

## Synthesis of $\mu$ -Oxo and Bis( $\mu$ -alkoxo) Bridged Diiron(III) Complexes Using a Tripodal Ligand, Bis(2-benzimidazolymethyl)ethanolamine with Mixed N/O Donor Atoms

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A  $\mu$ -oxo diiron(III) complex and two bis( $\mu$ -alkoxo) diiron(III) complexes with biomimetic tripodal ligand containing mixed N/O donor atoms were synthesized using a mononuclear iron(III) complex as starting material. Depending on the amounts and kinds of bases used, we obtained various kinds of diiron(III) complexes. The reaction of  $[\text{Fe}^{\text{III}}(\text{Hbba})\text{Cl}_2]\text{Cl}$ , **1**, with an equivalent amount of  $\text{KO}_2$  or  $\text{NaOAc}$  produced  $[\text{Fe}^{\text{III}}_2\text{O}(\text{Hbba})_2\text{Cl}_2]\text{Cl}_2$ , **2**. An additional equivalent amount of  $\text{NaOBz}$  or  $\text{NaOAc}$  converts complex **2** to complex **3** or complex **4** depending on the base used. The addition of two equivalent amounts of  $\text{NaOBz}$  or  $\text{NaOAc}$  directly converts complex **1** to  $[\text{Fe}^{\text{III}}_2(\text{bba})_2(\text{OBz})_2]\text{Cl}_2$ , **3**, or  $[\text{Fe}^{\text{III}}_2(\text{bba})_2(\text{OAc})_2]\text{Cl}_2$ , **4**, depending on the base used. Crystal data are as follows:  $[\text{Fe}^{\text{III}}_2\text{O}(\text{Hbba})_2\text{Cl}_2]\text{Cl}_2$ , **2**: monoclinic space group  $\text{P}2_1/n$ ,  $a = 8.421(1) \text{ \AA}$ ,  $b = 18.416(2) \text{ \AA}$ ,  $c = 13.736(1) \text{ \AA}$ ,  $\beta = 104.870(7)^\circ$ ,  $V = 2058.9(4) \text{ \AA}^3$ ,  $Z = 2$ ,  $R1 = 0.0469$  and  $wR2 = 0.1201$  for reflections with  $I > 2\sigma(I)$ .

### Introduction

Model systems that mimic the active sites of the metalloproteins are very important tools for understanding the reaction mechanism and properties of the metalloproteins and for the development of new low molecular weight biomimetic molecules. Many non-heme iron metalloproteins have diverse active site geometry, some with mononuclear iron centers<sup>1</sup> and the others with dinuclear iron centers<sup>2</sup>. Many biologically important iron centers have various mixed N/O donor atom environments. Thus, having a tool for the synthesis of various kinds of iron model complexes containing various mixed N/O donor ligands is very important. Most mixed N/O donor ligands contain carboxylate or phenolate oxygen donor atoms;<sup>3</sup> only a few ligands contain alcoholic oxygen atoms. Recently, we reported the synthesis and characterization of the mononuclear iron(III) complex  $[\text{Fe}(\text{Hbba})\text{Cl}_2]\text{Cl}_2$  using a biomimetic tripodal ligand, bis(2-benzimidazolymethyl)ethanolamine (Hbba), which had mixed N/O donor atoms with alcoholic oxygen atom.<sup>4</sup> The synthesis and characterization of the bis( $\mu$ -alkoxo) diiron(III) complex  $[\text{Fe}_2(\text{bba})_2(\text{OBz})_2]\text{ClO}_4$  was also reported by Que Jr. *et al.*, where the complex was synthesized using  $\text{Fe}(\text{ClO}_4)_3 \cdot x\text{H}_2\text{O}$ , an equivalent amount of Hbba,  $\text{Et}_3\text{N}$ , and benzoic acid in a methanolic solution.<sup>5</sup> In this study, we synthesized various diiron(III) complexes using the mononuclear iron(III) complex  $[\text{Fe}(\text{Hbba})\text{Cl}_2]\text{Cl}_2$  as starting material. We will discuss the synthesis and characterization of  $\mu$ -oxo and bis( $\mu$ -alkoxo) bridged diiron(III) complexes.

