Crystal Structure of Bis(μ -hydroxo)diiron(III) Complex with Tripodal Ligands Having a Terminal Carboxylate Group

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The structure of the dinuclear Fe(III) complex $[\text{Fe}_2(6\text{Me}_2\text{-BPP})_2(\text{OH})_2](\text{NO}_3)_{1.9553}\cdot\text{Br}_{0.0447}\cdot 8\text{H}_2\text{O}$ (**1**) was determined by X-ray crystallography, where 6Me₂-BPP is *N,N*-bis(6-methyl-2-pyridylmethyl)-3-aminopropionate. The compound crystallizes in a triclinic space group, $P\bar{1}$, with $a = 10.3845(15)$, $b = 11.1976(15)$, $c = 20.389(4)\text{\AA}$, $\alpha = 82.119(10)^\circ$, $\beta = 85.340(10)^\circ$, $\gamma = 68.871(7)^\circ$, $Z = 2$, $V = 2189.3(6)\text{\AA}^3$. The $R1$ [$I > 2\sigma(I)$] and $wR2$ (all data) values are 0.0342 and 0.0972, respectively, for all 9586 independent reflections. The complex has a bis(μ -hydroxo)diiron core structure.

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Hydroxo- or oxo-bridged non-heme diiron centers with terminal carboxylates are structural motifs found in metalloproteins, such as soluble methane monooxygenase (sMMO) and ribonucleotide reductase (RNR).¹⁻⁴ Synthetic diiron model complexes with $\text{Fe}_2(\text{OH})_2$, $\text{Fe}_2(\text{O})(\text{OH})$, and $\text{Fe}_2(\text{O})_2$ cores are of particular importance for obtaining fundamental insights into the structural and spectroscopic properties of the active centers in the metalloproteins mentioned above.²⁻⁴ Previously, we reported that the crystal structure of a (μ -oxo)(μ -hydroxo)diiron(III) complex, $[\text{Fe}_2(6\text{Me}_2\text{-BPP})_2(\text{O})(\text{OH})]^+$ (**2**),⁵ with a tetradentate tripodal ligand (6Me₂-BPP) having a terminal carboxylate, which was derived from deprotonation of its conjugate acid, $[\text{Fe}_2(6\text{Me}_2\text{-BPP})_2(\text{OH})_2]^{2+}$. In this paper, we report on the crystal structure of the bis(μ -hydroxo)diiron(III) complex $[\text{Fe}_2(6\text{Me}_2\text{-BPP})_2(\text{OH})_2](\text{NO}_3)_{1.9553}\cdot\text{Br}_{0.0447}\cdot 8\text{H}_2\text{O}$ (**1**) (Fig. 1).

A single crystal of $[\text{Fe}_2(6\text{Me}_2\text{-BPP})_2(\text{OH})_2](\text{NO}_3)_{1.9553}\cdot\text{Br}_{0.0447}\cdot 8\text{H}_2\text{O}$ (**1**) suitable for X-ray crystallography was obtained by the recrystallization of $[\text{Fe}_2(6\text{Me}_2\text{-BPP})_2(\text{OH})_2](\text{NO}_3)_2\cdot 4.5\text{H}_2\text{O}$ ⁵ from water. It was picked up on a hand-made cold copper plate mounted inside a liquid N₂ Dewar vessel and mounted on a glass rod at -80°C . 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)⁶ and expanded using a Fourier technique. The structure was refined by a full-matrix least-squares method by using the SHELXL 2014⁷ (Yadokari-XG).⁸ The asymmetric unit contains two very similar molecules that could be nearly related by each other with a translation symmetry in the $[0\ 1\ \bar{1}]$ direction. This could be interpreted as a structure with a half unit-cell volume. However, the counter anions (NO_3^- , Br^-) and crystallizing water molecules are located at different positions that could not be related by a translational symmetry. Also, the diffractions with $k + l = \text{odd}$ showed significant intensities (around 1/3 of those with $k + l = \text{even}$). Therefore, we concluded that the structure should have two

