Preparation, Structures and Properties of Novel Mono- and Trinuclear Iron(III) Complexes with Mixed Ligands

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Novel mono- and trinuclear iron(III) complexes with mixed ligands, $\mathrm{Fe^{III}}$(acac)(*N*-PhO-sal)(MeOH) **1** and $\mathrm{Fe^{III}_3}$(acac)(*N*-PhO-sal)$_4$ **2** have been prepared and characterized, where acacH and *N*-PhOH-salH denote acetylacetone and *N*-2-hydroxyphenyl-salicylideneamine, respectively. The variable temperature magnetic susceptibilities (2-350 K) for complex **2** indicate that there is an intramolecular antiferromagnetic interaction among the iron(III) ions, and that spin-crossover behavior may take place from S = 5/2, 5/2 and 5/2 ground states to S = 1/2, 5/2 and 1/2 (Fe1, Fe2 and Fe1*) near 60 K and below.

Polynuclear iron(III) complexes continue to be of interest in relation to oxidation and oxygenation of organic substances catalyzed by non-heme diiron enzymes such as methane monooxygenase (MMO), ribonucleotide reductase (RNR R2).[1] Recently, understanding the coordination environment around the iron ion, catalytic mechanism and magnetic properties for these systems have been gradually clarified by several analytical methods. In addition, the magnetic interaction representing spin-crossover behavior for iron complexes has been investigated in order to explain biological functions of iron active centers.[2] So far, the major part of iron(III) complexes exhibiting spin-crossover properties, however, has been limited for mononuclear or linear polynuclear complexes except few examples for a bent trinuclear complex.[2] In this paper, we describe the preparation, molecular structures and magnetic properties of the novel mono- and trinuclear iron(III) complexes.

The mononuclear iron(III) complex, $\mathrm{Fe^{III}}$(acac)(*N*-PhO-sal)(MeOH) **1** was obtained between ligand substitution reaction of $\mathrm{Fe^{III}}$(acac)$_3$ (0.965 g, 2.73 mmol) and *N*-PhOH-salH (0.584 g, 2.74 mmol) in methanol (MeOH) as black prismatic crystals (0.70 g, 70% yield), where acacH and *N*-PhOH-salH denote acetylacetone and *N*-2-hydroxyphenyl-salicylideneamine. On the other hand, when acetonitrile (MeCN), dichloromethane or cyclohexane was used as a solvent in place of MeOH, the trinuclear iron(III) complex, $\mathrm{Fe^{III}_3}$(acac)(*N*-PhO-sal)$_4$ **2** was obtained in 75% yield. Clearly, two types of different complexes are obtained depending on the solvents used. This may be caused by protecting further substitution reaction of acetylacetonato ligands with *N*-PhOH-salH by relatively strong coordination of MeOH molecules to the central iron(III) ion. These complexes were characterized by elemental analyses, spectroscopic methods, X-ray crystallography, and electrochemical and magnetic susceptibility measurements.[4,5] Moreover, the variable temperature magnetic susceptibilities for complex **2** were measured over the range of 2-350 K, and the data were fitted by applying the isotropic spin-exchange Hamiltonian and Van Vleck equation.

Figure 1 shows the molecular structure of complex **1** in which the central iron(III) ion adopts a six-coordinate tetragonally distorted octahedron: The NO_2 and O donor atoms of *N*-PhO-sal and acac, respectively, form an equatorial plane, and two O donor atoms of MeOH and the acac occupy the two axial posisitions.[6] The average of Fe-O (ca. 1.993 Å) and Fe-N (2.119 Å) distances are in the range normally observed for iron(III)-Schiff base complexes.[3] Moreover, the unit cell for the crystal structure of complex **1** has been found to consist of two crystallographically independent monomers of the same structure.

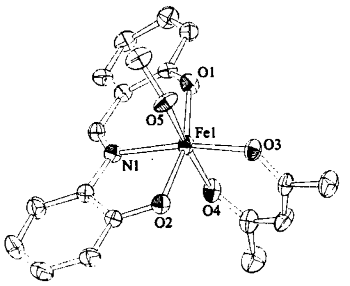

Figure 1. The molecular structure of [$\mathrm{Fe^{III}}$(acac)(*N*-PhO-sal)(MeOH)]; **1**. Hydrogen atoms are omitted for clarity. Selected bond lengths (Å) and angles (deg) are as follows: Fe1-O1 1.909(4), Fe1-O2 1.983(4), Fe1-O3 1.965(4), Fe1-O4 2.018(4), Fe1-O5 2.090(4), Fe1-N1 2.119(4), O1-Fe1-O2 163.0(2), O4-Fe1-O5 173.1(1), O3-Fe1-N1 170.0(2).