### Experimental Section

**Materials.** The following were used as received with no further purification: iron(III) chloride hexahydrate, potassium superoxide, sodium acetate, and sodium benzoate from Aldrich Inc.; methanol from Carlo Erba. Hbba was prepared according to the literature procedure.<sup>4</sup>

**Instrumentation.** The Elemental Analysis Laboratory of the Korean Institute of Basic Science performed C, H, N and Fe determinations. Infrared spectra were recorded as KBr pellets in the range  $4000\text{--}600 \text{ cm}^{-1}$  on a Bio-Rad FT-IR spectrometer. Absorption spectra were obtained using a Perkin Elmer Lambda spectrometer. Positive-ion FAB mass spectra were obtained using a JEOL HX110A/HX110A tandem mass spectrometer in a glycerol matrix. Room-temperature magnetic susceptibilities of well-ground solid samples were measured by using an Evans balance. The measurements were calibrated against a  $\text{Hg}[\text{Co}(\text{SCN})_4]$  standard.<sup>6</sup>

#### Synthesis.

**$[\text{Fe}^{\text{III}}(\text{Hbba})\text{Cl}_2]\text{Cl}$  (1):** Complex **1** was prepared according to literature procedure.<sup>4</sup>

**$[\text{Fe}^{\text{III}}_2\text{O}(\text{Hbba})_2\text{Cl}_2]\text{Cl}_2$  (2):** Method-A: Complex **1** (0.834 g, 1.72 mmol) was dissolved in 15 mL of methanol. Potassium superoxide (0.123 g, 1.73 mmol) in 15 mL of methanol was added to the solution. After 10 min of stirring, the solution was filtered. Slow evaporation of the filtrate solution over one week in a refrigerator produced red crystals (0.69 g, 83% yield). Method-B: Complex **1** (0.24 g, 0.50 mmol) was dissolved in 20 mL of methanol. Sodium acetate (0.050 g, 0.61 mmol) in 5 mL of methanol was added to the solution. After 10 min of stirring, the solution was filtered. Slow evaporation of the filtrate solution over 4 days produced red crystals (0.22 g, 91% yield). Anal. Calcd for  $[\text{Fe}^{\text{III}}_2\text{O}(\text{Hbba})_2\text{Cl}_2]\text{Cl}_2 \cdot 3\text{H}_2\text{O}$  ( $\text{Fe}_2\text{C}_{30}\text{H}_{44}\text{N}_{10}\text{O}_6\text{Cl}_4$ ) (fw =

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966.31); C, 44.75; H, 4.59; N, 14.49; Fe, 11.56%. Found: C, 44.56; H, 4.56; N, 14.61; Fe, 11.1%. FAB-MS,  $m/z$ :  $[\text{Fe}^{\text{III}}_2\text{O}(\text{Hbba})_2\text{Cl}_2\text{-H}]^+$ , 839; UV-Vis (MeOH)  $\lambda_{\text{max}}(\epsilon)$ : 236 nm ( $30300 \text{ M}^{-1}\text{cm}^{-1}$ ); 270 nm ( $35800 \text{ M}^{-1}\text{cm}^{-1}$ ); 277 nm ( $35000 \text{ M}^{-1}\text{cm}^{-1}$ ); 323.5 nm ( $8100 \text{ M}^{-1}\text{cm}^{-1}$ ).  $\mu_{\text{eff}}$ :  $2.38 \mu_{\text{B}}$  ( $1.68 \mu_{\text{B}}$ /metal).

