Formation of a Tetranuclear High–Spin Iron(II,III,II,III) Mixed Valence Complex

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A class II mixed valent Fe_4(II,III,II,III) complex $[Fe_4(Me_4\text{-tpdp})_2(\mu\text{-}F)_2(OH)_2(H_2O)_2](BF_4)_4$ was synthesized, where HMe_4-tpdp is *N,N,N',N'*-tetrakis[2-(6-methylpyridyl)methyl]-1,3-diamino-2-propanol. The crystal structure shows that the complex cation consists of two alkoxo-bridged dinuclear units which are connected by two fluoro bridges to form a bilayered structure (a box structure).

Di- and polynuclear high-spin iron mixed valence complexes have been shown to exist in various non-hem iron proteins such as hemerythrin (Hr), methane monooxygenase (MMO), purple acid phosphatase (PAP), and intermediates during ferritin core formation.[1] Recently various di- and polynuclear mixed valent complexes have been reported as models for the above iron proteins.[2,3]

Previously we found that dinuclear iron(II,II) complexes $[Fe_2(\text{bpmp or bzimp})(RCOO)_2]^+$ react with O_2 to form mixed valent complexes $[Fe_2(\text{bpmp or bzimp})(RCOO)_2]^{2+}$ (bpmp = 2,6-bis[bis(2-pyridylmethyl)aminomethyl]-4-methylphenolate and bzimp = 2,6-bis[bis(2-benzimidazolylmethyl)aminomethyl]-4-methylphenolate).[2a,2b] The dinuclear iron(II,II) complexes $[Fe_2(Me_4\text{-tpdp})(RCOO)]^{2+}$ reversibly bind molecular oxygen at -40 °C,[4] whereas at room temperature, irreversible oxidation occurred. In the presence of fluoride ion, autooxidation of iron(II,II) species at room temperature affords a novel tetranuclear mixed valent Fe_4(II,III,II,III) complex $[Fe_4(Me_4\text{-tpdp})_2(\mu\text{-}F)_2(OH)_2(H_2O)_2](BF_4)_4$. In this communication, we report the synthesis and the crystal structure of the complex.

The complex was prepared as follows: HMe_4-tpdp (0.5 mmol), triethylamine (0.5 mmol), and tetrabutylammonium fluoride (1 mmol) was dissolved in 10 cm^3 of ethanol and the resulting solution was added to a solution of $Fe(BF_4)_2 \cdot 6H_2O$ (1 mmol) in 5 cm^3 of ethanol under N_2. O_2 (8 cm^3, 0.33 mmol) was introduced into the above solution at room temperature to give a dark green solution. The resulting solution was allowed to stand for several days to give dark green crystals.[5] When the above reaction mixture was prepared under O_2, only brown powder was obtained, which could not be characterized. Although we tried to isolate $[Fe_4(Me_4\text{-tpdp})_2(\mu\text{-}F)_2(OH)_2(H_2O)_2](BF_4)_4$ from the reaction mixture containing equimolar amounts of Fe^{2+} and Fe^{3+} ions under N_2 in various conditions, all the attempts were in vain. Thus the complex was isolated only from the O_2 oxidation of the above reaction mixture containing iron(II) ion.