Figure 2 shows the molecular structure of complex **2** in which each of three iron(III) ions adopts a six-coordinate distorted octahedron.[6] Each of the two terminal iron(III) ions (Fe1 and Fe1*) is coordinated with two *N*-PhO-sal ligands and has a meridional configuration: both *N*-PhO-sal ligands bridge two iron ions (Fe1 and Fe2, or Fe1* and Fe2) by their phenolic oxygen donor atoms of *o*-aminophenol moiety. The average of

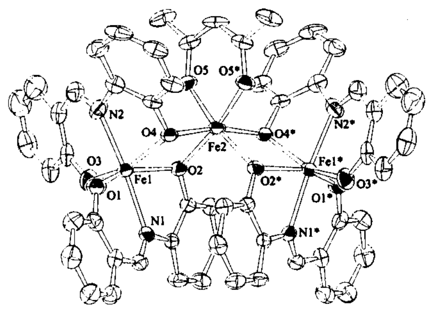

Figure 2. The molecular structure of [$\mathrm{Fe^{III}_3}$(acac)(*N*-PhO-sal)$_4$]; **2**. Hydrogen atoms are omitted for clarity. Selected bond lengths (Å) and angles (deg) are as follows: Fe1-Fe2 3.223(1), Fe1-O1 1.897(5), Fe1-O2 2.089(5), Fe1-O3 1.903(5), Fe1-O4 2.078(5), Fe1-N1 2.148(6), Fe1-N2 2.141(7), Fe2-O2 2.000(4), Fe2-O4 2.022(4), Fe2-O5 1.978(5), Fe1-Fe2-Fe1* 130.49(6), Fe1-O2-Fe2 104.0(2), O1-Fe1-O2 152.1(2), O3-Fe1-O4 152.3(2), N1-Fe1-N2 175.0(3), O4-Fe2-O4* 167.7(2), O2-Fe2-O5* 170.3(2).

non-bridging Fe-O distances (ca. 1.926 Å) is shorter than the average of bridging Fe-O distances (ca. 2.047 Å), and all of the bridging Fe-O distances are similar value (2.084 Å in Fe1 and 2.011 Å in Fe2). This means that the bridging oxygen donor atoms coordinate almost equally with both Fe1 (Fe1*) and Fe2, which provide distorted octahedral environments around the iron(III) centers. The Fe1-Fe2 distance (3.223 Å) falls within the range normally observed for μ-phenoxo iron(III) compounds.[3] The central iron(III) ion (Fe2) is coordinated with a O_6 donor set from the acac and two *N*-PhO-sal ligands. That is, the Fe1 and Fe2 are surrounded by clearly different coordination environments. The arrangement of three iron(III) ions is not linear (Fe1-Fe2-Fe1* 130.49(6)°), because of compelling them to adopt an octahedral configuration. Such a difference in coordination environment around the central iron(III) ions reflect their redox potentials: the redox couples of Fe(III) ⇔ Fe(II) are observed at the potentials of -0.59 and -1.02 V (vs. SCE) for complex **2** in MeOH which can be assigned to those of Fe2 and Fe1 (Fe1*), respectively. On the other hand, only the redox couple of Fe(III) ⇔ Fe(II) for complex **1** is observed at the potential of -0.61 V (vs. SCE).

Figure 3 shows the plots of the magnetic susceptibility and effective magnetic moment per complex **2** molecule against temperature over the range of 2-350 K, using a Quantum Design Model MPMS-5S superconducting quantum interference device (SQUID) in an applied magnetic field of 1000 G. The magnetic moments gradually decrease from 9.35 μ_B at 350 K to 6.81 μ_B near 60 K and then steeply to 6.24 μ_B at 15 K.[7] The magnetic data between 80 and 300 K are fairly fitted with the calculated values by the theoretical treatment derived from the isotropic spin-exchange Hamiltonian $H = -2JS1(S2+S3)$ and the Van Vleck equation, where all three iron(III) ions are S = 5/2. By assuming there is no magnetic interaction between the terminal iron(III) ions: $J_{11*} = 0$, we obtained $J_{12} = J_{1*2} = -3.54$ cm^{-1} and $g = 1.98$, where J_{12}, J_{1*2} and J_{11*} correspond to the magnetic exchange coupling parameters between Fe1-Fe2, Fe1*-Fe2 and Fe1-Fe1*, respectively. However, the magnetic data near 80 K and below deviated from the same calculation as mentioned above. Therefore, we presume that by cooling complex **2**, the spin states of the iron (III) ions may change from S = 5/2 (3Fe) to S = 1/2 (Fe1 and Fe1*) and S = 5/2 (Fe2). In complex **2**, the more reasonable fitting was obtained with assumption that the extent of the low-spin state (1/2) of Fe1 and Fe1* may increase with a decrease in the temperature. To clarify such a spin-crossover behavior Mössbauer spectra of complex **1** and complex **2** were measured at room temperature and 30 K. In both complexes the isomer shifts decreased and the quadrupole and splittings increased at lower temperature. The differences in their vales between both temperatures are considerably larger for complex **2** than for complex,[7] which is consistent with the spin-crossover behavior of complex **2**. The detailed magnetic behavior near 80 K and below is now in progress.

