used in this study, it is clear that a binuclear unit with μ-oxo bridge remains in the reaction mixture.

In our previous papers, we have shown that the peroxide

Table 1. Turn-over numbers of oxidized products[7] catalyzed by an iron(III) complex

ligand	cyclohexanol	cyclohexanone
(tfpy)	3.9	2.0
(epy)	2.4	1.7
(tpa)	0.0	0.0
(mopy)	0.2	0.2
(fpy)	0.6	0.2

Scheme 1.



anion coordinating to a metal ion with η^1-coordination mode (see Scheme 1, (b)) shows an electrophilic nature, tending to attack the carbon atom.[8] The MNDO/PM3 calculations[9] have shown that tetrahydrofuran or $CH_3CH_2OCH_3$ moiety has occupied C-H bonding orbitals with rather higher energy.[10] Based on these results, it seems reasonable to assume that at the first stage, the coordination of peroxide anion may occur at the site of chloride anion(Scheme 1, (b)); then the coordinating peroxide anion may interact with the C-H bond of the tetrahydrofuran ring through the charge transfer force[11](see Scheme 1, (c); in this case, the peroxide anion may act as an electron acceptor, i.e., an electrophile). The presence of the interaction assumed above may be supported by the fact that cyclohexanehydroperoxide forms in the reaction mixture of hydrogen peroxide, cyclohexane, and a binuclear iron(III) compound.[12] The lower energies of the σ-type C-H bond of the pyridine or furan ring may predict very weak interaction between the ring and peroxide adduct. Crystal structure determination on the (mopy) complex revealed that interaction between the peroxide adduct and C-H bond of the (mopy) ligand is unlikely because of the longer distance between them, which may be due to steric repulsion between the pyridine ring and morpholine ring. Above discussions and the results in Table 1 indicate that interaction between the iron(III)-peroxide adduct and the chemical group in the vicinity of the metal ion should control the activation of peroxide anion, and thus hydroxylation reaction of the alkanes. Our results may give valuable informations on elucidating the dioxygen activation in MMO.

References and Notes

1 A. L. Feig and S. J. Lippard, *Chem. Rev.*, **94**, 759(1994).

2 A. C. Rosenzweig, C. A. Frederick, S. J. Lippard, and P. Nordlund, *Nature*, **366**, 537(1993).

3 Crystal data of $[Fe_2OCl_2(tfpy)_2][FeCl_4]_2$: triclinic, P1, a=12.778(2), b=24.038(3), c=8.288(1) Å, α=97.47(1), β =98.46(1), γ=78.02(1)°, V=2449.7(6) $Å^3$, Z=2, Dx=1.65 Mgm^{-3}, R=0.102 for 4592 observed reflections.

4 T. Kojima, R. A. Leising, S. Yan, and L. Que, Jr., *J. Am. Chem. Soc.*, **115**, 11328(1993).

5 Crystal data of $Fe_2OCl_2(epy)_2(ClO_4)_2$: triclinic, P1, a=9.381(1), b=11.383(2), c=9.147(2) Å, α=96.15(2), β =104.58(1), γ=83.75(1)°, V=935.7(2) $Å^3$, Z=1, Dx=1.53 Mgm^{-3}, R=0.076 for 3251 observed reflections.

6 Crystal data of $Fe_2OCl_2(mopy)_2(ClO_4)_2$: monoclinic, $P2_1/n$, a=12.71(2), b=15.779(2), c=21.939(3) Å, β= 95.40(5)°, V=4385(6) $Å^3$, Z=4, Dx=1.546 Mgm^{-3}, R=0.063 for 3306 observed reflections.

7 In a typical run, an acetonitrile solution(20 ml) containing iron(III) complex(0.05 mmole) and cyclohexane(0.840 g) was added to an acetonitrile solution(10 ml) containing hydrogen peroxide(1.13 g of 30% aqueous solution), and after 13 hours the products were determined by GC. Cyclopentanone was used as an internal standard. In the case of (tfpy) complex, $Fe_2OCl_2(tfpy)_2(ClO_4)_2$ was used.

8 Y. Nishida, N. Tanaka, and M. Okazaki, *Polyhedron*, **13,** 2245(1994); Y. Nishida, H. Itoh, and A. Yamazaki, *Polyhedron*, **13**, 2473(1994).

9 J. J. J. Stewart, *J. Comput. Chem.*, **10**, 209, 221(1989).

10 Energies of MO containing C-H bonds; tetrahydrofuran, -12.41; methylethyl ether, -12.06; furan, -13.49 eV.

11 R. S. Mulliken, *J. Am. Chem. Soc.*, **74,** 811(1952).

12 R. H. Fish, M. S. Konings, K. J. Oberhausen, R. H. Fong, W. M. Yu, G. Christou, J. B. Vincent, D. K. Koggin, and R. M. Buchannan, *Inorg. Chem.*, **30,** 3002(1991).