**$[\text{Fe}^{\text{III}}_2(\text{bbca})_2(\text{OBz})_2]\text{Cl}_2$  (3):** Method-A: Complex **1** (0.24 g, 0.50 mmol) was dissolved in 60 mL of MeOH. Potassium superoxide (0.036 g, 0.50 mmol) and sodium benzoate (0.072 g, 0.50 mmol) were added to the solution. After 30 min of stirring, slow evaporation of the solution over one week produced reddish crystals (0.20 g, 70% yield). Method-B: Complex **1** (0.24 g, 0.50 mmol) was dissolved in 20 mL of MeOH. Sodium acetate (0.041 g, 0.50 mmol) and sodium benzoate (0.070 g, 0.49 mmol) were added to the solution. After 30 min of stirring, the solution was filtered and a red powder was obtained (0.16 g, 56% yield). Slow evaporation of the filtrate solution over 2 weeks produced reddish crystals (0.09 g, 32% yield). The IR spectrum of the crystal was identical to that of the red powder sample. Method-C: Complex **2** (0.145 g, 0.150 mmol) was dissolved in 10 mL of MeOH. Sodium benzoate (0.043 g, 0.30 mmol) was added to the solution. After 30 min of stirring, slow evaporation of the solution over one week produced reddish crystals (0.15 g, 88% yield). Anal. Calcd for  $[\text{Fe}_2(\text{bbca})_2(\text{OBz})_2]\text{Cl}_2 \cdot 4\text{H}_2\text{O}$  ( $\text{Fe}_2\text{C}_{50}\text{H}_{54}\text{N}_{10}\text{O}_{10}\text{Cl}_2$ ) ( $f_w = 1137.64$ ): C, 52.79; H, 4.78; N, 12.31; Fe, 9.82. Found: C, 52.25; H, 4.47; N, 12.31; Fe, 10.9. FAB-MS,  $m/z$ :  $[\text{Fe}^{\text{III}}_2(\text{bbca})_2\text{-H}]^+$ , 751;  $[\text{Fe}^{\text{III}}(\text{bbca})]^+$ , 376. UV-Vis (MeOH)  $\lambda_{\text{max}}(\epsilon)$ : 229 nm ( $41300 \text{ M}^{-1}\text{cm}^{-1}$ ); 271 nm ( $31900 \text{ M}^{-1}\text{cm}^{-1}$ ); 277.5 nm ( $30800 \text{ M}^{-1}\text{cm}^{-1}$ ); 328 nm ( $7900 \text{ M}^{-1}\text{cm}^{-1}$ ).  $\mu_{\text{eff}}$ :  $5.23 \mu_{\text{B}}$  ( $3.70 \mu_{\text{B}}$ /metal).

**$[\text{Fe}^{\text{III}}_2(\text{bbca})_2(\text{OAc})_2]\text{Cl}_2$  (4):** Method-A: Complex **1** (0.24 g, 0.50 mmol) was dissolved in 20 mL of MeOH. Potassium superoxide (0.036 g, 0.51 mmol) and sodium acetate (0.041 g, 0.50 mmol) in 5 mL of methanol were added to the solution. After 30 min of stirring, slow evaporation of the solution over one week produced reddish crystals (0.19 g, 75% yield). Method-B: Complex **1** (0.24 g, 0.50 mmol) was dissolved in 20 mL of MeOH. Sodium acetate (0.082 g, 1.0 mmol) in 5 mL of methanol was added to the solution. After 30 min of stirring, slow evaporation of the solution over one week produced reddish crystals (0.23 g, 91% yield). Method-C: Complex **2** (0.145 g, 0.15 mmol) was dissolved in 10 mL of MeOH. Sodium acetate (0.025 g, 0.30 mmol) was added to the solution. After 30 min of stirring, slow evaporation of the solution over 10 days produced reddish crystals (0.13 g, 86% yield). Anal. Calcd for  $[\text{Fe}_2(\text{bbca})_2(\text{OAc})_2]\text{Cl}_2 \cdot 4\text{H}_2\text{O}$  ( $\text{Fe}_2\text{C}_{40}\text{H}_{50}\text{N}_{10}\text{O}_{10}\text{Cl}_2$ ) ( $f_w = 1013.50$ ): C, 47.40; H, 4.97; N, 13.82; Fe, 11.02. Found: C, 47.81; H, 4.67; N, 13.41; Fe, 11.2. FAB-MS,  $m/z$ :  $[\text{Fe}^{\text{III}}_2(\text{bbca})_2\text{-2H}]^+$ , 750;  $[\text{Fe}^{\text{III}}(\text{bbca}) + \text{nba} - \text{H}]^+$ , 528;  $[\text{Fe}^{\text{III}}(\text{bbca})]^+$ , 376. UV-Vis (MeOH)  $\lambda_{\text{max}}(\epsilon)$ : 238 nm ( $22000 \text{ M}^{-1}\text{cm}^{-1}$ ); 271 nm ( $26600 \text{ M}^{-1}\text{cm}^{-1}$ ); 277.5 nm ( $26100 \text{ M}^{-1}\text{cm}^{-1}$ ); 330 nm ( $6800 \text{ M}^{-1}\text{cm}^{-1}$ ).  $\mu_{\text{eff}}$ :  $4.68 \mu_{\text{B}}$  ( $3.31 \mu_{\text{B}}$ /metal).

