Synthesis and Crystal Structure of the Bis(μ -hydroxo)diiron(II) Complex with Tridentate Ligands Having a Sterically Bulky Imidazolyl Group

Reiko YAGUCHI,^{*1} Hideki FURUTACHI,^{*1†} Sanae SHIROTSUKI,^{*1} Xi ZHANG,^{*1} Takanao ISHIKAWA,^{*1} Shigehisa AKINE,^{*1,*2} Takehiko TOSHA,^{*3} Shuhei FUJINAMI,^{*1} Masatatsu SUZUKI,^{*1} and Teizo KITAGAWA^{*4}

^{*1} Department of Chemistry, Division of Material Sciences, Graduate School of Natural Science and Technology, Kanazawa University, Kakuma-machi, Kanazawa 920-1192, Japan

^{*2} Nano Life Science Institute (WPI-NanoLSI), Kanazawa University, Kakuma-machi, Kanazawa 920-1192, Japan

^{*3} Biometal Science Laboratory, RIKEN SPring-8 Center, Kouto, Sayo, Hyogo 679-5148, Japan

^{*4} Picobiology Institute, Graduate School of Life Science, University of Hyogo, Ako-gun, Hyogo 678-1297, Japan

The structure of the dinuclear Fe(II) complex $[\text{Fe}_2(\text{OH})_2(\text{L})_2](\text{ClO}_4)_2$ (**1**) was determined by X-ray crystallography, where L is bis(1-methyl-2-phenyl-4-imidazolylmethyl)benzylamine. The compound crystallizes in a monoclinic space group, $P2_1$, with $a = 11.007(2)$, $b = 11.5591(12)$, $c = 12.534(2)\text{\AA}$, $\alpha = 63.254(12)$, $\beta = 86.458(19)$, $\gamma = 79.581(7)^\circ$, $Z = 1$, $V = 1400.4(4)\text{\AA}^3$. The $R1$ [$I > 2\sigma(I)$] and $wR2$ (all data) values are 0.00328 and 0.0862, respectively, for all 6735 independent reflections. The complex has a bis(μ -hydroxo)diiron core structure.

(Received December 26, 2018; January 10, 2019; Published on web May 10, 2019)

The Fe_2/O_2 -mediated arene hydroxylation is of current interest for understanding the reaction mechanism of a dioxygen activating non-heme dinuclear iron enzyme, such as toluene monooxygenase (TMO).¹⁻³ Previously, we reported on intramolecular aromatic ligand hydroxylation *via* the decay of (μ -peroxo)diiron(III) complexes with the dinucleating ligands having a phenyl group as a reaction probe.⁴⁻⁶ In this study, we synthesized the bis(μ -hydroxo)diiron(II) complex $[\text{Fe}_2(\text{OH})_2(\text{L})_2](\text{ClO}_4)_2$ (**1**) with a tridentate ligand (L) having 2-phenylimidazolyl groups in order to examine the Fe_2/O_2 -mediated arene hydroxylation (Fig. 1). In this paper, we report on the crystal structure of **1** together with the reactivity toward dioxygen.

The tridentate ligand L-H₂O was synthesized according to a literature method.⁷ The diiron(II) complex with L was prepared under a N₂ atmosphere. A mixture of $\text{Fe}(\text{CF}_3\text{SO}_3)_2 \cdot 2\text{CH}_3\text{CN}$ ⁸ (0.436 g, 1.0 mmol) and L-H₂O (0.456 g, 1.0 mmol) in dry-THF/ CH_2Cl_2 (1:1, 20 mL) was added a THF solution (3 mL) containing H₂O (18 μL , 1.0 mmol) and triethylamine (138 μL , 1.0 mmol) to give a yellow-green solution. Diethyl ether (20 mL) was added to the resulting yellow-green solution to give a yellow-green powder, which was filtered and washed with diethyl ether. Yield: 0.32 g, 47%. *Anal.* Found: C, 52.51; H, 4.43; N, 10.18%. Calcd for $[\text{Fe}_2(\text{OH})_2(\text{L})_2](\text{CF}_3\text{SO}_3)_2 \cdot 2\text{H}_2\text{O}$, $\text{C}_{60}\text{H}_{64}\text{Fe}_2\text{N}_{10}\text{O}_{10}\text{S}_2$: C, 52.41; H, 4.69; N, 10.19%. Single crystals of $[\text{Fe}_2(\text{OH})_2(\text{L})_2](\text{ClO}_4)_2$ (**1**) suitable for X-ray crystallography were obtained by slow diffusion of diethyl ether onto a dry- $\text{CH}_2\text{Cl}_2/\text{MeCN}$ (1:1) solution of a yellow-green powder containing $(n\text{-Bu})_4\text{NClO}_4$.

