

Crystal Structure of μ -Phenoxo- μ -benzoate-bridged Dinuclear Fe(II) Complex with a Dinucleating Ligand Having a Sterically Bulky Imidazolyl Group

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The structure of the dinuclear Fe(II) complex $[\text{Fe}_2(\text{Ph-bimp})(\text{PhCO}_2)(\text{CH}_3\text{CN})](\text{BF}_4)_2 \cdot 2\text{CH}_3\text{CN} \cdot 3\text{CH}_3\text{CH}_2\text{OH}$ (**1**) was determined by X-ray crystallography, where Ph-bimp is 2,6-bis[bis{2-(1-methyl-4,5-diphenylimidazolyl)methyl}-aminomethyl]-4-methylpenolate. The compound crystallizes in a monoclinic space group *Cc* with $a = 15.5690(10)$, $b = 23.8260(8)$, $c = 24.821(1)\text{\AA}$, $\beta = 95.3460(3)^\circ$, $Z = 4$, $V = 9167.2(10)\text{\AA}^3$. The $R1$ [$I > 2\sigma(I)$] and $wR2$ (all data) values are 0.0336 and 0.0850, respectively, for all 16812 independent reflections. The complex has a μ -phenoxo- μ -benzoate-bridged diiron(II) core structure.

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The end-off type compartmental ligands, having a phenolic and alcoholic oxygen as an endogenous bridge, have been used for modeling bimetallic active sites of metalloproteins,¹⁻⁴ such as hemerythrin (Hr)⁵ and methane monooxygenase (MMO).⁶ We have demonstrated that the thermal stability of (μ -peroxo) diiron(III) complexes and the oxygenation-deoxygenation reversibility are highly dependent on the nature of the end-off type compartmental ligands.^{4,7-11} Previously, we reported the crystal structure of a (μ -peroxo)diiron(III) complex, $[\text{Fe}_2(\text{Ph-bimp})(\text{PhCO}_2)(\text{O}_2)]^{2+}$, with a dinucleating ligand (Ph-bimp) bearing a sterically bulky imidazolyl group,⁸ which was obtained in a reversible reaction of the corresponding diiron(II) precursor complex, $[\text{Fe}_2(\text{Ph-bimp})(\text{PhCO}_2)](\text{BF}_4)_2 \cdot 3\text{H}_2\text{O}$, with dioxygen in acetonitrile at ambient temperature. In this paper, we report details of the crystal structure of the diiron(II) precursor complex $[\text{Fe}_2(\text{Ph-bimp})(\text{PhCO}_2)(\text{CH}_3\text{CN})](\text{BF}_4)_2 \cdot 2\text{CH}_3\text{CN} \cdot 3\text{CH}_3\text{CH}_2\text{OH}$ (**1**) (Fig. 1).

A single crystal of $[\text{Fe}_2(\text{Ph-bimp})(\text{PhCO}_2)(\text{CH}_3\text{CN})](\text{BF}_4)_2 \cdot 2\text{CH}_3\text{CN} \cdot 3\text{CH}_3\text{CH}_2\text{OH}$ (**1**) suitable for X-ray crystallography was obtained by recrystallization of $[\text{Fe}_2(\text{Ph-bimp})(\text{PhCO}_2)](\text{BF}_4)_2 \cdot 3\text{H}_2\text{O}$ from a mixture of acetonitrile/ethanol at ambient temperature under N_2 . It was picked up on a hand-made cold copper plate mounted inside a liquid N_2 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 $\text{Mo K}\alpha$ radiation at 108 K. The structure was solved by a direct method (SIR 92)¹² and expanded using a Fourier technique. The structure was refined by a full-matrix least-squares method by using SHELXL 2014¹³ (Yadokari-XG).¹⁴ All non-hydrogen atoms were refined with anisotropic displacement parameters (ADP) and all hydrogen

atoms were included using a riding model. The occupancy factors were also refined for the two BF_4^- anions, one acetonitrile molecule, and three ethanol molecules, which were disordered over two or three orientations. Distance/ADP restraints were applied to the disordered atoms in the anions and solvents. The crystal data is summarized in Table 1.

