Characterization of a Fluoride-bridged Mixed-valent Tetrairon(II,II,III,III) Complex

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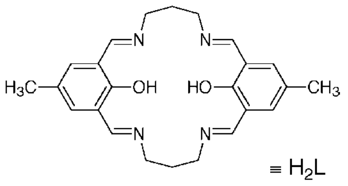
A di-μ-fluoride mixed-valent tetrairon(II,II,III,III) complex, $[\{Fe_2(L)(dnba)\}_2(\mu\text{-}F)_2](BF_4)_2$, was synthesized and characterized by X-ray structural analysis, UV–vis–NIR spectroscopy, and Mössbauer measurement.

Mixed-valent iron clusters play a most important role for the maintenance of life in biology, for example, respiration and electron-transfer processes,[1,2] and their spin-delocalized systems show interesting physicochemical properties.[3–5] Therefore, many mixed-valent iron clusters, which are mainly bridged by O- or S-donor ligands such as hydroxo, phenolate, carboxylate, and thiolate, have been reported.[6,7] However, these reports on mixed-valent tetrairon clusters except for iron–sulfur clusters are scarce although there are many reports of dinuclear clusters. Previously, we reported the preparation of a series of oxo- and phenolate-bridged tetrairon(III) complexes, $[\{Fe_2(L)(L')\}_2(\mu\text{-}O)_2](PF_6)_2$, and their mixed-valent $Fe_4{}^{II,II,III,III}$ derivatives, where L^{2-} was a phenol-based dinucleating macrocyclic ligand derived from the cyclic [2 + 2] condensation of 2,6-diformyl-4-methylphenol and 1,3-diaminopropane (Scheme 1) and $(L')^-$ was a bidentate end-cap ligand such as a carboxylate, a phosphate, or a diethyldithiophosphate.[8] These tetrairon structures were prepared by dimerization of two diiron units, $[Fe_2(L)(L')]^{3+}$, using an oxo bridge, leading us to expect that a new tetrairon structure with other bridging ligand instead of oxo would be prepared. This paper describes preparation and characterization of intramolecular electron-transfer properties of a mixed-valent di-μ-fluoride $Fe_4{}^{II,II,III,III}$ complex, $[\{Fe_2(L)(dnb)\}_2(\mu\text{-}F)_2](BF_4)_2\cdot 2H_2O$ ($\mathbf{1}\cdot 2H_2O$), where dnb^- as end-cap ligand is 3,5-dinitrobenzoate.

$\mathbf{1}\cdot 2H_2O$ was obtained by the reaction of $Fe(BF_4)_2\cdot 6H_2O$, Na_2L, and sodium 3,5-dinitrobenzoate (Na(dnb)) in a 2:1:1 molar ratio in methanol solution under nitrogen atmosphere (yield: 63%), where the incorporation of two fluoride anions into the cationic portion of **1** was confirmed by ESI/TOF-MS measurement (obsd $m/z = 744.072$, calcd $m/z = 744.073$) in MeCN.[9] Furthermore, ESI/TOF-MS data also shows that the tetranuclear structure is maintained in MeCN solution.[10] The bridging fluoride ion must arise from the decomposition of $BF_4{}^-$ ion.[11] The effective magnetic moment of $\mathbf{1}\cdot 2H_2O$ is 10.26 BM per molecule at 300 K, indicating that the present complex has mixed-valent $Fe_4{}^{II,II,III,III}$ ($\mu_{S.O.} = 10.86$).[10] Single crystals suitable for X-ray crystallography ($[\{Fe_2(L)(dnb)\}_2(\mu\text{-}F)_2](BF_4)_2$ (**1**)) were obtained upon recrystallization from dry-DMF/diethyl ether.[9] The structure of the cationic portion of **1** determined at 183 K is shown in Figure 1. The Fe atoms in the dinuclear $\{Fe_2(L)(dnb)\}^{2+}$ unit are bridged by two phenolic oxygen atoms of L^{2-} and the carboxylate group of dnb^-, and the two dinuclear units are connected by two fluoride ions to afford a tetranuclear di-μ-fluoride-bis[di-μ-phenolatodiiron(II,III)] core. There is an inversion center at the center of the two bridging fluoride anions, and two Fe atoms in the dinuclear unit (Fe(1) and Fe(2)) are crystallographically not equivalent but have a similar pseudo octahedral geometry with the N_2O_2 donor atoms of L^{2-} on the equatorial plane and a carboxylate oxygen and a fluoride ion at the axial sites. The geometric features of the dinuclear unit somewhat resemble those of the related a spin-delocalized mixed-valent



Scheme 1. Chemical structure of H_2L.

