Heteronuclear $Fe^{III}Mn^{II}Fe^{III}$ and Homonuclear $Fe^{III}Fe^{III}Fe^{III}$ Complexes with a Tripodal Tetradentate Ligand

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The reaction of a tripodal tetradentate ligand (H_2L = *N,N*-bis(2-hydroxybenzyl)-*N′,N′*-dimethylethylenediamine) with $Fe(ClO_4)_2 \cdot 6H_2O$ and a carboxylic acid in basic methanol generates an iron(III) species under aerobic conditions. Further addition of an Mn^{2+} cation gave a heterotrinuclear complex, $[\{Fe^{III}(L)(carboxylato)(OCH_3)\}_2Mn^{II}]$. On the other hand, an additional Fe^{2+} cation gave a μ_3-oxo homotrinuclear complex, $[\{Fe^{III}(L)(carboxylato)\}_2OFe^{III}(OCH_3)]$. Drastic changes in the structure were induced by the addition of metal ions.

Heteronuclear complexes are of interest in connection with their physical properties and relevance to bioinorganic chemistry. In particular, the magnetic study has been an important research field for elucidating the mechanism of the spin-exchange interactions. Di- and trinuclear heterometallic systems have been extensively studied.[1-3] One type of the heterotrinuclear complexes is a linear molecule of MM'M. Most compounds in the MM'M system are structurally rigid in order to distinguish M and M'. Our recent work has provided a variety of bridging structures for polynuclear manganese complexes with Mn^{III} and Mn^{II} using tripodal tetradentate ligands.[4,5] The structure of an $Mn^{III}Mn^{II}Mn^{III}$ complex with a tripodal tetradentate ligand (L, Figure 1) is also linear. However, a combination of Mn and Fe allowed diverse overall structures. Here, we report an expansible heterotrinuclear complex containing an $Fe^{III} \cdots Mn^{II} \cdots Fe^{III}$ arrangement supported by the L ligand. When an additional iron ion was used for the central manganese core, a μ_3-oxo homotrinuclear complex was obtained.

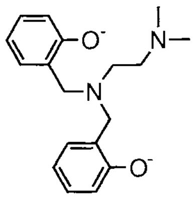

Figure 1. Structure of the tripodal tetradentate ligand (L).

The reaction of the H_2L ligand (1 equiv) with $Fe(ClO_4)_2 \cdot 6H_2O$ (1 equiv) and *m*-chlorobenzoic acid (Hmcba, 1 equiv) in basic methanol gave a red-brown solution. After addition of $Mn(ClO_4)_2 \cdot 6H_2O$ (0.5 equiv), the reaction mixture was stirred. The resulting brown precipitate was collected and recrystallized from dichloromethane-methanol to give the heterotrinuclear complex, $[\{Fe^{III}(L)(mcba)(OCH_3)\}_2Mn^{II}]$ (**1**).[6] The yield was 63%. The electronic spectrum shows an intense band at 20.8 × 10^3 cm^{-1} (ε = 6960 $M^{-1}cm^{-1}$, 1 M = 1 mol dm^{-3}) which is assigned to a phenolate to iron(III) charge transfer (LMCT).

The X-ray analysis of $[\{Fe^{III}(L)(mcba)(OCH_3)\}_2Mn^{II}]$ (**1**) revealed that two geometrical isomers exist in a unit cell. Figure 2 shows the structures of isomers **1A** and **1B**. Both structures consist of a central manganese core and flanking iron cores coordinated by the tripodal tetradentate ligand (L). The Fe and Mn cores are bridged by a μ-phenolato, a μ-alkoxo, and a μ-carboxylato ligand. Isomer **1A** has a center of inversion on the central manganese ion. This structural feature is similar to $[\{Mn^{III}(L)(mcba)(OCH_3)\}_2Mn^{II}]$ which was reported previously.[4] Isomer **1B** has pseudo C_2 symmetry, and the arrangement of Fe···Mn···Fe is not linear (153.37(9)°). Although the overall structures of **1A** and **1B** are quite different, the Fe···Mn separations are almost identical: the distances are 3.111(2) Å in isomer **1A**, and 3.143(3) and 3.144(3) Å in isomer **1B**. These distances are also similar to the $Mn^{III} \cdots Mn^{II}$ separation of $[\{Mn^{III}(L)(mcba)(OCH_3)\}_2Mn^{II}]$ (3.1720(7) Å). The structural differences between **1** and $[\{Mn^{III}(L)(mcba)(OCH_3)\}_2Mn^{II}]$ are