independent molecules in the asymmetric unit. All non-hydrogen atoms were refined with anisotropic displacement parameters. The hydrogen atoms in the μ -hydroxo groups and water molecules were restrained to ensure reasonable distances (0.84 Å) by applying the default values for O-H DFIX restraints. 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 two halves of complex cations, $[\text{Fe}_2(6\text{Me}_2\text{-BPP})_2(\text{OH})_2]^{2+}$ (molecules A and B), 1.9553 nitrate ions, 0.0447 bromide ion, and eight water molecules. The partial content of the bromide ion appears to be due to the preparation route of the 6Me₂-BPPH ligand, which was obtained from the reaction of bis(6-methyl-2-pyridylmethyl)amine with 3-bromopropionic acid in the presence of triethylamine.⁵

ORTEP drawing of the complex cation $[\text{Fe}_2(6\text{Me}_2\text{-BPP})_2(\text{OH})_2]^{2+}$ (molecule A) is shown in Fig. 2. Selected bond distances (Å) and angles ($^\circ$) are given in Table 2. Only the

Fig. 1 Chemical diagram of the complex cation, $[\text{Fe}_2(6\text{Me}_2\text{-BPP})_2(\text{OH})_2]^{2+}$ of **1**.

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Table 1 Crystal and experimental data

Chemical formula: $C_{34}H_{58}Br_{0.04}Fe_2N_{7.96}O_{19.87}$	
Formula weight = 1011.38	
$T = 123\text{ K}$	
Crystal system: triclinic	Space group: $P\bar{1}$
$a = 10.3845(15)\text{ \AA}$	$\alpha = 82.119(10)^\circ$
$b = 11.1976(15)\text{ \AA}$	$\beta = 85.340(10)^\circ$
$c = 20.389(4)\text{ \AA}$	$\gamma = 68.871(7)^\circ$
$V = 2189.3(6)\text{ \AA}^3$	$Z = 2$
$D_x = 1.534\text{ g/cm}^3$	
Radiation: Mo $K\alpha$ ($\lambda = 0.71073\text{ \AA}$)	
$\mu(\text{Mo } K\alpha) = 0.791\text{ cm}^{-1}$	
$F(0\ 0\ 0) = 1060$	
Crystal size = $0.40 \times 0.40 \times 0.20\text{ mm}^3$	
No. of reflections collected = 23558	
No. of independent reflections = 9586	
θ range for data collection = 3.028 to 27.483°	
Data/Restraints/Parameters = 9586/82/661	
Goodness-of-fit on $F^2 = 1.091$	
R indices [$I > 2\sigma(I)$]: $R1 = 0.0342$, $wR2 = 0.0920$	
R indices (all data): $R1 = 0.0481$, $wR2 = 0.0972$	
$(\Delta/\sigma)_{\text{max}} = 0.002$	
$(\Delta\rho)_{\text{max}} = 0.321\text{ e \AA}^{-3}$ ($\Delta\rho)_{\text{min}} = -0.343\text{ e \AA}^{-3}$	
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: CCDC 1879204

Fig. 2 ORTEP drawing of the complex cation, $[Fe_2(6Me_2-BPP)_2(OH)_2]^{2+}$ (molecule A) of **1**, showing 50% probability ellipsoids. The hydrogen atoms are omitted for clarity.

molecular structure of molecule A is discussed here in detail, since the structural features of the two molecules are similar (Table 2 and Figs. 2 and 3). The diiron(III) center is doubly bridged by exogenous hydroxo groups to form a bis(μ -hydroxo)-diiron(III) core, as found for closely related bis(μ -hydroxo)-diiron(III) complexes with bidentate,^{9,10} tridentate,¹¹ and tetradentate ligands.^{12–14} Each iron has an octahedral structure with an N_3O_3 donor set, where three nitrogen atoms of 6Me₂-BPP are in a *mer*-arrangement. The Fe–OH bond *trans* to the carboxylate oxygen (Fe1–O3: 1.9867(10) Å) is slightly longer than the corresponding bond *trans* to the amino nitrogen (Fe1–O3*: 1.9400(11) Å) owing to the *trans* effect of the stronger