X-ray diffraction measurements were made on a Rigaku CCD Mercury diffractometer with graphite-monochromated Mo $K\alpha$ radiation at 123 K. The structure was solved by a direct method (SHELXS 97)⁹ and expanded using a Fourier technique. The

structure was refined by a full-matrix least-squares method by using a SHELXL 2014¹⁰ (Yadokari-XG).¹¹ All non-hydrogen atoms were refined with anisotropic displacement parameters. The μ -hydroxo hydrogen atoms were refined using distance restraints with U_{iso} constrained to 1.2-times the U_{eq} of the parent oxygen atoms. Other hydrogen atoms were included using a riding model. The crystal data are summarized in Table 1.

X-ray crystallography of **1** reveals that the asymmetric unit contains a half of the complex cation $[\text{Fe}_2(\text{OH})_2(\text{L})_2]^{2+}$ and a perchlorate anion. The molecular structure of the complex cation $[\text{Fe}_2(\text{OH})_2(\text{L})_2]^{2+}$ of **1** is shown in Fig. 2. Selected bond distances ($\text{\AA}$) and angles ($^\circ$) are given in Table 2. The complex cation $[\text{Fe}_2(\text{OH})_2(\text{L})_2]^{2+}$ of **1** has a centrosymmetric bis(μ -hydroxo)diiron(II) diamond core, as found for a closely related five-coordinated bis(μ -hydroxo)diiron(II) complex $[\text{Fe}_2(\text{OH})_2$ -

Fig. 1 Chemical diagram of the complex cation $[\text{Fe}_2(\text{OH})_2(\text{L})_2]^{2+}$ of **1**.

[†] To whom correspondence should be addressed.

E-mail: h-furutachi@se.kanazawa-u.ac.jp

Table 1 Crystal and experimental data

Chemical formula: $C_{58}H_{60}Cl_2Fe_2N_{10}O_{10}$	
Formula weight = 1239.76	
$T = 123\text{ K}$	
Crystal system: triclinic	Space group: $P\bar{1}$
$a = 11.007(2)\text{ \AA}$	$\alpha = 63.254(12)^\circ$
$b = 11.5591(12)\text{ \AA}$	$\beta = 86.458(19)^\circ$
$c = 12.534(2)\text{ \AA}$	$\gamma = 79.581(17)^\circ$
$V = 1400.4(4)\text{ \AA}^3$	$Z = 1$
$D_x = 1.470\text{ g/cm}^3$	
Radiation: Mo $K\alpha$ ($\lambda = 0.71073\text{ \AA}$)	
$\mu(\text{Mo } K\alpha) = 6.83\text{ cm}^{-1}$	
$F(0\ 0\ 0) = 644$	
Crystal size = $0.25 \times 0.20 \times 0.08\text{ mm}^3$	
No. of reflections collected = 15351	
No. of independent reflections = 6735	
θ range for data collection = 2.647 to 30.519°	
Data/Restraints/Parameters = 6735/1/375	
Goodness-of-fit on $F^2 = 1.046$	
R indices [$I > \sigma(I)$]: $R1 = 0.0328$, $wR2 = 0.0847$	
R indices (all data): $R1 = 0.0349$, $wR2 = 0.0862$	
$(\Delta/\sigma)_{\max} = 0.001$	
$(\Delta\rho)_{\max} = 0.339\text{ e \AA}^{-3}$ ($\Delta\rho)_{\min} = -0.481\text{ e \AA}^{-3}$	
Measurement: Rigaku CCD Mercury Diffractometer	
Data collection & cell refinement program: CrystalClear	
Structure solving program: SHELXS 97	
Structure determination: SHELXL 2014	
Refinement: full-matrix least squares against F^2	
CCDC deposition number: 1887314

Fig. 2 ORTEP drawing of the complex cation $[Fe_2(OH)_2(L)_2]^{2+}$ of **1**, showing 50% probability ellipsoids. The hydrogen atoms are omitted for clarity.

