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cis-μ-1,2-Peroxo Diiron Complex: Structure and Reversible Oxygenation

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The chemistry of diiron−dioxygen complexes[2] is of particular importance to gain insight into the structure and functions of hemerythrin (Hr),[3] the R2 protein of ribonucleotide reductase (RNR),[4] and methane monooxygenase (MMO).[5] Hr plays the role of a dioxygen transport, and it binds O_2 reversibly in a hydroperoxo fashion. The reduced forms of RNR R2 and MMO activate O_2 to oxidize tyrosine to tyrosine radical and to hydroxylate methane to methanol, respectively. Recently, a "peroxo intermediate" (compound **L**) has been detected as an intermediate of dioxygen activation by the diiron center in MMO.[6]

Only a few iron(II) complexes that bind O_2 in a μ-peroxo fashion have been known.[7−9] We have demonstrated that dinuclear cobalt(II) and iron(II) complexes $[Co_2$ or $Fe_2(L)(RCOO)]^{2+}$ form μ-peroxo species, and that the dioxygen affinity and thermal stability of the μ-peroxo species toward irreversible oxidation are highly dependent on the stereochemistry of the bridging skeleton, electron donor ability, and steric bulkiness of the dinucleating ligands (L = an N_6O donor ligand with a phenolate or alkoxide bridging group).[9−11] Que et al. pointed out that polar solvents such as DMSO greatly stabilize μ-peroxo species.[8] In this communication, we describe the preparation and crystal structure of a novel μ-peroxo diiron complex, $[Fe_2(\text{Ph-bimp})(C_6H_5COO)(O_2)](BF_4)_2{\cdot}2CH_3CN{\cdot}C_2H_5OC_2H_5{\cdot}H_2O$ (**1**). The complex shows a higher thermal stability toward irreversible oxidation than the previously reported μ-peroxo diiron complexes and has a very high dioxygen affinity. This is the first example of a crystallographically characterized *cis*-μ-1,2-peroxo diiron complex that binds O_2 reversibly at ambient temperature.

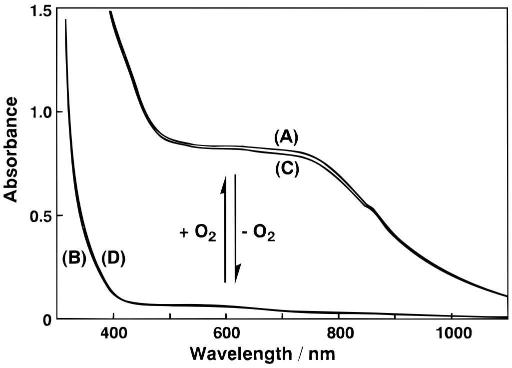

Figure 1. Absorption spectral changes for $[Fe_2(\text{Ph-bimp})(C_6H_5COO)(O_2)]^{2+}$ (**1**) in acetonitrile at 20 °C demonstrating the reversible oxygenation−deoxygenation cycles. Spectrum (a) under O_2; (b) after deoxygenation by boiling the solution under N_2; (c) after reoxygenation under O_2; (d) after redeoxygenation by boiling the acetonitrile solution under N_2.

The reaction of 2 equiv of $Fe(BF_4)_2{\cdot}6H_2O$ with 1 equiv of HPh-bimp[12] and C_6H_5COONa in EtOH under N_2 gave $[Fe_2(\text{Ph-bimp})(C_6H_5COO)](BF_4)_2{\cdot}3H_2O$ (**2**). Two iron centers in **2** are coordinatively unsaturated and readily react with O_2 in acetonitrile to generate an oxygenated complex **1**. The electronic spectrum of **2** in acetonitrile displays two d−d bands at 853 nm ($\epsilon = 12$ dm^3 mol^{-1} cm^{-1}) and 1900 nm ($\epsilon = 22$ dm^3 mol^{-1} cm^{-1}), typical of high-spin five-coordinate iron(II) centers.[9,13]

The complex **1** has an intense dark green color, its electronic spectrum in CH_3CN at 20 °C showing a broad absorption band at 800−500 nm (ϵ = ca. 1700 dm^3 mol^{-1} cm^{-1}), as seen in Figure 1 (spectrum A). Boiling the CH_3CN solution of **1** under N_2 resulted in decolorization of the solution (spectrum B). Bubbling of O_2 through the solution restored the original dark green color (spectrum C). Thus, complex **1** is substantially thermally stable toward irreversible oxidation compared to the μ-peroxo complexes reported so far.

