Bis(μ-oxo)(μ-hydroxo)triiron(III) and (μ-oxo)(μ-hydroxo)diiron(III) Core Complexes with Tripodal Ligands Having a Terminal Carboxylate Group

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(Received July 13, 2000; CL-000668)

The tripodal ligands (6Me$_2$-BPG and BPG) containing the carboxylate donor afford two types of $Fe_2(O)(OH)$ and $Fe_3(O)_2(OH)$ core complexes, depending upon the methyl-substituent effect on the 6-position of the pyridyl ring.

Bimetallic oxo frameworks $M_2(\mu\text{-}O)_2$ have been shown as a common motif of a reactive high valent bimetallic species of $Cu^{III}{}_2$, $Fe^{III}Fe^{IV}$, $Ni^{III}{}_2$, and $Co^{III}{}_2$ and a key intermediate for oxygenation of C–H bond in ligands.[1] Especially, an $Fe_2(O)_2$ core[2] has been proposed as a key intermediate in the process of dioxygen activation by diiron centers in methane monooxygenase (MMOH) and ribonucleotide reductase (RNR), whose coordination environments are carboxylate-rich relative to that of hemerythrin (Hr).[3] Recently Que et al. have reported the structures and properties of the $Fe_2(O)_2$, $Fe_2(O)(OH)$, and $Fe_3(O)_3$ core complexes with the tetradentate ligands having four nitrogen donors,[4] but there is no structurally characterized $Fe_2(O)_2$, $Fe_2(O)(OH)$, and $Fe_3(O)_3$ core complexes with a terminal carboxylate oxygen donor. Therefore, it is important to explore how the nature of carboxylate donor in a terminal ligand influences the structures and properties of the cores mentioned above. Here we report the structures and properties of a (μ-oxo)(μ-hydroxo)diiron(III) and a bis(μ-oxo)(μ-hydroxo)triiron(III) complex with the tripodal ligands (6Me$_2$-BPG and BPG)[5] containing the carboxylate group.

Reaction of $[Fe_2(6Me_2\text{-}BPG)_2(O)(AcO)]ClO_4$ (**1**) with 2 equiv of Et_3N in methanol affords red crystals, $[Fe_2(6Me_2\text{-}BPG)_2(O)(OH)]ClO_4$ (**2**).[6] An ORTEP view of **2** is shown in Figure 1.[7] Two Fe ions are bridged by oxo and hydroxo oxygens to form a (μ-oxo)(μ-hydroxo)diiron(III) core. **2** is the first structurally characterized (μ-oxo)(μ-hydroxo)diiron(III) complex with the carboxylate oxygen donor, while three structurally characterized $Fe_2(O)(OH)$ complexes, $[Fe_2(X)_2(O)(OH)](ClO_4)_3$ (X = 6Me$_3$-TPA (**3**), BQPA (**4**), BPEEN (**5**)), with the N_4 tetradentate ligands have been reported.[4] Each Fe ion in **2** has an octahedral geometry consisted of N_3O_3 donor set, where three N donor atoms are in a mer-arrangement. The Fe···Fe separation is 2.899(2) Å, which is in the middle of the range for the $Fe_2(O)(OH)$ core complexes (2.835(1)–2.948(3) Å).[4] The Fe–O–Fe and Fe–OH–Fe angles are 103.9(4) and 91.5(3)°, respectively, which are comparable to those of **5** (Fe–O–Fe: 100.2(2); Fe–OH–Fe: 91.1(2)°).[4c] The $Fe–O_{oxo}$ and $Fe–O_{OH}$ bonds trans to the carboxylate oxygens (Fe(1)–O(6): 1.873(8) Å, Fe(2)–O(5): 2.083(9) Å) are significantly longer than their respective bonds trans to the amino nitrogens (Fe(2)–O(6): 1.807(7) Å, Fe(1)–O(5): 1.962(6) Å) owing to the trans effect of the stronger electron donor ability of the carboxylate oxygen. The observed asymmetry of the $Fe–O_{oxo}$ (Δr = 0.066 Å) and $Fe–O_{OH}$ (Δr = 0.121 Å) bonds in **2** is significantly larger than those in **5** ($Fe–O_{oxo}$: Δr = 0.004 Å, $Fe–O_{OH}$: Δr = 0.017 Å).[4] Thus the terminal carboxylate donor gives rise to a significant distortion of the $Fe_2(O)(OH)$ diamond core as compared with the pyridyl nitrogen donor in N_4 tetradentate ligands.[4] It is noted that deprotonation of the bridging hydroxide ion from the $Fe_2(O)(OH)$ core in **3** takes place to produce a $Fe_2(O)_2$ core,[4a] whereas **2** does not afford a $Fe_2(O)_2$ core even under more basic conditions. This fact suggests that the terminal carboxylates lower a Lewis acidity of the Fe center in **2**, which make the deprotonation of the bridging hydroxide ion difficult.

