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A Mononuclear Peracetatoiron(III) Complex: Structural and Spectroscopic Characterization, and Oxidation Reactivity

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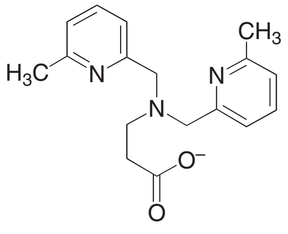
A mononuclear peracetatoiron(III) complex [Fe(6Me_2-BPP)($CH_3C(O)O_2$)]$^+$ (**2**) with a tripodal ligand (6Me_2-BPP) was prepared in the reaction of an iron(II) complex [Fe(6Me_2-BPP)(H_2O)]$^+$ (**1**) with peracetic acid. **2** is the first example of a structurally and spectroscopically well-defined non-heme type peracetatoiron(III) complex and has modest oxidation ability toward triphenyl phosphine, some olefins, and the tertiary C–H bond of adamantane.



6Me_2-BPP

Chart 1.

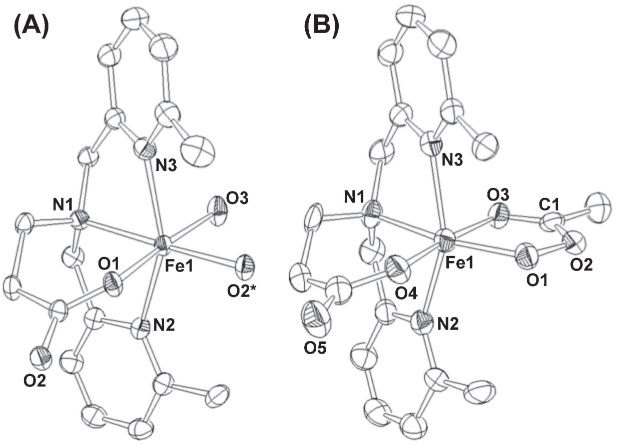


Figure 1. ORTEP views (50% probability) of **1**•BF_4•CH_3CN (A) and **2**•ClO_4 (B). Selected bond distances (Å) and angles (deg) for **2**•ClO_4: Fe1–O1, 1.912(2); Fe1–O3, 2.080(2); Fe1–O4, 1.904(2); Fe1–N1, 2.135(2); Fe1–N2, 2.210(2); Fe1–N3, 2.169(2); O1–O2, 1.443(3); Fe1–O1–O2, 115.7(1); O1–Fe1–O3, 77.74(8).

Combination of peroxycarboxylic acid such as peracetic acid with non-heme type iron complexes has been shown to be competent for selective epoxidation of some olefins such as cyclooctene,[1,2] oxidation of C–H bonds of alkanes,[3,4] and hydroxylation of arenes.[5–7] In these oxidation reactions, high-valent iron(IV or V) oxo species have been suggested as reactive intermediates. Non-heme type acylperoxoiron(III) complex has not been identified despite its important role in the oxidation reactions mentioned above,[1–7] although non-heme type mononuclear peroxo–, hydroperoxo–, and alkylperoxoiron(III) complexes have been spectroscopically and/or structurally well characterized.[8–10] However, acylperoxoiron(III) porphyrin complexes have been spectroscopically characterized[11] and in some cases, they have been shown to generate iron(IV) porphyrin π-cation radicals which are responsible for some oxidation reactions. Furthermore, some acylperoxoiron(III) porphyrin complexes have also been suggested to directly epoxidize olefins as well as iron(IV) porphyrin π-cation radical.[11d,11g,11h,12,13] Thus, it is of particular interest to investigate structural and spectroscopic properties, and oxidation reactivity of the non-heme type acylperoxoiron(III) species. Herein, we report the first example of a structurally and spectroscopically well-defined non-heme type peracetatoiron(III) complex [Fe(6Me_2-BPP)($CH_3C(O)O_2$)]$^+$ (**2**) with a tripodal ligand (6Me_2-BPP) (Chart 1)[14] generated in the reaction of an iron(II) complex [Fe(6Me_2-BPP)(H_2O)]$^+$ (**1**) with peracetic acid, and its oxidation reactivity toward some olefins and alkanes.

The iron(II) complex **1** was obtained by treatment of $Fe(ClO_4)_2$•$6H_2O$ in methanol with 6Me_2-BPPH under N_2 atmosphere, which has a distorted octahedral structure with an N_3O_3 donor set (Figures 1A and S1[22]), where the terminal carboxylate oxygen of 6Me_2-BPP bridges an adjacent Fe(II) ion forming a polymer structure (Figure S2[22]).