A single crystal suitable for X-ray crystallography was obtained by a diffusion of diethyl ether into an acetonitrile solution of **2** under O_2 at −20 °C. The molecular structure of the dinuclear cation of **1** is shown in Figure 2. The complex has a triply bridged structure with *cis*-1,2-μ-peroxide, μ-phenolate of Ph-bimp, and μ-benzoate, which is quite similar to that of a μ-peroxo dicobalt complex, $[Co_2(\text{bpmp})(C_6H_5COO)(O_2)](BF_4)_2{\cdot}H_2O$ (**3**).[10a] Such a *cis*-μ-1,2-peroxo coordination mode has been suggested for $[Fe_2(N\text{-Et-HPTB})(C_6H_5COO)$-

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[11] Abbreviations of ligands used: Ph-bimp = 2.6-bis[bis{2-(1-methyl-4,5-diphenylimidazolyl)methyl}aminomethyl]-4-methylphenolate; Me$_4$-tpdp = *N*,*N*,*N′*,*N′*-tetrakis{2-(6-methylpyridyl)methyl}-1,3-diaminopropan-2-olate; bimp = 2,6-bis[bis{2-(1-methylimidazolyl)methyl}aminomethyl]-4-methylphenolate; Ph-tidp = *N*,*N*,*N′*,*N′*-tetrakis{2-(1-methyl-4,5-diphenylimidazolyl)methyl}-1,3-diaminopropan-2-olate; tpdp = *N*,*N*,*N′*,*N′*-tetrakis(2-pyridylmethyl)-1,3-diaminopropan-2-olate; *N*-Et-HPTB = *N*,*N*,*N′*,*N′*-tetrakis{2-(1-ethylbenzimidazolyl)methyl}-1,3-diaminopropan-2-olate.

[12] Synthesis of HPh-bimp will be submitted for publication. Calcd for $C_{77}H_{72}N_{10}O_2$ (HPh-bimp·H_2O): C, 79.08; H, 6.21; N, 11.98. Found: C, 78.92; H, 5.93; N, 11.97. MS: *m*/*z* 1152 $[MH]^+$.

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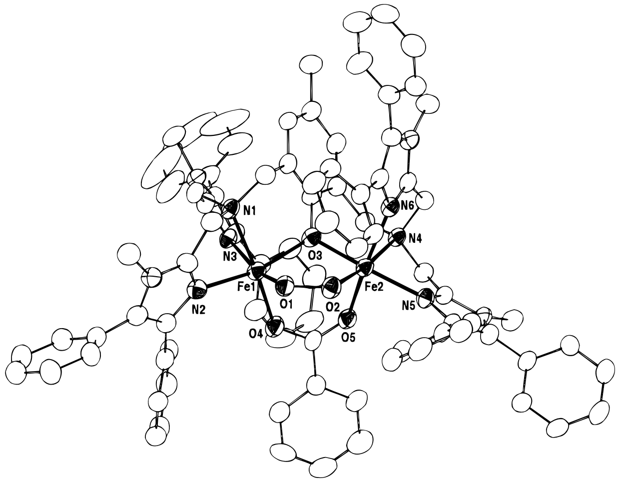

Figure 2. ORTEP view of $[Fe_2(Ph\text{-}bimp)(C_6H_5COO)(O_2)]^{2+}$ (**1**). Hydrogen atoms are omitted for clarity. Selected bond distances (Å) and angles (deg): Fe1−O1, 1.944(4); Fe1−O3, 2.018(5); Fe1−O4, 1.998(5); Fe1−N1, 2.252(4); Fe1−N2, 2.110(5); Fe1−N3, 2.237(5); Fe2−O2, 1.864(4); Fe2−O3, 2.001(4); Fe2−O5, 2.102(5); Fe2−N4, 2.325(4); Fe2−N5, 2.097(5); Fe2−N6, 2.178(6); O1−O2, 1.426(6); Fe1−Fe2, 3.327(2); Fe1−O3−Fe2, 111.7(2); Fe1−O1−O2, 118.1(3); Fe2−O2−O1, 121.4(3); Fe1−O1−O2−Fe2, 9.89.