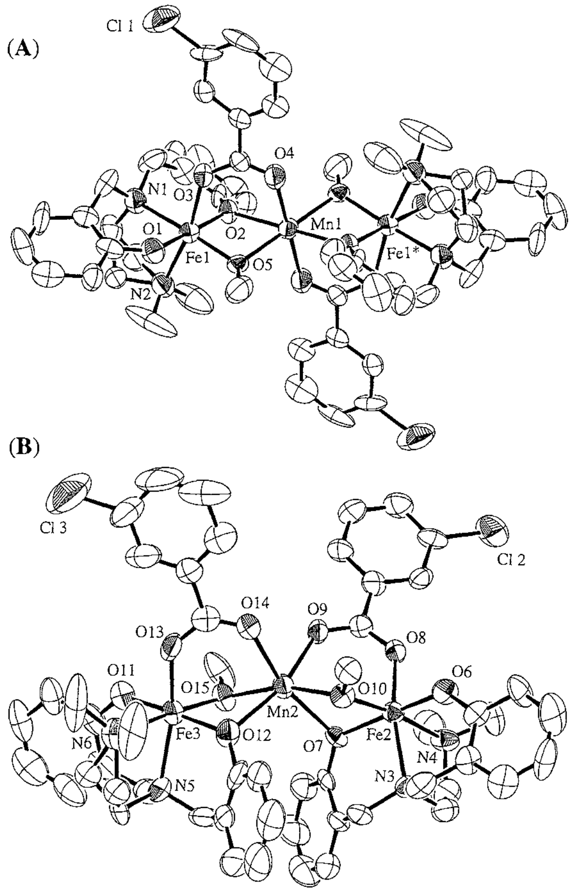

Figure 2. ORTEP views of two structures of $[\{Fe^{III}(L)(mcba)(OCH_3)\}_2Mn^{II}]$ (**1**).

observed in Fe—N and Mn—N bond distances. In the Mn^{III}Mn^{II}Mn^{III} complex, Mn—N(central) is 2.110(3) Å and Mn—N(terminal) is 2.390(3) Å.[4] The large Mn—N(terminal) distance stems from the Jahn-Teller elongation of the high-spin d^4 compound. In the Fe^{III}Mn^{II}Fe^{III} complex (**1**), Fe1—N1(central) is 2.19(1) Å and Fe1—N2(terminal) is 2.28(1) Å for isomer **1A**. The similar situation is observed for isomer **1B**: Fe2—N3(central) = 2.21(1) Å, Fe2—N4(terminal) = 2.29(1) Å, Fe3—N5(central) = 2.23(1) Å, Fe3—N6(terminal) = 2.29(1) Å. The Jahn-Teller effect is not expected for the high-spin iron(III) moieties.

The effective magnetic moment of **1** is 8.88 μ_B at 297 K. Because the local bridging frameworks of **1A** and **1B** are similar to each other, the magnetic properties will be similar for these isomers. The temperature dependence was interpreted as a 5/2-5/2-5/2 spin system using an isotropic spin Hamiltonian ($H = -2[J_{12}(S_1 \cdot S_2) + J_{23}(S_2 \cdot S_3) + J_{13}(S_1 \cdot S_3)]$ where $S_1 = S_2 = S_3 = 5/2$ for the S_1-S_2-S_3 arrangement). The fitting gives $J\ (=J_{12} = J_{23}) = -7.28$ cm^{-1}, $g = 1.98$, and $\Theta = -0.39$ K, where the interaction between the terminal Fe^{III} ions was excluded ($J_{13} = 0$). On the other hand, in [{Mn^{III}(L)(carboxylato)(OCH$_3$)}$_2$Mn^{II}], the values of spin-exchange interactions between Mn^{III} and Mn^{II} range from −0.25 cm^{-1} to 1.9 cm^{-1}.[4] These magnetic properties corroborate the Fe^{III}···Mn^{II}···Fe^{III} arrangement.

The homotrinuclear complex, [{Fe^{III}(L)(mcba)}$_2$OFe^{III}(OCH$_3$)] (**2**), was obtained by the same procedure as that for **1** except that Fe(ClO$_4$)$_2$·6H$_2$O (0.5 equiv) was added instead of Mn(ClO$_4$)$_2$·6H$_2$O (yield: 60%).[7] The electronic spectrum shows an intense band at 20.8 × 10^3 cm^{-1} (ε = 8860 M^{-1}cm^{-1}). This band is at the same position as that of **1**, and is also assigned to a phenolate to iron(III) CT band. Since the crystals of **2** were not suitable for X-ray analysis, we prepared analogous complexes. A successful X-ray structure determination was performed for [{Fe^{III}(L)(3,5-dcba)}$_2$OFe^{III}(OCH$_3$)] (**3**) where 3,5-dcba denotes 3,5-dichlorobenzoate(1−).[8] Figure 3 shows the structure of **3**. This molecule is composed of two Fe(L) units and an inserted iron(III) core. They are connected by an oxo, two phenolato, and two carboxylato bridges. The Fe(1)O(1)O(2)N(1) and Fe(2)O(3)O(4)N(3) least-squares planes in the Fe(L) units twist to form a dihedral angle of 41.8°. The μ-oxo ligand is shared by the three Fe^{III} cores and is in the Fe$_3$ plane. The bond distances (Å) and angles (°) around the μ_3-oxo center are as follows: Fe(1)—O(10) = 1.866(6), Fe(2)—O(10) = 1.853(6), Fe(3)—O(10) = 2.016(6); Fe(1)—O(10)—Fe(2) = 152.8(4), Fe(1)—O(10)—Fe(3) = 103.3(3), Fe(2)—O(10)—Fe(3) = 103.8(3). Because of the μ-oxo bridge, a strong antiferromagnetic interaction was observed between Fe(1) and Fe(2): $J_{\mathrm{Fe(1)\text{-}Fe(2)}} = -48.0$ cm^{-1}, $J_{\mathrm{Fe(1)\text{-}Fe(3)}} = J_{\mathrm{Fe(2)\text{-}Fe(3)}} = -7.3$ cm^{-1}, and $g = 2.03$.[9]