Reaction of **1**•$C_4F_9SO_3$ in acetonitrile at −40 °C with ≈1 equivalent of commercially available peracetic acid which consists of 32 wt % peracetic acid, ≈6 wt % H_2O_2, and 40–45 wt % acetic acid[2,15] gave a yellow acetatoiron(III) complex [Fe(6Me_2-BPP)($CH_3C(O)O$)]$^+$ (**3**: *m*/*z* 413.1), which can be further converted into a yellow peracetatoiron(III) complex [Fe(6Me_2-BPP)($CH_3C(O)O_2$)]$^+$ (**2**: *m*/*z* 429.1) by addition of ≈9 equivalents of peracetic acid (Figure S5[22]), indicating that the complex **2** is preferentially generated even in the presence of H_2O_2 and acetic acid. Generation of **2** is also observed in the reaction of **1** with H_2O_2/acetic acid (d_4-acetic acid) mixture in acetonitrile at 0 °C (Figure S6[22]), implying that the iron center mediates in situ generation of peracetic acid from acetic acid and H_2O_2,[2,16] although the amount of **2** (d_3-**2**) generated seems to be poor judging from ESI-TOF-MS measurements.

We also attempted to prepare [Fe(6Me_2-BPP)(*m*-CPBA)]$^+$ from the reaction of **1**•$C_4F_9SO_3$ with ≈10 equivalents of *m*-chloroperbenzoic acid (*m*-CPBA) in acetonitrile at −40 °C. The ESI-TOF-MS of the reaction solution suggested the formation of [Fe(6Me_2-BPP)(*m*-CPBA)]$^+$ (*m*/*z* 525.1), although the amount of [Fe(6Me_2-BPP)(*m*-CPBA)]$^+$ generated seems to be very poor judging from ESI-TOF-MS (Figure S7[22]) and it could not be isolated.

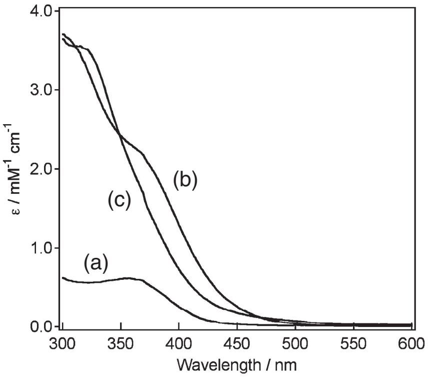


Figure 2. Electronic spectra of (a) $\mathbf{1}\cdot C_4F_9SO_3$, (b) an isolated sample of $\mathbf{2}\cdot C_4F_9SO_3$, and (c) its decomposed species (decomposed at 20 °C) in acetonitrile at −40 °C.

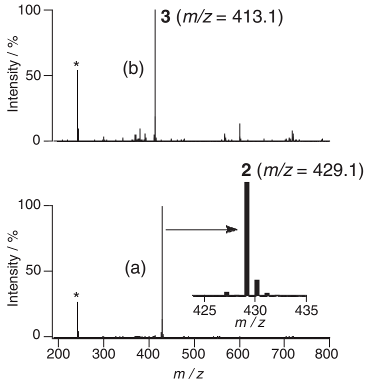


Figure 3. ESI-TOF-MS of (a) an isolated sample of $\mathbf{2}\cdot C_4F_9SO_3$ in acetonitrile at −40 °C and (b) its decomposed species at 20 °C. Asterisk is $(n\text{-butyl})_4N^+$ cation used as an internal standard ($m/z = 242.3$). See details in Figure S8.[22]

The crystal structure of $\mathbf{2}\cdot ClO_4$ showed that the complex cation has a distorted octahedral structure with an N_3O_3 donor set composed of a bidentate peracetate and a tetradentate tripodal ligand (Figures 1B and S3[22]). The peracetate forms a five-membered chelate ring with the O1–Fe1–O3 angle of 77.74(8)° similar to that of the peroxocarbonate group in $[Fe(qn)_2(O_2C(O)O)]^-$ (78.8(1)°).[10a] The peroxo oxygen is trans to a tertiary amine nitrogen, and the carbonyl oxygen is trans to a carboxylate oxygen. The peroxo O–O bond length of $\mathbf{2}\cdot ClO_4$ (O1–O2: 1.443(3) Å) is comparable to those of $[Fe(qn)_2(O_2C(O)O)]^-$ (1.455(5) Å), $[Cu_2(XYL\text{-}O)(m\text{-}CPBA)]^{2+}$ (1.463(12) Å),[17] and the (μ-peroxo)diiron(III) complexes (1.396(5)–1.426(6) Å).[18] The iron–peroxo bond length (Fe1–O1: 1.912(2) Å) is slightly shorter than that of $[Fe(qn)_2(O_2C(O)O)]^-$ (1.936(3) Å).