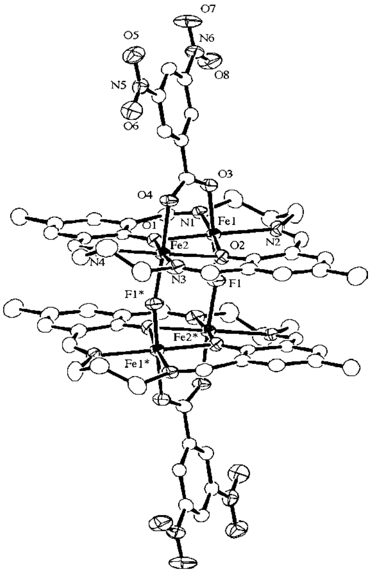


Figure 1. An ORTEP structure of cation part of **1** at 183 K drawn with the 40% thermal ellipsoids. Selected bond lengths [Å] and angles [°]: Fe(1)···Fe(2) 2.835(1); Fe(1)···Fe(2*) 3.892(1); Fe(1)–N(1) 2.115(3); Fe(1)–N(2) 2.132(3); Fe(1)–O(1) 2.004(3); Fe(1)–O(2) 2.023(2); Fe(1)–O(3) 2.065(3); Fe(1)–F(1) 1.976(2); Fe(2)–N(3) 2.127(3); Fe(2)–N(4) 2.134(3); Fe(2)–O(1) 1.993(2); Fe(2)–O(2) 2.012(3); Fe(2)–O(4) 2.072(3); Fe(2)–F(1*) 1.966(2); Fe(1)–O(1)–Fe(2) 90.4(1); Fe(1)–O(2)–Fe(2) 89.3(1); Fe(1)–F(1)–Fe(2*) 161.8(1).

diiron(II,III) complex, $[Fe_2(L)(AcO)_2](ClO_4)$ (av Fe–donor (in-plane) 2.087 Å, Fe–Ophenolate–Fe: 84.83°, Fe···Fe′: 2.741 Å).[4] In addition, the Fe–F distance of **1** (av 1.971 Å) is intermediate between the Fe^{III}–F (1.938 Å) and Fe^{II}–F (2.068 Å) bond distances for the valence-trapped $Fe_4{}^{II,II,III,III}$ complex, $[Fe_4(Me_4\text{-tpdp})_2(\mu\text{-F})_2(OH)_2(H_2O)_2](BF_4)_4$ ($Me_4\text{-tpdp}^- =$ *N*,*N*,*N*′,*N*′-tetrakis[2-(6-methylpyridyl)methyl]-1,3-diamino-2-propanol).[12]