(HB(3,5-*i*Pr₂Pz)₃)₂] with a tridentate ligand (HB(3,5-*i*Pr₂Pz)₃ = hydrotris(3,5-diisopropylpyrazol-1-yl)-borate).¹² Both of the iron atoms in **1** have a distorted five-coordinate structure that is intermediate between a trigonal bipyramid and a square-pyramid ($\tau = 0.44$)¹³ with an N_3O_2 donor set, where three nitrogen atoms of **L** are in a facial array. The structural distortion around the iron atoms is much larger than that observed in $[Fe_2(OH)_2(HB(3,5-*i*Pr_2Pz)_3)_2]$ ($\tau = 0.003$), which is probably due to unfavorable steric interactions among 2-phenylimidazolyl groups of the tridentate ligands. The Fe-OH bond *trans* to the imidazole

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

Fe1-O1	1.9807(11)	Fe1-O1*	2.0394(12)
Fe1-N1	2.2971(12)	Fe1-N2	2.0916(12)
Fe1-N4	2.1076(12)	Fe1...Fe1*	3.0488(9)
O1-Fe1-O1*	81.36(5)	O1-Fe1-N1	93.00(5)
O1-Fe1-N2	142.82(5)	O1-Fe1-N4	109.61(5)
O1*-Fe1-N1	169.40(4)	O1*-Fe1-N2	100.53(5)
O1*-Fe1-N4	114.06(5)	N1-Fe1-N2	78.53(5)
N1-Fe1-N4	76.25(5)	N2-Fe1-N4	103.44(5)
Fe1-O1-Fe1*	98.64(5)		

Symmetry operation *: $-x, -y+1, -z+1$.

Fig. 3 Electronic spectra of (a) $[Fe_2(OH)_2(L)_2](ClO_4)_2$ (**1**) and (b) $[Fe_2(O)(O_2)(L)_2]^{2+}$ (**2**) generated by the reaction of **1** with O_2 in $CH_2Cl_2/MeCN$ (3:1) at -80°C .

nitrogen (Fe1-O1: 1.9807(11)Å) is slightly shorter than the corresponding bond *trans* to the amino nitrogen (Fe1-O1*: 2.0394(12)Å), giving rise to a slightly asymmetric diamond core ($\Delta r = 0.06\text{ \AA}$). Unlike **1**, the Fe-OH bonds are almost equivalent in $[Fe_2(OH)_2(HB(3,5-*i*Pr_2Pz)_3)_2]$ (2.04 and 2.016 Å; $\Delta r = 0.02\text{ \AA}$) with the capping ligand having identical donor atoms. The average Fe-OH bond distance (2.01 Å) of **1** is comparable to those in five-coordinated bis(μ -hydroxo)diiron(II) complexes (2.00 – 2.03 Å),^{5,12} but is slightly shorter than those in six-coordinated bis(μ -hydroxo)diiron(II) complexes (2.04 – 2.08 Å).^{14,15} The Fe-Fe separation is 3.0488(9)Å, which is on the short side of the range reported for related bis(μ -hydroxo)diiron(II) complexes (3.010 – 3.187 Å).^{5,12,14,15} The Fe-OH bond distances as well as the Fe-O-Fe and O-Fe-O angles are in the range of those observed for related bis(μ -hydroxo)diiron(III) complexes. The Fe-ligand bond distances observed for **1** are consistent with the complexes having high spin Fe(II) ions.^{4,5,12,14,15}

The reaction of **1** with O_2 in $CH_2Cl_2/MeCN$ (3:1) at -80°C generated a dark-green peroxo species (**2**), which exhibits an intense absorption band at 630 nm ($\epsilon = 930\text{ M}^{-1}\text{ cm}^{-1}$) that can be assigned to the CT transition from O_2^{2-} to Fe(III) center,³ together with bands at $\sim 460\text{ nm}$ (sh, $\epsilon = 810\text{ M}^{-1}\text{ cm}^{-1}$) and $\sim 825\text{ nm}$ ($\epsilon = 235\text{ M}^{-1}\text{ cm}^{-1}$) (Fig. 3). The spectral feature of **2** is quite similar to those of well-characterized (μ -oxo)(μ -peroxo)-diiron(III) complexes.^{3,14-16} The resonance Raman (rR) spectra of **2** showed two isotope-sensitive bands at 839 cm^{-1} ($^{16-18}\Delta = 49\text{ cm}^{-1}$) and 486 cm^{-1} ($^{16-18}\Delta = 22\text{ cm}^{-1}$) in $CH_2Cl_2/MeCN$ (3:1) at -80°C with a 607-nm laser excitation (Fig. S1). These bands can be assigned to $\nu(\text{O-O})$ and $\nu_s(\text{Fe-O})$ vibrations, respectively,

which are also similar to those of well-characterized (μ -oxo) (μ -peroxo)diiron(III) complexes.^{3,14-16} Thus, these data indicate that **2** has a (μ -oxo)(μ -peroxo)diiron(III) core (Scheme S1).