Unfortunately, $\mathbf{2}\cdot ClO_4$ was insoluble in common organic solvents at −40 °C. Therefore, we prepared $\mathbf{2}\cdot C_4F_9SO_3$, which is soluble in acetonitrile. The crystal structure of $\mathbf{2}\cdot C_4F_9SO_3$ is almost the same as that of $\mathbf{2}\cdot ClO_4$.[19] Isolation of $\mathbf{2}\cdot C_4F_9SO_3$ allowed us to investigate spectroscopic characterization and oxidation reactivity of peracetatoiron(III) species in solution state in the absence of acetic acid and H_2O_2 which are commonly present in commercially available peracetic acid. **2** is stable for at least 4 h in acetonitrile at −40 °C, but it decays in several minutes at 20 °C to afford acetatoiron(III) complex **3** (Figures 2, 3, and S8[22]) together with a bis(μ-hydroxo)diiron(III) complex $[Fe_2(OH)_2(6Me_2\text{-}BPP)_2]^{2+}$ (**4**), $\{6Me_2\text{-}BPPH + H^+\}^+$, and unidentified species observed at m/z 379.1, 568.2, and 718.2 (relative intensities are <5–10% compared to that of **3**). It was also found that the exchange of the acetyl moiety [*CH₃C(O)*–O–O] in **2** occurs as observed for that of the CO_2 moiety in peroxocarbonatoiron(III) complex $[Fe(qn)_2(O_2C(O)O)]^-$,[10b] which was confirmed by the reaction with $CD_3C(O)OD$ by ESI-TOF-MS (Figure S9[22]). This result indicates that the peroxo moiety of peracetate in **2** has a strong nucleophilic character (eq 1).

$$[Fe(6Me_2\text{-}BPP)(CH_3C(O)O_2)]^+(\mathbf{2}) + CD_3C(O)OD \rightleftarrows$$
$$[Fe(6Me_2\text{-}BPP)(CD_3C(O)O_2)]^+(\mathbf{2}\text{-}d_3) + CH_3C(O)OD \qquad (1)$$

The EPR spectrum of a frozen acetonitrile/toluene solution of **2** at 78 K shows a signal at $g = 4.3$, arising from a rhombic high-spin iron(III) center (Figure S10[22]) as observed for $[Fe(qn)_2(O_2C(O)O)]^-$.[10a] It should be noted that unlike mononuclear peroxo–, hydroperoxo–, and alkylperoxoiron(III) complexes,[8–10] and peroxodiiron(III) complexes,[18] **2** has no intense color. The UV–vis spectrum of **2** shows a featureless absorption band around 300–450 nm with a shoulder at 367 nm ($\varepsilon = 2260$ $M^{-1}\,cm^{-1}$) as shown in Figure 2b. Thus, unlike mononuclear hydroperoxo-, alkylperoxo-, and peroxocarbonatoiron(III) complexes which exhibit the LMCT transitions at 440–640 nm irrespective of their spin states (low- or high-spin),[8–10] the complex **2** has no LMCT transition at least up to ≈370 nm. Such a significant blue shift of the LMCT band of **2** seems to be partly attributable to the lowering of the π_v^* orbital energy of the peroxo moiety due to the stronger electron-withdrawing nature of acetyl moiety compared with that of hydrogen, alkyl, or CO_2 moieties. For fuller understanding of such a significant blue shift of the LMCT transition, further study is needed. We also tried to further characterize **2** by resonance Raman spectroscopy, but the ν(O–O) and ν(Fe–O) bands have not been observed with 351.4, 363.8, 406.7, and 514.5 nm laser excitations.