**X-ray Crystallography.** Because crystals of **2** lose their

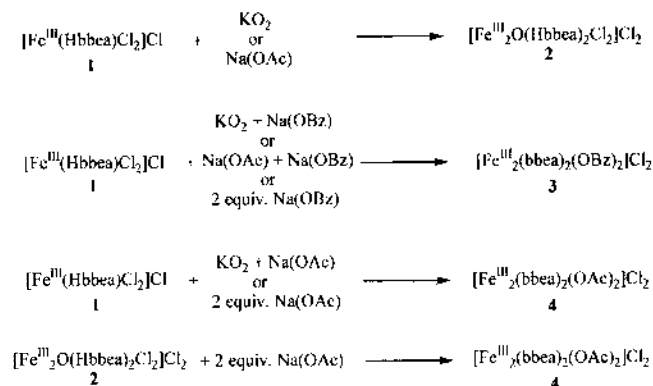
**Table 1.** Crystal Data and Structure Refinement for **2**

formula	$\text{C}_{36}\text{H}_{43}\text{Cl}_2\text{Fe}_2\text{N}_{10}\text{O}_5$
$f_w$	961.89
temp	293(2) K
wavelength	0.71069 Å
cryst system, space group	monoclinic, $P2_1/n$
unit cell dimens	$a = 8.421(1) \text{ Å}$ , $\alpha = 90^\circ$ $b = 18.416(2) \text{ Å}$ , $\beta = 104.870(7)^\circ$ $c = 13.736(1) \text{ Å}$ , $\gamma = 90^\circ$
$V$	$2058.9(4) \text{ Å}^3$
$Z$ , Calcd density	2, 1.552 Mg/m <sup>3</sup>
abs coeff	$1.022 \text{ mm}^{-1}$
crystal size	$0.57 \times 0.50 \times 0.42 \text{ mm}$
$\theta$ range for data collen	1.89 to $24.97^\circ$
reflens colled/unique	3865/3614 [ $R(\text{int}) = 0.0267$ ]
data/restraints/params	3614/0/278
goodness-of-fit on $F^2$	1.182
final $R$ indices [ $I > 2\sigma(I)$ ]	$R1 = 0.0469$ , $wR2 = 0.1201$
$R$ indices (all data)	$R1 = 0.0549$ , $wR2 = 0.1250$
largest diff peak and hole	0.638 and $-0.206 \text{ e Å}^{-3}$

solvate molecules of crystallization within a few minutes, it was mounted in a glass capillary with the mother liquor to prevent the loss of the solvate molecules during data collections. Preliminary examination and data collection were performed with Mo  $K\alpha$  radiation ( $= 0.71069 \text{ Å}$ ) on an Enraf-Nonius CAD4 computer-controlled  $\kappa$ -axis diffractometer equipped with a graphite crystal, incident-beam monochromator. Cell constants and orientation matrix for data collection were obtained from least-squares refinement, using the setting angles of 25 reflections. Data were collected at room temperature using the  $\omega$  scan technique. Three standard reflections were monitored every hour, but no intensity variations were monitored. Lorentz and polarization corrections were applied to the data; however, no correction was made for absorption. The structure was solved by direct methods using SHELXS-86<sup>7a</sup> and refined by full-matrix least-squares calculation with SHELXL-97.<sup>7b</sup> All non-hydrogen atoms were refined anisotropically. All hydrogen atoms were allowed to ride on geometrically ideal positions with isotropic temperature factors 1.2 times those of the attached non-hydrogen atoms in the refinement of crystal structure **2**. Crystal and intensity data are given in Table 1.