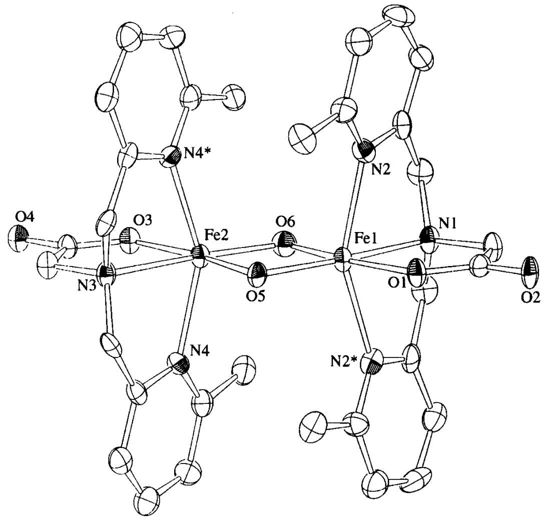

Figure 1. An ORTEP drawing of the cationic part of $[Fe_2(6Me_2\text{-}BPG)_2(O)(OH)]ClO_4$ (**2**). Selected Bond Distances (Å) and Angles (deg): Fe1 – O1 2.007(7); Fe1 – O5 1.962(6); Fe1 – O6 1.873(8); Fe1 – N1 2.179(8); Fe1 – N2 2.232(5); Fe2 – O3 2.053(7); Fe2 – O5 2.083(9); Fe2 – O6 1.807(7); Fe2 – N3 2.218(8); Fe2 – N4 2.185(5); Fe1···Fe2 2.899(2). Fe1 – O5 – Fe2 91.5(3); Fe1 – O6 – Fe2 103.9(4).

The Mössbauer spectrum of **2** at 84 K consists of a sharp single quadrupole doublet with δ = 0.51, ΔE_Q = 2.19, and Γ_{ave} = 0.43 mm/s, which is characteristic of high spin (μ-oxo)diiron(III) complexes.[8] The value of ΔE_Q for **2** is significantly larger than that of **3** (ΔE_Q = 1.66 mm/s),[4b] implying a larger electric field gradient around the iron(III) ions, probably due to perturbation from the terminal carboxylate group in 6Me$_2$-BPG.

Reaction of $[Fe_2(BPG)_2(O)(AcO)]ClO_4$ (**7**) with 2 equiv of Et_3N in methanol affords black crystals, $[Fe_3(BPG)_3(O)_2(OH)]ClO_4$ (**8**·ClO_4).[9] X-ray crystallography of $[Fe_3(BPG)_3(O)_2(OH)]CF_3SO_3$ (**8**·CF_3SO_3),[10] reveals that **8**·CF_3SO_3 has the first example of a bis(μ-oxo)(μ-hydroxo)triiron(III) core with a hexagon-like ring (Figure 2). Each Fe ion assumes an octahedral geometry with the N_3O_3 donor set, where three N donor atoms are in a mer-arrangement as observed for **2**. The average Fe–O_{oxo} bond distance (1.82 Å) is slightly shorter than that of **2** (1.84 Å) and the average Fe–O_{OH} bond distance (1.98 Å) is also shorter than that of **2** (2.02 Å). The average Fe–O–Fe angle (142.7°) is much larger than the Fe–OH–Fe angle (129.4(2)°). The Fe–O_{oxo} and Fe–O_{OH} bond distances are also substantially affected by the terminal carboxylate in the trans-position as observed for **2**; the Fe–O_{oxo} and Fe–O_{OH} bonds trans to the carboxylate oxygens (Fe(1)–O(3): 2.012(4) Å, Fe(2)–O(1): 1.873(4) Å, Fe(3)–O(2): 1.811(4) Å) are significantly elongated compared with those trans to the amino nitrogens (Fe(3)–O(3): 1.938(4) Å, Fe(2)–O(2): 1.784(4) Å, Fe(1)–O(1): 1.795(4) Å).