It is noted that the EPR and UV–vis spectral features of **2** and its decomposed product(s) are quite similar (Figures 2 and S10[22]). Thus, it is difficult to identify the formation and decomposition of **2** by only UV–vis and EPR spectra, however, it can be identified by ESI-TOF-MS. Therefore, the absence of reports of non-heme type acylperoxoiron(III) species is probably due to difficulty in detecting it by standard spectroscopic methods (UV–vis and EPR).

Oxidation reactivity of **2** toward some substrates, PPh_3, cyclooctene, styrene, *cis*-stilbene, adamantane, and cyclohexane was investigated (details are given in the Supporting Information[22]). The oxidation products determined by GC-MS are listed in Table S1.[22] Complex **2** acts as an oxo-transfer reagent to produce $O{=}PPh_3$ (≈94%) in acetonitrile at 20 °C. Reaction of **2** with a 2000-fold excess of cyclooctene and styrene in acetonitrile at 20 °C under N_2 afforded the corresponding epoxides in moderate yields (48 and 40%, respectively)[20] and no other oxidation product was observed, indicating that **2** has selective epoxidation ability as found for $[Fe_2(phen)_4(O)(H_2O)_2]^{4+}$[1,2] and $[Fe(TPA\text{ or }BPMEN)(CH_3CN)_2]^{2+}$,[2] although oxidation ability of **2** is modest. However, no epoxidation of *cis*-stilbene was observed. We have also investigated the C–H bond oxidation of adamantane and cyclohexane. Regioselective oxidation of adamantane (≈100 equivalents in CH_2Cl_2) occurred to give 1-adamantanol (7%), 2-adamantanol (1.5%), and 2-adamantanone (0.3%), although their yields are poor.[20] The regioselectivity between the tertiary (3°) and the secondary (2°) carbons (3°/2°) is ≈12, which is derived from the amount of 1-adamantanol divided by the amounts of 2-adamantanol and 2-adamantanone and multiplied by 3 to correct for the number of the tertiary C–H bonds and the number of the secondary C–H bonds. The value is in the range of those obtained for metal-based oxidation (3.5–33),[21] suggesting that the oxidation of adamantane also proceeds through a metal-based oxidation pathway. However, **2** is not capable of oxidizing the C–H bond of cyclohexane under the same conditions.

In summary, we have succeeded in the first structural and spectroscopic characterization of a mononuclear peracetato–iron(III) complex **2** obtained from the reaction of **1** with peracetic acid. **2** has no intense color (LMCT band) in the visible region, which is in contrast to those of other peroxoiron(III) complexes. Although the oxidation ability of complex **2** is modest, **2** is capable of not only epoxidizing some olefins but also oxidizing the tertiary C–H bond of adamantane.

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14 Abbreviations used: 6Me$_2$-BPP, *N*,*N*-bis(6-methyl-2-pyridylmethyl)-3-aminopropionate; *m*-CPBA, *m*-chloroperbenzoic acid; qn, quinaldinate; XYL-O, 2,6-bis{bis[2-(2-pyridyl)ethyl]aminomethyl}phenolate; phen, 1,10-phenanthroline; TPA, tris(2-pyridylmethyl)amine; BPMEN, *N*,*N*′-dimethyl-*N*,*N*′-bis(2-pyridylmethyl)-1,2-ethylenediamine.

15 In the course of this study, 32 wt % peracetic acid (Aldrich) was not commercially available. Thus, synthesis and isolation of **2**$\cdot C_4F_9SO_3$ were made in the reaction of **1**$\cdot C_4F_9SO_3$ with 15% peracetic acid (AppliChem; this reagent also contains 24% H_2O_2, 15% acetic acid, and 40% water according to the reagent description). See Supporting Information.[22]

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19 Crystal structure of **2**$\cdot C_4F_9SO_3$ was also determined by X-ray crystallography. X-ray crystallography of **2**$\cdot C_4F_9SO_3$ revealed that an asymmetric unit contains two independent molecules (Figure S4[22]).

20 Control experiments of cyclooctene (≈2000 equiv), styrene (≈2000 equiv), and adamantane (≈100 equiv) with 1 equiv of peracetic acid (32 wt %, Aldrich) in the absence of **2** were also carried out. The yields of cyclooctene oxide and styrene oxide (based on peracetic acid) were ≈24 and ≈20%, respectively. Thus, the epoxide yields in the presence of **2** are ≈2 times higher than those of control experiments. No oxidation products of adamantane were observed in the control experiment.

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22 Supporting Information is available electronically on the CSJ-Journal Web site, http://www.csj.jp/journals/chem-lett/index.html.