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

Molecule A		Molecule B	
Fe1–O1	1.9271(10)	Fe2–O4	1.9352(10)
Fe1–O3	1.9867(10)	Fe2–O6	1.9800(10)
Fe1–O3* ^a	1.9400(11)	Fe2–O6* ^b	1.9417(11)
Fe1–N1	2.1591(12)	Fe2–N4	2.1575(13)
Fe1–N2	2.2410(12)	Fe2–N5	2.2309(13)
Fe1–N3	2.1945(12)	Fe2–N6	2.2016(13)
Fe1–Fe1* ^a	3.0886(6)	Fe2–Fe2* ^b	3.0869(6)
Fe1–O3–Fe1* ^a	103.72(5)	Fe2–O6–Fe2* ^b	103.84(5)
O3–Fe1–O3* ^a	76.28(5)	O6–Fe2–O6* ^b	76.17(5)

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

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

Fig. 3 ORTEP drawing of the complex cation, $[Fe_2(6Me_2-BPP)_2(OH)_2]^{2+}$ (molecule B) of **1**, showing 50% probability ellipsoids. The hydrogen atoms are omitted for clarity.

electron-donor ability of the carboxylate oxygen (Fe1–O1: 1.9271(10) Å), giving rise to a slightly asymmetric diamond core ($\Delta r = 0.05\text{ \AA}$). A similar deformation of the diamond core was made for bis(μ -hydroxo)diiron(III) complexes with tridentate ($\Delta r = 0.05 - 0.06\text{ \AA}$)¹¹ and tetradentate ligands ($\Delta r = 0.03 - 0.09\text{ \AA}$),^{12–14} except for the complexes with bidentate ligands ($\Delta r = \sim 0.01\text{ \AA}$).^{9,10} The Fe–Fe separation is 3.0886(6) Å, which is on the short side of the range reported for related bis(μ -hydroxo)diiron(III) complexes (3.008 – 3.172 Å),^{9–14} which is probably due to the stacking between the pyridine rings in **1** ($\sim 3.6\text{ \AA}$). The Fe–OH bond distances as well as the Fe–OH–Fe angle are in the range of those observed for related bis(μ -hydroxo)diiron(III) complexes.^{9–14} The Fe–ligand bond distances for **1** are characteristic of high-spin Fe(III) complexes,^{3,4} which are consistent with the Mössbauer spectrum of **1** ($\delta(\Delta E_Q) = 0.42$ (1.16) mm/s).⁵

The structural feature of **1** is quite similar to that of its conjugate base, $[Fe_2(6Me_2-BPP)_2(O)(OH)]^+$ (**2**), but protonation of **2** to **1** results in opening the Fe–O(H)–Fe angle from 100.2(1) to 103.72(5)° and lengthening the Fe–Fe distance from 2.969(1) to 3.0886(6) Å. The Fe–O (carboxylate) and Fe–N (amine) bonds *trans* to the hydroxo/oxo oxygens and the ΔE_Q values are also affected by protonation. The Fe–O (carboxylate) and Fe–N (amine) bonds in **2** (1.979(3) and 2.175(3) Å) become shorter in **1** (1.9271(10) and 2.1591(12) Å). The ΔE_Q value for **1**

(1.16 mm/s) is smaller than that of **2** ($\Delta E_Q = 1.56$ mm/s),⁵ implying that the bridging hydroxo group does not cause a larger electric field gradient around the Fe(III) ions, as compared with the bridging oxo group.

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Supporting Information

A cif format file. This material is available free of charge on the Web at <http://www.jsac.or.jp/xraystruct/>.

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