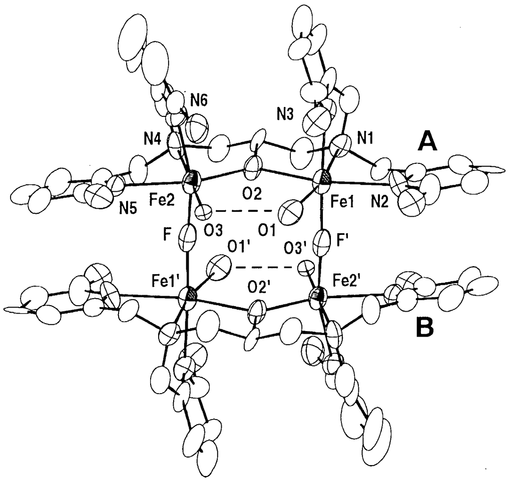

Figure 1. Molecular structure of $[Fe_4(Me_4\text{-tpdp})_2(\mu\text{-}F)_2(OH)_2(H_2O)_2]^{4+}$ complex cation. The selected bond distances (l/Å) and angles (φ/°) are as follows; Fe1-F' 2.068(8), Fe1-O1 2.089(8), Fe1-O2 2.243(8), Fe1-N1 2.18(1), Fe1-N2 2.30(1), Fe1-N3 2.25(1), Fe2-F 1.938(8), Fe2-O2 1.918(8), Fe2-O3 1.856(7), Fe2-N4 2.16(1), Fe2-N5 2.25(1), Fe2-N6 2.20(1), Fe1···Fe2 3.871(3), Fe1···Fe2' 4.002(3), O1···O3 2.61(1), Fe1-F'-Fe2' 175.3(4), Fe1-O2-Fe2 136.8(4).

The crystal structure consists of discrete tetranuclear complex cation and BF_4^- anions.[6] The complex cation which possesses an inversion center contains two alkoxo-bridged dinuclear units which are connected by nearly linear two fluoro bridges to form a bilayered structure (a rectangular structure) as shown in Figure 1. Similar Fe_4(III,III,III,III) complexes which are assembled from two dinuclear units by two oxo bridges and/or two carboxylato bridges have been reported.[7] For those complexes, oxo bridges prefer the (III,III,III,III) oxidation state. For the present complex, Me_4-tpdp which is a relatively weaker electron donor and the fluoro bridges seem to stabilize the mixed valent state. Two pairs of pyridyl rings (A and B in Figure 1) are faced each other and the distances between them are ca. 3.7 Å, suggesting the presence of pairwise stacking interaction of pyridyl rings, which seems to contribute to assemble two dinuclear units. The coordination geometries around Fe atoms are distorted octahedral with the N_3O_2F donor set where three N donors are in a *mer*-arrangement. Two iron sites, Fe1 and Fe2, are inequivalent: the bond distances around Fe2 are significantly shorter than those around Fe1, indicating that the Fe1 site is iron(II) form and the Fe2 site is iron(III) one. Coordination of water and hydroxide ion was deduced from the elemental analysis, the charge balance of the complex cation, and the bond distances. Hydroxide ion is assumed to be coordinated to iron(III) moiety and water molecule to iron(II) moiety. Those two oxygen atoms, O1(water) and O3-(hydroxo), are separated by 2.61(1) Å, indicating the presence of hydrogen bonding interaction.

The effective magnetic moment of the complex at 300 K is 8.65 μ_B and decreases to 2.24 μ_B at 9 K (the spin only value of high-spin Fe_4(II,III,II,III) is 10.87 μ_B), indicating the presence of antiferromagnetic interaction between high-spin iron ions. Analysis of the magnetism is under investigation. Mössbauer spectrum of the complex at 78 K exhibits two sets of quadrupole doublets with an almost 1 : 1 intensity ratio, i.e., ΔE_Q = 3.13 mm s^{-1} and δ = 1.55 mm s^{-1}, and ΔE_Q = 0.81 mm s^{-1} and δ = 0.39

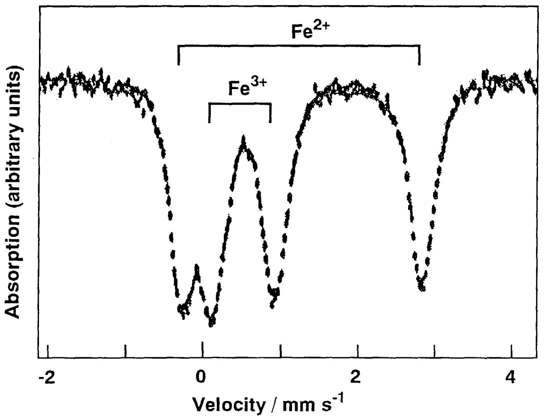

Figure 2. Mössbauer spectrum of $[Fe_4(Me_4\text{-tpdp})_2(\mu\text{-}F)_2(OH)_2(H_2O)_2](BF_4)_4$ at 78 K.