The molecular structure of complex cation $[\text{Fe}_2(\text{Ph-bimp})(\text{PhCO}_2)(\text{CH}_3\text{CN})]^{2+}$ of **1** is shown in Fig. 2. Selected bond distances (\AA) and angles ($^\circ$) are given in Table 2. The diiron(II) center is doubly bridged by phenoxide oxygen of Ph-bimp and benzoate oxygens, as found for closely related diiron(II) complexes: $[\text{Fe}_2(\text{Ph-tidp})(\text{PhCO}_2)]^{2+}$ (**2**) (Ph-tidp = *N,N,N',N'*-tetrakis(1-methyl-4,5-diphenyl-2-imidazolyl)methyl-1,3-diamino-2-propanolate),⁹ $[\text{Fe}_2(\text{L}^{\text{Ph4}})(\text{PhCO}_2)]^{2+}$ (**3**) (L^{Ph4} = *N,N,N',N'*-tetrakis(1-methyl-2-phenyl-4-imidazolyl)methyl-1,3-diamino-2-propanolate),¹⁰ and $[\text{Fe}_2(\text{N-Et-HPTB})(\text{PhCO}_2)]^{2+}$ (**4**) (*N-Et-HPTB* = *N,N,N',N'*-tetrakis(1-ethyl-2-benzimidazolyl)methyl-1,3-diamino-2-propanolate).¹⁵ The two iron atoms in **1** have different coordination geometries. The five-coordinate iron

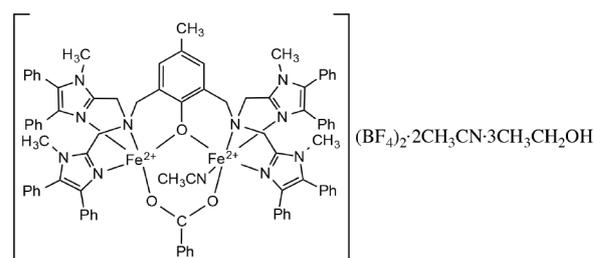


Fig. 1 Chemical diagram of $[\text{Fe}_2(\text{Ph-bimp})(\text{PhCO}_2)(\text{CH}_3\text{CN})](\text{BF}_4)_2 \cdot 2\text{CH}_3\text{CN} \cdot 3\text{CH}_3\text{CH}_2\text{OH}$ (**1**).

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Table 1 Crystal and experimental data

Chemical formula: C ₉₆ H ₁₀₁ B ₂ F ₈ Fe ₂ N ₁₃ O ₆	
Formula weight = 1818.21	
T = 108 K	
Crystal system: monoclinic	Space group: Cc
a = 15.5690(10) Å	
b = 23.8260(8) Å	β = 95.3460(3)°
c = 24.821(2) Å	
V = 9167.2(10) Å ³	Z = 4
D _x = 1.317 g/cm ³	
Radiation: Mo Kα (λ = 0.71073 Å)	
μ(Mo Kα) = 3.94 cm ⁻¹	
F(0 0 0) = 3800	
Crystal size = 0.5 × 0.3 × 0.3 mm ³	
No. of reflections collected = 42650	
No. of independent reflections = 16812	
θ range for data collection = 2.362 to 27.484°	
Data/Restraints/Parameters = 16812/623/1482	
Goodness-of-fit on F ² = 1.029	
Flack parameter = 0.007(4)	
R indices [I > 2σ(I)]: R1 = 0.0336, wR2 = 0.0825	
R indices (all data): R1 = 0.0367, wR2 = 0.0850	
(Δ/σ) _{max} = 0.001	
(Δρ) _{max} = 0.502 eÅ ⁻³ (Δρ) _{min} = -0.312 eÅ ⁻³	
Measurement: Rigaku CCD Mercury Diffractometer	
Data collection & cell refinement program: CrystalClear	
Structure solving program: SIR 92	
Structure determination: SHELXL 2014	
Refinement: full-matrix least squares against F ²	
CCDC deposition number: CCDC 1872404	

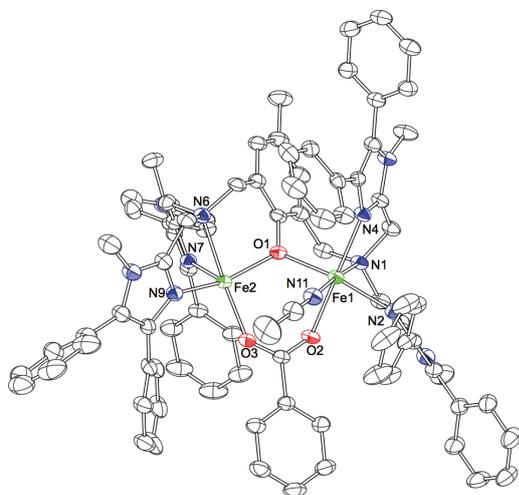


Fig. 2 ORTEP drawing of a complex cation, [Fe₂(Ph-bimp)(PhCO₂)-(CH₃CN)]²⁺, of **1**, showing 50% probability ellipsoids. The hydrogen atoms are omitted for clarity.

atom (Fe2) has a square-pyramidal structure ($\tau = 0.08$)¹⁶ with the nitrogen atom (N7) of Ph-bimp at the apex. The six-coordinate iron atom (Fe1) contains an additional coordinated acetonitrile molecule to form a distorted octahedral structure with an N₄O₂ donor set. Bridging benzoate coordinates *trans* to the tertiary amine nitrogen atom of Ph-bimp in Fe2, whereas *trans* to the imidazolyl nitrogen atom of Ph-bimp in Fe1. Unlike **1**, each iron center in **2** - **4** has a five-coordinate structure and bridging benzoate coordinates *trans* to the tertiary amine nitrogen atoms of dinucleating ligands. The Fe-ligand bond