For the L ligand, an oxo bridged iron dimer has not been isolated. We presume that the additional iron ion shortens the distance between the two Fe(L) units to generate the μ-oxo bridge. Another role of the additional Fe^{2+} ion is underlined by the fact that the addition of the Mn^{2+} ion gives no μ-oxo compound. The redox potential of the additional ion may be important. The different structures of the Fe^{III}Mn^{II}Fe^{III} and Fe^{III}Fe^{III}Fe^{III} complexes imply that the additional metal ions can give rise to different characters for the same mononuclear unit.

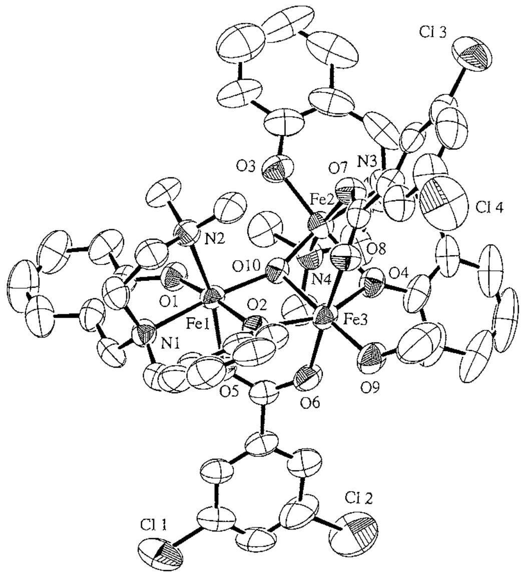

Figure 3. ORTEP view of [{Fe^{III}(L)(3,5-dcba)}$_2$OFe^{III}(OCH$_3$)] (**3**).

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6 Anal. Found: C, 54.38; H, 5.02; N, 5.04%. Calcd for [{Fe(L)(mcba)(OCH$_3$)}$_2$Mn] = C$_{52}$H$_{58}$Cl$_2$Fe$_2$MnN$_4$O$_{10}$: C, 54.95; H, 5.14; N, 4.93%. Crystallographic data for **1**: formula weight 1136.57, triclinic, space group $P\bar{1}$, a = 13.926(3), b = 24.879(7), c = 12.136(4) Å, α = 102.82(3), β = 93.76(3), γ = 75.89(2)°, V = 3976(2) Å^3, Z = 3, D_c = 1.42 g cm^{-3}, μ(Mo $K\alpha$) = 9.34 cm^{-1}, 14014 unique reflections ($2\theta_{\max}$ = 50°), 4707 ($I > 2\sigma(I)$) used in the refinement, R = 0.082, R_w = 0.065.

7 Anal. Found: C, 54.43; H, 4.95; N, 5.08%. Calcd for [{Fe(L)(mcba)}$_2$OFe(OCH$_3$)] = C$_{51}$H$_{55}$Cl$_2$Fe$_3$N$_4$O$_{10}$: C, 54.57; H, 4.94; N, 4.99%.

8 Anal. Found: C, 51.42; H, 4.32; N, 4.85%. Calcd for [{Fe(L)(3,5-dcba)}$_2$OFe(OCH$_3$)] = C$_{51}$H$_{53}$Cl$_4$Fe$_3$N$_4$O$_{10}$: C, 51.42; H, 4.48; N, 4.70%. Crystallographic data for **3**·2CH$_3$OH·3H$_2$O: formula weight 1309.46, monoclinic, space group $P2_1/c$, a = 15.499(11), b = 21.839(5), c = 19.802(4) Å, β = 95.22(3)°, V = 6675(4) Å^3, Z = 4, D_c = 1.30 g cm^{-3}, μ(Mo $K\alpha$) = 8.62 cm^{-1}, 13489 unique reflections ($2\theta_{\max}$ = 52°), 5715 ($I > 2\sigma(I)$) used in the refinement, R = 0.080, R_w = 0.089.

9 The magnetic property of **3** was interpreted as a 5/2-5/2-5/2 spin system.