## Results and Discussion

**Preparation and Characterization of Diiron(III) Complexes.** The  $\mu$ -oxo diiron(III) complex **2**,  $[\text{Fe}_2\text{O}(\text{Hbba})_2\text{-Cl}_2]\text{Cl}_2$ , could be obtained by a reaction of a mononuclear iron(III) complex  $[\text{Fe}^{\text{III}}(\text{Hbba})\text{Cl}_2]\text{Cl}$ , **1** and an equivalent amount of potassium superoxide in methanol. (Scheme 1) When we use an equivalent amount of sodium acetate instead of potassium superoxide, we could also get complex **2**. The IR spectra of complexes **1** and **2** are similar to each other. The only difference is the band at  $844 \text{ cm}^{-1}$  that is assigned as a Fe-O-Fe asymmetric stretching band.<sup>8</sup> The



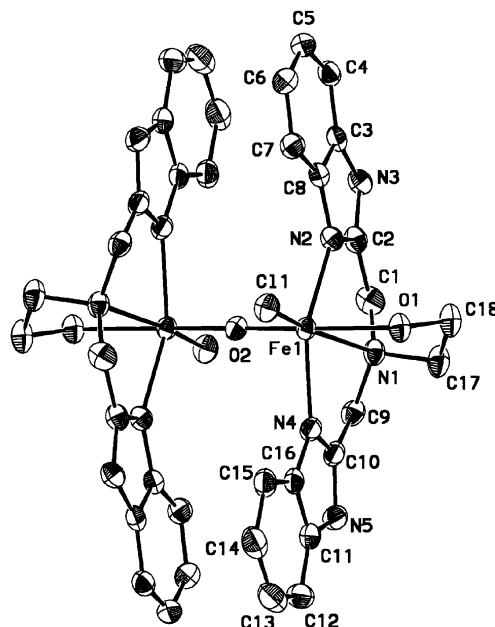
**Scheme 1**

magnetic moment of complex **2** at room temperature, 2.38  $\mu_B$  (1.68  $\mu_B$ /metal), corresponds to the value of oxo-bridged linear diiron(III) complexes.<sup>8b</sup>

Complex **3**,  $[\text{Fe}_2(\text{bbea})_2(\text{OBz})_2]\text{Cl}_2$ , could be obtained by a reaction of complex **2** with one equivalent amount of potassium superoxide and an equivalent amount of sodium benzoate in methanol. (Scheme 1) When we use one equivalent amount of sodium acetate instead of potassium superoxide or two equivalent amounts of sodium benzoate instead of one equivalent amount of potassium superoxide and one equivalent amount of sodium benzoate, we could also get complex **3**. The cation part of complex **3**<sup>9</sup> is identical to the previously reported bis( $\mu$ -alkoxo) diiron(III) complex  $[\text{Fe}_2(\text{bbea})_2(\text{OBz})_2]\text{ClO}_4$ .<sup>5</sup>

Complex **4**,  $[\text{Fe}_2(\text{bbea})_2(\text{OAc})_2]\text{Cl}_2$ , could be obtained by a reaction of complex **1** with one equivalent amount of potassium superoxide and sodium acetate in methanol. (Scheme 1) When we use two equivalent amounts of sodium acetate instead of an equivalent amount of potassium superoxide and an equivalent amount of sodium acetate, we could also get complex **4**. Complex **4** could also be obtained by a reaction of complex **2** and two equivalents amount of sodium acetate in methanol. The IR spectra of complexes **3** and **4** are very similar to each other. The only difference is in the bands at 1575 and 1394  $\text{cm}^{-1}$  that are assigned as the bands of the acetate group. The magnetic moment of complex **4** at room temperature is 4.68  $\mu_B$  (3.31  $\mu_B$ /metal).