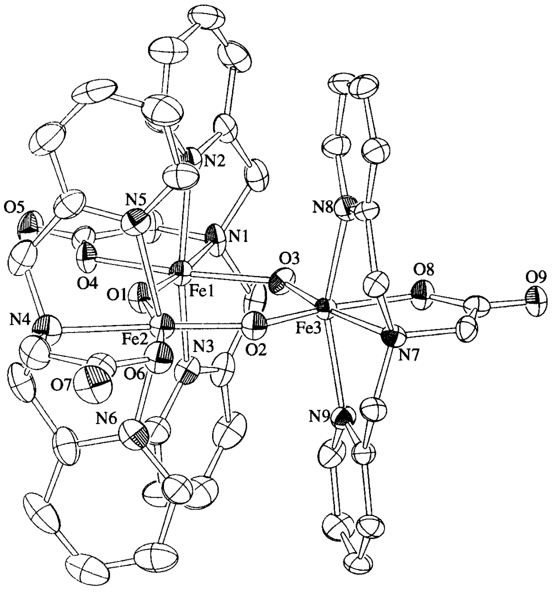

Figure 2. An ORTEP drawing of the cationic part of $[Fe_3(BPG)_3(O)_2(OH)]CF_3SO_3{\cdot}2H_2O$ (**8**·CF_3SO_3). Selected Bond Distances (Å) and Angles (deg): Fe1 – O1 1.795(4); Fe1 – O3 2.012(4); Fe1 – O4 2.049(4); Fe1 – N1 2.287(5); Fe1 – N2 2.209(5); Fe1 – N3 2.227(5); Fe2 – O1 1.873(4); Fe2 – O2 1.784(4); Fe2 – O6 2.069(4); Fe2 – N4 2.250(6); Fe2 – N5 2.248(5); Fe2 – N6 2.240(6); Fe3 – O2 1.811(4); Fe3 – O3 1.938(4); Fe3 – O8 2.087(4); Fe3 – N7 2.207(5); Fe3 – N8 2.198(5); Fe3 – N9 2.194(5); Fe1···Fe2 3.478(1); Fe1···Fe3 3.572(1); Fe2···Fe3 3.404(2). Fe1 – O1 – Fe2 143.0(2); Fe2 – O2 – Fe3 142.4(2); Fe1 – O3 – Fe3 129.4(2)

Recently, Que et al. reported a tri(μ-oxo)triiron(III) complex, $[Fe_3(5Et_3\text{-}TPA)_3(O)_3]^{3+}$ (**9**) with four nitrogen donors.[4c] In contrast to the formation of the $Fe_3(O)_3$ core in **9**, the $Fe_3(O)_2(OH)$ core is formed in **8**. This fact also reflects the stronger electron donor ability of the terminal carboxylate oxygen. It must be noted that introduction of the methyl groups into the 6-position of the pyridyl ring causes a remarkable structural change between **2** and **8**, i.e., **2** has the $Fe_2(O)(OH)$ core, whereas **8** has the $Fe_3(O)_2(OH)$ core. Such a change of the core structure reflects the unfavorable steric interaction between 6-methyl groups on the pyridyl ring.

The Mössbauer spectrum of **8**·CF_3SO_3 at 293 K exhibits a broad single quadrupole doublet with $\delta = 0.35$, $\Delta E_Q = 1.62$, and $\Gamma_{ave} = 0.76$ mm/s, which is due to overlapping of closely spaced two sets of quadrupole doublets attributable to the bis(μ-oxo)Fe^{III} and the (μ-oxo)(μ-hydroxo)Fe^{III} moieties. It should be noted that Mössbauer spectrum of **8**·CF_3SO_3 at 293 K significantly differs from that at 95 K; the two peaks becomes broader at 95 K. The spectral change may be explained by the relaxation effect due to a long Fe···Fe distance (3.404(2)–3.572(1) Å). Further, the peak of lower energy side is broader than that of higher energy side at 95 K. Since the broaden peak is observed at a lower energy side, the quadrupole splitting parameter e^2qQ is negative, i.e., | ± 3/2> state in Mössbauer excited state is lower than | ± 1/2> state.