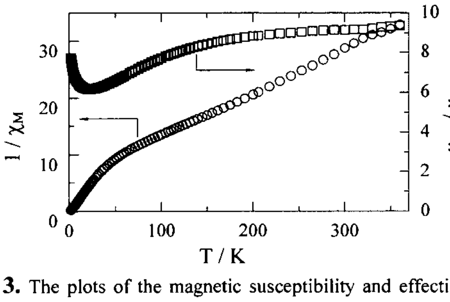

Figure 3. The plots of the magnetic susceptibility and effective magnetic moment per complex **2** molecule versus temperature in the 2-350 K range.

References and Notes

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4 Physicochemical data for **1**: UV-visible spectra (MeOH): λ_{max} = 487 nm (log ε = 3.47). Cyclic voltammogram (MeOH): $E_{1/2}$ = -0.61 V (III⇔II)(vs. SCE). Magnetic moment: 5.91 μ_B (297 K). Anal. Found: C, 57.30; H, 5.07; N, 3.55; Fe, 14.06%. Calcd for **1**, $C_{19}H_{20}FeNO_5$: C, 57.30; H, 5.06; N, 3.52; Fe, 14.03%.

5 Physicochemical data for **2**: UV-visible spectra (MeOH): λ_{max} = 480 nm (log ε = 3.96). Cyclic voltammogram (MeOH): $E_{1/2}$ = -0.59 and -1.02 V (III⇔II)(vs. SCE). Magnetic moment per trimer: 9.14 μ_B (297 K). Anal. Found: C, 61.49; H, 4.20; N, 7.00; Fe, 14.98%. Calcd for **2**·2MeCN, $C_{61}H_{49}Fe_3N_6O_{10}$: C, 61.38; H, 4.14; N, 7.04; Fe, 15.04%.

6 Crystal data for **1**: formula = $C_{19}H_{20}FeNO_5$, F_W = 398.22, triclinic, space group $P\bar{1}$, a = 11.145(3), b = 17.548(5), c = 9.904(2) Å, α = 103.42(2), β = 99.94(1), γ = 93.32(2)°, Z = 4, V = 1841.8(9) Å^3, d_{calcd} = 1.436 gcm^{-3}, μ(Mo-K$_\alpha$) = 8.47 cm^{-1}, T = 277 K, crystal dimensions 0.20_0.30_0.45 mm^3, 8473 reflections measured(2θ_{max} = 55.0º), 3609[$I > 3.00\sigma(I)$] used in the refinement, R = 0.046, R_W = 0.061.

Crystal data for **2**·2MeCN: $C_{61}H_{49}Fe_3N_6O_{10}$, F_W = 1193.63, monoclinic, space group $C2/c$, a = 26.121(4), b = 12.204(4), c = 19.407(5) Å, β = 116.57(1)°, Z = 4, V = 5533(2) Å^3, d_{calcd} = 1.433 gcm^{-3}, μ(Mo-Kα) = 8.41 cm^{-1}, T = 293 K, crystal dimensions 0.10 × 0.10 × 0.30 mm^3, 6655 reflections measured(2θ_{max} = 55.0°), 2167[$I > 3.00\sigma(I)$] used in the refinement, R = 0.049, R_W = 0.065. Intensity data were collected on a Rigaku AFC7R diffractometer using graphite-monochromated Mo-K$_\alpha$ radiation. The structure was solved by the direct method; SHELXS86 and refined by the full-matrix least-squares method using a teXsan program package.

7 The isomer shifts and quadrupole splittings measured at room temperature (at 30 K) are 0.40 (0.33) and 0.53 (0.67) mms^{-1} for complex 1, and 0.51 (0.09) and 0.35 (0.56) mms^{-1} for complex **2**, respectively.