**Molecular Structure of Complex 2.** An ORTEP drawing of complex **2** is shown in Figure 1. Complex **2** belongs to the *C*<sub>2</sub> point group and is similar to the reported  $\mu$ -oxo diiron(III) complex  $[\text{Fe}_2\text{O}(\text{ntb})_2\text{Cl}_2](\text{ClO}_4)_2$  (where ntb is tris(2-benzimidazolylmethyl)amine).<sup>10</sup> The  $\mu$ -oxo oxygen atom is at the crystallographic inversion center. The alcoholic oxygen atom in the Hbbea ligand replaced one of the benzimidazole nitrogen donor atoms in the ntb ligand. The bond distance between the iron(III) ion and the oxygen atom of the alcohol group is 2.207 Å, which corresponds to the distance between the iron(III) ion and the alcoholic oxygen atom, not the alkoxy oxygen atom. The alcoholic oxygen atom is at a trans-position of the bridging oxo oxygen atom. Each metal center has a distorted octahedral geometry. Two nitrogen atoms of the benzimidazole groups and an oxygen



**Figure 1.** ORTEP drawing of the cation of complex **2**,  $[\text{Fe}_2\text{O}(\text{Hbbea})_2\text{Cl}_2]^{2+}$ .

**Table 2.** Selected Bond Lengths [Å] and Angles [°] for **2**

Fe(1)-O(1)	2.207(3)	Fe(1)-N(2)	2.119(3)
Fe(1)-O(2)	1.7747(5)	Fe(1)-N(4)	2.123(3)
Fe(1)-N(1)	2.290(3)	Fe(1)-Cl(1)	2.3043(10)
O(2)-Fe(1)-O(1)	171.65(8)	O(2)-Fe(1)-Cl(1)	101.94(3)
O(1)-Fe(1)-N(1)	75.20(10)	N(2)-Fe(1)-N(1)	76.04(12)
N(2)-Fe(1)-O(1)	85.38(11)	N(4)-Fe(1)-N(1)	75.25(12)
N(4)-Fe(1)-O(1)	88.00(11)	N(1)-Fe(1)-Cl(1)	161.19(8)
O(1)-Fe(1)-Cl(1)	86.12(8)	N(2)-Fe(1)-N(4)	151.28(12)
O(2)-Fe(1)-N(1)	96.81(8)	N(2)-Fe(1)-Cl(1)	105.13(9)
O(2)-Fe(1)-N(2)	90.37(9)	N(4)-Fe(1)-Cl(1)	102.25(9)
O(2)-Fe(1)-N(4)	92.34(8)	Fe(1)#1 <sup>a</sup> -O(2)-Fe(1)	180.0

<sup>a</sup>Symmetry transformations used to generate equivalent atoms: #1 [-x+1, -y-1, -z]

**Hydrogen Bonds.**

D-H <sup>b</sup>	d(D-H)	d(H...A)	<DHA	d(D...A) <sup>b</sup>	O3 [-x+1, y-1/2, -z+1/2]
N3-H3	0.860	2.003	169.83	2.853	O3 [x+1, y, z]
N5-H5	0.860	2.085	161.72	2.914	O3 [-x+1, y+1/2, -z+1/2]
O1-H1O	0.860	2.201	163.08	3.034	O3 [-x+1, y+1/2, -z+1/2]
O3-H3O1	0.944	2.191	158.11	3.088	O3 [-x+1, y+1/2, -z+1/2]
O3-H3O2	0.962	2.383	158.78	3.298	O11

<sup>b</sup>D: Hydrogen atom donor; H: Hydrogen atom; A: Hydrogen atom acceptor.