$(O_2)]^{2+}$ and its analogs on the basis of spectroscopic studies.[8,9,14] Each iron center has a distorted octahedral geometry with a facial-N_3O_3 donor set, but the two iron centers are not equivalent (vide infra). The O1−O2 bond length is 1.426(6) Å, which is comparable to those of **3** [1.43(3) Å] and shorter than that in $[Fe_6(O_2)(O)_2(C_6H_5COO)_{12}(H_2O)_2]$ [1.480(12) Å][15] and in the range observed for the μ-peroxo transition metal complexes.[16] The Fe−O(peroxide) bonds are asymmetric [Fe1−O1 = 1.944(4) and Fe2−O2 = 1.864(4) Å] and significantly shorter than the average Fe−O(phenolate and benzoate) lengths [2.030(5) Å]. The Mössbauer spectrum of a powdered sample of **1** at 77 K exhibited two sets of quadrupole doublets ($\delta_1 = 0.58$ mm s^{-1} and $\Delta E_{Q1} = 0.74$ mm s^{-1}, and $\delta_2 = 0.65$ mm s^{-1} and $\Delta E_{Q2} = 1.70$ mm s^{-1}, ratio of areas = 1.1:1), which can be assigned to two distinct high-spin iron(III) centers. Thus the O−O bond length and Mössbauer data suggest the $Fe^{3+}-O_2^{2-}-Fe^{3+}$ formulation.[17] The average Fe−O(peroxide, phenolate, and benzoate) bond length [1.988(5) Å] in **1** is slightly longer than that of the iron(III) site of a mixed-valence complex $[Fe_2(bimp)(C_6H_5COO)_2]^{2+}$ (**4**) [Fe−O(phenolate and benzoate) = 1.973(2) Å].[18] The average Fe−N(imidazole) bond length of **1** [2.156(5) Å] is substantially longer than that of either iron(III) site [2.097(2) Å] or iron(II) site [2.124(3) Å] in **4**. Such a significant elongation of the Fe−N(imidazole) bonds seems to be due to unfavorable steric interaction between the hydrogen atoms of the 4-phenyl group of the coordinated imidazole groups and the oxygen atoms of the bridging peroxide (O2) and benzoate (O4). A similar elongation of the Fe−N bonds due to 6-methyl groups of pyridyl groups was previously observed for $[Fe_2(Me_4\text{-}tpdp)(C_6H_5COO)(H_2O)](BF_4)_2$.[9] Phenyl groups at the fourth position of the imidazole groups coordinated to Fe2 form a hydrophobic pocket in which the peroxide resides (Figure S1, supporting information).

Previously, we found that a dinucleating ligand which has weaker electron donor atoms and sterically bulkier substituents providing a hydrophobic environment around the O_2 binding site suppresses the irreversible oxidation.[9] The phenyl groups in Ph-bimp appear to have both effects: 4-phenyl groups of imidazole groups cause an elongation of the Fe−N(imidazole) bonds that weakens the electron donor ability of the imidazole groups[19] and form a hydrophobic pocket surrounding the coordinated peroxide. These two effects are expected to suppress the irreversible oxidation and facilitate the reversible oxygenation.

The equilibrium constant (K) of eq 1 for the oxygenation of **2** was measured by spectrophotometric titration in CH_3CN at 20 °C under various partial O_2 pressures (Figure S2, supporting information). $K[P(O_2)_{1/2} = 1/K]$ of **2** was estimated to be ca.

$$[Fe_2] + O_2 \overset{K}{\rightleftharpoons} [Fe_2(O_2)] \tag{1}$$

0.5 $Torr^{-1}$ (ca. 2 Torr). The dioxygen affinity of **2** is significantly higher than that of $[Fe_2(Me_4\text{-}tpdp)(C_6H_5COO)]^{2+}$ (**5**) and $[Fe_2(Ph\text{-}tidp)(C_6H_5COO)]^{2+}$ (**6**), which have 1,3-diamino-2-propanolate bridging skeletons [$P(O_2)_{1/2}$ = ca. 6 Torr at −41 °C in CH_2Cl_2 for **5** and $P(O_2)_{1/2}$ = ca. 17 Torr at −40 °C in CH_2Cl_2 for **6**].[9,20] Such an increased dioxygen affinity was also observed for the corresponding cobalt complex **3** compared to $[Co_2(tpdp)(CH_3COO)]^{2+}$.[10b,c] Thus the dioxygen affinity of the present type of complex is highly dependent on the stereochemistry of the bridging skeleton; a 2,6-bis(aminomethyl)phenolate bridging skeleton appears to be suitable for the formation of an additional μ-peroxo bridge compared to a 1,3-diamino-2-propanolate bridging skeleton.

In summary, sterically bulky substitutents of the present type of dinucleating ligands which weaken the electron donor ability and form a hydrophobic pocket for an O_2 binding site would suppress irreversible oxidation and facilitate reversible oxygenation. In addition, the dioxygen affinity seems to be highly dependent on the stereochemistry of the bridging skeleton of the dinucleating ligands. Further studies are needed in order to fully understand the basis of the observed high thermal stability toward irreversible oxidation and high dioxygen affinity in this system.

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Supporting Information Available: Analytical data of **1** and **2**, experimental data for structural determination, tables of fractional atomic coordinates, thermal parameters, and bond lengths and angles for **1**, a space-filling view of **1** showing a hydrophobic cavity surrounding the O_2 binding site (Figure S1), and plot of $P(O_2)$ vs $P(O2)/(A - A_0)$ for **1** (Figure S2) (21 pages). This material is contained in many libraries on microfiche, immediately follows this article in the microfilm version of the journal, can be ordered from the ACS, and can be downloaded from the Internet; see any current masthead page for ordering information and Internet access instructions.

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