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

Fe1-O1	2.043(2)	Fe2-O1	2.0160(19)
Fe1-O2	2.1955(19)	Fe2-O3	2.017(2)
Fe1-N1	2.260(2)	Fe2-N6	2.329(2)
Fe1-N2	2.126(3)	Fe2-N7	2.118(2)
Fe1-N4	2.194(2)	Fe2-N9	2.117(2)
Fe1-N11	2.137(3)	Fe1-Fe2	3.5350(6)
Fe1-O1-Fe2	121.10(9)		

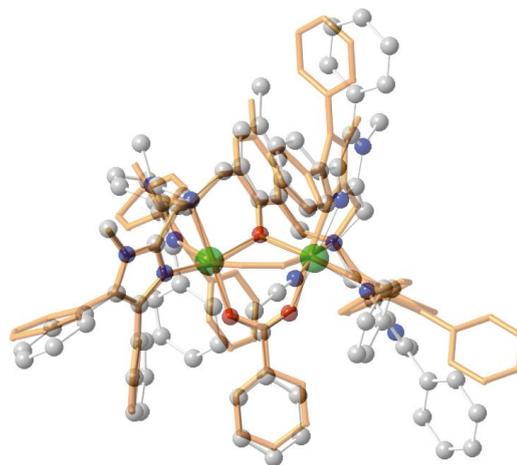


Fig. 3 Overlays of [Fe₂(Ph-bimp)(PhCO₂)(CH₃CN)]²⁺ (ball-and-stick) and [Fe₂(Ph-bimp)(PhCO₂)(O₂)]²⁺ (orange tube).

distances for **1** are characteristic of high spin Fe(II) complexes.^{4,7,9,10,15} The average Fe-N(imidazole) bond distance of **1** is 2.14 Å is substantially longer than the average Fe-N(benzimidazole) bond distance of **4** (2.07 Å).¹⁵ The elongation in **1** is possibly due to unfavorable steric interactions among phenyl groups of Ph-bimp, the bridging benzoate and the acetonitrile molecule (Fig. 2 and Figs. S2 - S3 (Supporting Information)). A similar observation was made for **2** (2.12 Å)⁹ and **3** (2.12 Å),¹⁰ which have also sterically bulky phenyl groups.

A comparison of the molecular structure of deoxy-form **1** and oxy-form [Fe₂(Ph-bimp)(PhCO₂)(O₂)]²⁺ (Fig. 3 and Figs. S2 - S3, and Table S1 (Supporting Information)) provides some suggestive information concerning the dioxygen affinity and the reversible oxygenation. The structure around two iron atoms in both forms are almost superimposed (Fig. 3), indicating that deoxy-form **1** has a suitable dioxygen binding site on the diiron center in a μ -1,2-peroxo fashion. Furthermore, the dioxygen binding site is in a hydrophobic pocket surrounded by phenyl groups of Ph-bimp (Fig. S3). This stereochemistry provided by the 2,6-bis(aminomethyl)phenolate bridging skeleton seems to be responsible for the high dioxygen affinity and thermal stability compared with that provided by 1,3-diamino-2-propanolate skeleton.⁴ The oxygenation of **1** to [Fe₂(Ph-bimp)(PhCO₂)-(O₂)]²⁺ results in a closing of the Fe-O(phenolate)-Fe angle from 121.10(9)° to 111.7(2)° and a shortening the Fe-Fe distance from 3.5350(6) Å to 3.327(2) Å. However, the average Fe-ligand (Fe-N(tertiary amine), Fe-N(imidazole), and Fe-O(phenolate), except for Fe-O(benzoate)) bond distances for **1** are comparable to those for [Fe₂(Ph-bimp)(PhCO₂)(O₂)]²⁺ (Table S1), indicating that Ph-bimp stabilizes the Fe(II) oxidation state, which would facilitate the reversible oxygenation. The resonance Raman

spectrum of $[\text{Fe}_2(\text{Ph-bimp})(\text{PhCO}_2)(\text{O}_2)]^{2+}$ showed an isotope sensitive band at 874 cm^{-1} ($^{16-18}\Delta = 49\text{ cm}^{-1}$) in CH_2Cl_2 at -90°C (Fig. S4, Supporting Information), which can be assigned to the $\nu(\text{O-O})$ vibration,^{1,3,4} which was not detected in a previous study.⁸

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Supporting Information

A cif format file, Table S1, and Figs. S1 - S4. These materials are available free of charge on the Web at <http://www.jsac.or.jp/xraystruct/>.

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