atom of the alcohol group in the Hbbea, and a bridging oxo anion formed the base of the octahedral geometry. (Table 2) An apical nitrogen atom of Hbbea occupied one of two axial positions and a chloride anion occupied the remaining site. The bond distance between the iron(III) ion and the apical tertiary nitrogen atom (N1) is about 0.17 Å longer than the bond distances between the iron(III) ion and the basal nitrogen atoms of the benzimidazole groups (Table 2). Similar elongations were also observed in the other iron complexes

of tripodal tetradentate ligands with the benzimidazolymethyl group.<sup>11</sup>

The  $\mu$ -oxo diiron(III) complex **2**,  $[\text{Fe}_2\text{O}(\text{Hbbca})_2\text{Cl}_2]\text{Cl}_2$ , could be obtained by a reaction of a mononuclear iron(III) complex **1** and an equivalent amount of potassium superoxide in methanol. When we use an equivalent amount of sodium acetate as a base instead of potassium superoxide, we could also get complex **2**. A superoxide radical might behave as a base in methanol. The superoxide radical is a weak base whose  $\text{pK}_b$  is 4.8.<sup>12</sup> Similar behavior was already reported in our previous reactivity study on a mononuclear iron(III) complex  $[\text{Fe}^{\text{III}}(\text{ntb})\text{Cl}_2]\text{Cl}$ , **5** in methanol.<sup>10</sup> When we used an equivalent amount of base whether it was superoxide, acetate or hexamethylenediamine, we could have gotten the same complex  $[\text{Fe}^{\text{III}}(\text{ntb})\text{Cl}_2]\text{Cl}$ , **5**. However, when we use an equivalent amount of base (whether it is potassium superoxide, sodium acetate or sodium benzoate) and an additional equivalent amount of sodium benzoate, we could get the bis( $\mu$ -alkoxo) diiron(III) complex,  $[\text{Fe}_2(\text{bbca})_2(\text{OBz})_2]\text{Cl}_2$ , **3** with a benzoate at a monodentate binding mode to each metal center. The base was used to deprotonate the hydrogen atom of the coordinated alcohol group, the resulting alkoxy oxygen atom served as a bridging atom. We could synthesize the acetate analogue complex  $[\text{Fe}_2(\text{bbca})_2(\text{OAc})_2]\text{Cl}_2$ , **4** using sodium acetate instead of sodium benzoate. Complex **4** could be also synthesized starting with a  $\mu$ -oxo diiron(III) complex **2**. Two equivalent amounts of sodium acetate convert the  $\mu$ -oxo diiron(III) complex **2** to a bis( $\mu$ -alkoxo) diiron(III) complex,  $[\text{Fe}_2(\text{bbca})_2(\text{OAc})_2]\text{Cl}_2$ , **4**.

In conclusion, we synthesized various kinds of biologically important diiron(III) model complexes, one  $\mu$ -oxo diiron model complex and two bis( $\mu$ -alkoxo)/carboxylato diiron model complexes, with mixed a N/O donor atom environment. The  $\mu$ -oxo diiron(III) complex and the bis( $\mu$ -alkoxo)/carboxylato diiron(III) complexes with a biomimetic tripodal ligand containing mixed N/O donor atoms were synthesized using the mononuclear iron(III) complex as starting material. Depending on amounts and kinds of bases used, we could get various kinds of diiron(III) complexes. The reaction of a mononuclear iron(III) complex **1** with one equivalent amount of  $\text{KO}_2$  or  $\text{NaOAc}$  produced oxo diiron(III) complex **2**. An additional equivalent amount of  $\text{NaOBz}$  or  $\text{NaOAc}$  converts complex **2** to a bis( $\mu$ -alkoxo)/benzoato diiron(III) complex **3** or bis( $\mu$ -alkoxo)/acetato diiron(III) complex **4** depending on the base used. The addition of two equivalent amounts of  $\text{NaOBz}$  or  $\text{NaOAc}$  directly converts complex **1** to complex **3** or complex **4** depending on the base used. Currently, we are investigating the reactivity of complex **1** with other bases.

**Supplementary Material.** The following are available on request from the correspondence author: Tables giving

the structure determination summary, atomic coordinates, temperature factors, bond lengths, bond angles, and anisotropic thermal parameters for non-hydrogen atoms and atomic coordinates for hydrogen atoms and  $F_o/F_c$  tables for **2** and **3**.