mm s^{-1}, and $A_{Fe(III)}/A_{Fe(II)}$ = 1.06 as shown in Figure 2. The former is assigned to the high spin Fe^{2+} moiety and the latter to the high spin Fe^{3+} one. A similar spectrum was observed at room temperature (ΔE_Q = 2.47 mm s^{-1} and δ = 1.21 mm s^{-1}, and ΔE_Q = 0.77 mm s^{-1} and δ = 0.37 mm s^{-1}). These spectra clearly indicate that the complex is a mixed valent one and the electrons are localized within Mössbauer time scale at these temperatures.

The reflectance spectrum displays three absorption bands at 8100 cm^{-1}, 11100 cm^{-1}, and 16600 cm^{-1} in near infrared and visible region as shown in Figure 3, which is quite similar to that of the mixed valent complex $Fe_2F_5\cdot 2H_2O$.[8] The former two bands can be assigned to the d-d transitions of $^5T_{2g} \rightarrow {}^5E_g$ (in octahedral symmetry) which splits into two bands due to a lower symmetry. The band at 16600 cm^{-1} is assignable to the intervalence band ([II,III] → [III,II]*) as found for $Fe_2F_5\cdot 2H_2O$ ($\tilde{\nu}_{IT}$ = ca. 14000 cm^{-1}). The presence of the IT band indicates that the complex belongs to the class II mixed valence system. The energy of the IT band of the present complex is higher than those of $[Fe_2(bpmp\ or\ bzimp)(RCOO)_2]^{2+}$ ($\tilde{\nu}_{IT}$ = 7000 - 8000 cm^{-1})[2a,2b] and $Fe_2F_5\cdot 2H_2O$,[8] indicating that the extent of the electron delocalization of the present complex is relatively small compared to those of the above complexes.

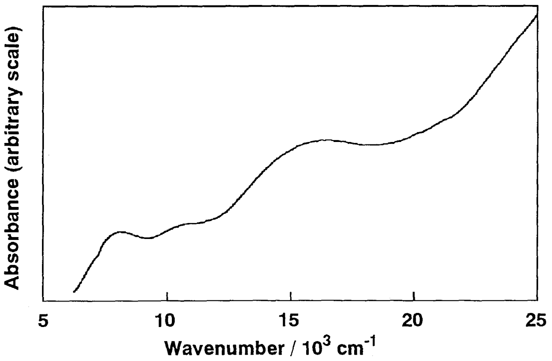

Figure 3. Reflectance spectrum of $[Fe_4(Me_4\text{-tpdp})_2(\mu\text{-}F)_2(OH)_2(H_2O)_2](BF_4)_4$.

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5 Yield: 690 mg (82%). Anal. Found: C, 43.61; H, 4.80; N, 9.64%. Calcd for $C_{62}H_{80}N_{12}B_4F_{18}Fe_4O_6$: C, 43.86; H, 4.75; N, 9.90.

6 Crystal data: $C_{62}H_{80}N_{12}B_4F_{18}Fe_4O_6$, F.W. = 1698.0, monoclinic, $P2_1/n$ with a = 15.281(7)Å, b = 13.578(7)Å, c = 17.627(7)Å, β = 102.52(3), V = 3570 (3) Å^3, Z = 2, D_c = 1.50, μ = 8.37. A Rigaku AFC-5R diffractometer with Mo-Kα radiation (λ = 0.71073 Å) was used in the ω-2θ scan mode to collect 7324 unique reflections (2θ < 60.0°), of which 1651 reflections with $I \geq 3.00\ \sigma(I)$ were used in the solution and refinement. The structure was solved by direct methods. Refinement yielded R = 0.064 and Rw = 0.051. The largest peak in a final difference map was 0.20 e/Å^3.

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