In conclusion, the tripodal ligands containing the carboxylate donor afford two types of $Fe_2(O)(OH)$ and $Fe_3(O)_2(OH)$ cores, depending upon the methyl-substituent effect on the 6-position of the pyridyl ring. The stronger electron donor ability of the terminal carboxylate causes a significant asymmetric distortion for the rhomb $Fe_2(O)(OH)$ and hexagon $Fe_3(O)_2(OH)$ cores.

This work was supported by a Grants-in-Aid for Scientific Research, from the Ministry of Education, Science, Sports and Culture, Japan (M. S.), and by the JSPS Research Fellowships for Young Scientists (H. F.).

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5 Abbreviations used: BPG, *N,N*-bis(2-pyridylmethyl)glycinate; $6Me_2$-BPG, *N,N*-bis(6-methyl-2-pyridylmethyl)glycinate; $6Me_3$-TPA, tris(6-methyl-2-pyridylmethyl)amine; BQPA, bis(2-quinolylmethyl)(2-pyridylmethyl)amine; $5Et_3$-TPA, tris(5-ethyl-2-pyridylmethyl)amine; BPEEN, *N,N*-diethyl-*N,N*-bis(2-pyridylmethyl)ethane-1,2-diamine.

6 **1**·$4.5H_2O$: Anal. Calcd for $C_{34}H_{74}ClFe_2N_6O_{15.5}$: C, 43.63; H, 5.17; N, 8.98 %. Found: C, 43.43; H, 4.74; N, 9.02 %. **2**: Calcd for $C_{32}H_{37}ClFe_2N_6O_{10}$: C, 47.29; H, 4.59; N, 10.34 %. Found: C, 47.17; H, 4.57; N, 10.35 %. Reflectance spectrum of **2** (λ / nm): 378, 522, 740 (complex **2** was insoluble in common organic solvents).

7 Crystal data for $[Fe_2(6Me_2\text{-}BPG)_2(O)(OH)]ClO_4$ at –150 °C. Red plate, fw = 812.83, orthorhombic, space group $Pmn2_1$ with $Z = 2$, $a = 14.973(2)$, $b = 14.998(2)$, $c = 7.693(3)$ Å, $V = 1727.6(5)$ Å^3, $D_c = 1.562$ g cm^{-3}. $R = 0.047$ and $R_w = 0.065$ for 1575 data.

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9 **7**·$3H_2O$: Calcd for $C_{30}H_{37}ClFe_2N_6O_{14}$: C, 42.25; H, 4.37; N, 9.85 %. Found: C, 42.50; H, 4.12; N, 9.90 %. **8**·$ClO_4{\cdot}5H_2O$: Calcd for $C_{42}H_{53}ClFe_3N_9O_{18}$: C, 42.94; H, 4.55; N, 10.73 %. Found: C, 42.95; H, 4.44; N, 10.95 %. **8**·$CF_3SO_3{\cdot}3H_2O$: Calcd for $C_{43}H_{49}F_3Fe_3N_9O_{15}S$: C, 43.46; H, 4.16; N, 10.61 %. Found: C, 43.31; H, 4.10; N, 10.57 %. Absorption spectrum of **8**·$CF_3SO_3{\cdot}3H_2O$ [λ / nm (ε / M^{-1} cm^{-1})] in water: 466 (470), 500 (sh, 385), 565 (sh, 255), 650 (sh, 145); reflectance spectrum (λ / nm): 415 (sh), 468, 565 (sh), 650 (sh).

10 Crystal data for $[Fe_3(BPG)_3(O)_2(OH)]CF_3SO_3{\cdot}2H_2O$ at –110 °C. Dark green prisms, fw = 1170.49, trigonal, space group $P\bar{3}$ with $Z = 6$, $a = 23.963(2)$, $c = 15.164(3)$ Å, $V = 7540(1)$ Å^3, $D_c = 1.546$ g cm^{-3}. $R = 0.034$ and $R_w = 0.044$ for 2813 data. Three water molecules per asymmetric unit were suggested by the elemental analysis, although we could not locate one water molecule.