Peroxo species $[\text{Fe}_2(\text{O})(\text{O}_2)(\text{L})_2]^{2+}$ (**2**) gradually decomposes in $\text{CH}_2\text{Cl}_2/\text{MeCN}$ (3:1) at -80°C , but quickly decays at -60°C . The decomposition of **2** obeys first-order kinetics (Fig. S2), where the k_d value (first-order rate constant of self-decomposition) is $1.2 \times 10^{-3} \text{ s}^{-1}$. However, **2** showed no intramolecular aromatic ligand hydroxylation (Scheme S1). This result is in sharp contrast to the intramolecular aromatic ligand hydroxylation initiated by (μ -peroxo)diiron(III) complexes with dinucleating ligands.⁴⁻⁶ The origin of such a difference is not clear at the present time. For a fuller understanding of such different reactivity, further comprehensive functional model studies are needed.

Acknowledgements

This work was supported by Grants-in-Aid for Scientific Research from the Ministry of Education, Culture, Sports, Science and Technology, Japan, and the Kanazawa University SAKIGAKE Project.

Supporting Information

A cif format file, Figs. S1 and S2, and Scheme S1. These materials are available free of charge on the Web at <http://www.jsac.or.jp/xraystruct/>.

References

1. M. H. Sazinsky and S. J. Lippard, *Acc. Chem. Res.*, **2006**, 39, 558.
2. J. F. Acheson, L. J. Bailey, T. C. Blunold, and B. G. Fox, *Nature*, **2017**, 544, 191.
3. A. J. Jasiewicz and L. Que Jr., *Chem. Rev.*, **2018**, 118, 2554.
4. M. Yamashita, H. Furutachi, T. Tosha, S. Fujinami, W. Saito, Y. Maeda, K. Takahashi, K. Tanaka, T. Kitagawa, and M. Suzuki, *J. Am. Chem. Soc.*, **2007**, 129, 2.
5. M. Sekino, H. Furutachi, K. Tasaki, T. Ishikawa, S. Mori, S. Fujinami, S. Akine, Y. Sakata, T. Nomura, T. Ogura, T. Kitagawa, and M. Suzuki, *Dalton Trans.*, **2016**, 45, 469.
6. M. Sekino, H. Furutachi, R. Tojo, A. Hishi, H. Kajikawa, T. Suzuki, K. Suzuki, S. Fujinami, S. Akine, Y. Sakata, T. Ohta, S. Hayami, and M. Suzuki, *Chem. Commun.*, **2017**, 53, 8838.
7. K. Itoh, H. Hayashi, H. Furutachi, T. Matsumoto, S. Nagatomo, T. Tosha, S. Terada, S. Fujinami, M. Suzuki, and T. Kitagawa, *J. Am. Chem. Soc.*, **2005**, 127, 5212.
8. K. S. Hagen, *Inorg. Chem.*, **2000**, 39, 5867.
9. G. M. Sheldrick, SHELXS-97, Program for the Solution of Crystal Structures, University of Göttingen, Germany, **1997**.
10. G. M. Sheldrick, *Acta. Crystallogr.*, **2008**, A64, 112.
11. C. Kabuto, S. Akine, T. Nemoto, and E. Kwon, *J. Cryst. Soc. Jpn.*, **2009**, 51, 218.
12. N. Kitajima, N. Tamura, M. Tanaka, and Y. Moro-oka, *Inorg. Chem.*, **1992**, 31, 3342.
13. A. W. Addison, T. N. Rao, J. Reedijk, J. van. Rijn, and G. C. Verschoor, *J. Chem. Soc., Dalton Trans.*, **1984**, 1349.
14. V. L. MacMurdo, H. Zheng, and L. Que Jr., *Inorg. Chem.*, **2000**, 39, 2254.
15. S. V. Kryatov, S. Taktak, I. V. Korendovych, E. V. Rybak-Akimova, J. Kaizer, S. Torelli, X. Shan, S. Mandal, V. L. MacMurdo, A. M. i. Payeras, and L. Que Jr., *Inorg. Chem.*, **2005**, 44, 85.
16. X. Zhang, H. Furutachi, S. Fujinami, S. Nagatomo, Y. Maeda, Y. Watanabe, T. Kitagawa, and M. Suzuki, *J. Am. Chem. Soc.*, **2005**, 127, 826.