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## References

1. Que, L., Jr.; Ho, R. Y. N. *Chem. Rev.* **1996**, *96*, 2607-2624.
2. (a) Wallar, B. J.; Lipscomb, J. D. *Chem. Rev.* **1996**, *96*, 2625-2657. (b) Yoshizawa, K.; Ohta, T.; Yamabe, T.; Hoffmann, R. *J. Am. Chem. Soc.* **1997**, *119*, 12311-12321.
3. (a) Herold, S.; Lippard, S. J. *J. Am. Chem. Soc.* **1997**, *119*, 145-156. (b) Hemmert, C.; Verelst, M.; Tuchagues, J.-P. *J. Chem. Soc. Chem. Commun.* **1996**, 617-618. (c) Sanders-Loehr, J.; Wheeler, W. D.; Shiemke, A. K.; Averill, B. A.; Loehr, T. M. *J. Am. Chem. Soc.* **1989**, *111*, 8084-8093. (d) Lambert, E.; Chabut, B.; Chardon-Noblat, S.; Deronzier, A.; Chottard, G.; Bousseksou, A.; Tuchagues, J.-P.; Laugier, J.; Bardet, M.; Latour, J.-M. *J. Am. Chem. Soc.* **1997**, *119*, 9424-9437. (e) Neves, A.; de Brito, M. A.; Vencayo, I.; Drago, V.; Griesar, K.; Haase, W. *Inorg. Chem.* **1996**, *35*, 2360-2368. (f) Borovik, A. S.; Hendrich, M. P.; Holman, T. R.; Mümek, E.; Papaefthymiou, V.; Que, L., Jr. *J. Am. Chem. Soc.* **1990**, *112*, 6031-6038.
4. Kwak, B.; Rhee, H.; Lah, M. S. *Bull. Korean Chem. Soc.* **1999**, *20*, 1235-1237.
5. Menage, S.; Que, Jr., L. *Inorg. Chem.* **1990**, *29*, 4293-4297.
6. Evans, D. F. *J. Chem. Soc.* **1958**, 2003-2005.
7. (a) Sheldrick, G. M. *Acta Crystallogr.* **1990**, *A46*, 467-473. (b) Sheldrick, G. M. *SHELXL97*; University of Göttingen: Göttingen, Germany, 1997.
8. (a) Cohen, J. D.; Payne, S.; Hagen, K. S.; Sanders-Loehr, J. *J. Am. Chem. Soc.* **1997**, *119*, 2960-2961. (b) Wang, S.; Luo, Q.; Wang, X.; Wang, L.; Yu, K. *J. Chem. Soc., Dalton Trans.* **1995**, 2045-2055.
9. Crystallographic data for complex **3**: monoclinic,  $C2/c$ ,  $a = 15.039(6)$ ,  $b = 18.292(8)$ ,  $c = 23.965(11)$  Å,  $\beta = 97.86(3)^\circ$ ,  $V = 6531(5)$  Å<sup>3</sup>,  $Z = 8$ ,  $D_{\text{calc}} = 1.279$  g/cm<sup>3</sup>. Final R factors were  $R1 = 0.0836$  and  $wR2 = 0.2571$  for 3039 observed reflections ( $I > 2\sigma(I)$ ).
10. Kwak, B.; Cho, K. W.; Pyo, M.; Lah, M. S. *Inorg. Chim. Acta* **1999**, *290*, 21-27.
11. (a) Buchanan, R. M.; O'Brien, R. J.; Richardson, J. F.; Latour, J.-M. *Inorg. Chim. Acta* **1993**, *214*, 33-40. (b) Wang, S.; Luo, Q.; Wang, X.; Wang, L.; Yu, K. *J. Chem. Soc. Dalton Trans.* **1995**, 2045-2055.
12. Behar, D.; Czapski, G.; Rabani, J.; Dorfman, L. M.; Schwarz, H. A. *J. Phys. Chem.* **1970**, *74*, 3209-3213.