The electronic absorption spectrum in acetonitrile at room temperature shows three absorption bands at 348 nm (ε: 18350 $M^{-1}\,cm^{-1}$), 480 nm (ε: 4200 $M^{-1}\,cm^{-1}$), and 1202 nm (ε: 1150 $M^{-1}\,cm^{-1}$) attributable to the π–π^* transition band associated with the azomethine group of L^{2-}, the LMCT band from the phenolate oxygen to Fe^{III} center, and the intervalence transition (IT) band, respectively.[6,7,13] The position and intensity of the IT band resemble those of related $[Fe_2(L)(AcO)_2]ClO_4$ ($\lambda = 1060$ nm, $\varepsilon = 1250\ M^{-1}\,cm^{-1}$).[4] According to Hush's theory, the classification of a mixed-valent system is defined as follows; (i) the correlation between the half-band width ($\Delta\nu_{1/2}$) of the observed IT band and calculated from the band maximum frequency ν_{max} as $\Delta\nu_{1/2} = (2310 \times \nu_{max})^{1/2}$ and (ii) the solvent dependency of the position and intensity of the IT band.[14] The half-band width of the band at 1200 nm is 4700 cm^{-1}, that agrees with the calculated value (4510 cm^{-1}) by the above equation. In addition, the position and intensity of the IT band show solvent dependence (1124 nm and 719 $cm^{-1}\,M^{-1}$ in DMF). Thus, the present complex belongs to Class II in the classification by Robin and Day.[15] The electron delocalization coefficient, α^2, can be calculated by the equation, $\alpha^2 = (4.25 \times 10^{-4}) \times \varepsilon_{max}\Delta\nu_{1/2}/\nu_{max}r^2$, where r is the inter-metal separation. From crystallographic analysis of **1**, the Fe···Fe separation within a dinuclear unit (2.835(1) Å) is shorter than that between dinuclear units (3.893(1) Å). Thus, the electron-transfer rate for the present complex is mainly dominated within dinuclear units rather than between dinuclear units because the electron-tranfer rate depends on the M···M separation.[5] The α^2 value of the present complex was evaluated to be 0.031 using $r = 2.835$ Å, $\Delta\nu_{1/2} = 4500\ cm^{-1}$, $\nu_{max} = 8800\ cm^{-1}$, and $\varepsilon_{max} = 1150\ M^{-1}\,cm^{-1}$. In addition, the rate constant (k_{et}) for electron transfer between phenolate-bridged Fe centers within a dinuclear unit was estimated to be $1.3 \times 10^{12}\ s^{-1}$.[14]

The Mössbauer spectrum at 180 K is shown in Figure 2 and consists of an asymmetric doublet with an isomer shift of $\delta = 0.79\ mm\,s^{-1}$ and a quadrupole splitting of $\Delta E_Q = 2.04\ mm\,s^{-1}$. The isomer shift and the quadrupole splitting of **1** are close to those of the spin-delocalized $Fe^{II}Fe^{III}$ complex, $[Fe_2(L)(AcO)_2]ClO_4$ ($\delta = 0.71\ mm\,s^{-1}$, $\Delta E_Q = 1.89\ mm\,s^{-1}$), indicating that the valence of **1** is formally delocalized at 180 K.[4] The spectrum at 5 K shows the presence of two doublets: (A) $\delta = 0.68\ mm\,s^{-1}$ and $\Delta E_Q = 1.89\ mm\,s^{-1}$ and (B) $\delta = 1.04\ mm\,s^{-1}$ and $\Delta E_Q = 2.23\ mm\,s^{-1}$, which are attributable to the discrete Fe^{III} and Fe^{II} sites, respectively.[10] Namely, the valence state at 5 K is localized. A relatively large ΔE_Q for Fe^{III} component compared with typical Fe^{III} ions may be resulted from the large electric field gradient.[6a]

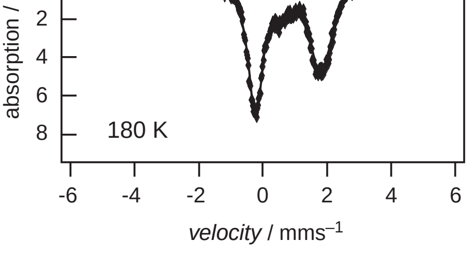


Figure 2. Mössbauer spectrum of $\mathbf{1}\cdot 2H_2O$ at 180 K.

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9 Elemental analysis data of $\mathbf{1}\cdot 2H_2O$: Calcd for $C_{62}H_{62}N_{12}O_{18}Fe_4B_2F_{10}$: C, 43.85; H, 3.68; N, 9.90%. Found: C, 43.78; H, 3.68; N, 9.90%. ESI/TOF-MS data of $\mathbf{1}\cdot 2H_2O$ in MeCN: $m/z = 744.072$, calcd $m/z = 744.073$ for $[\{Fe_2(L)(dnb)\}_2(F)_2]^{2+}$. Crystallographic data of **1** at 183 K: monoclinic, space group $P2_1/n$ (#14), $a = 12.028(1)$, $b = 24.455(2)$, $c = 12.728(1)$ Å, $\beta = 116.779(4)°$, $V = 3342.4978$ Å^3, $Z = 2$, $D_{calcd} = 1.645\ g\,cm^{-1}$, R (all data) = 0.082, Rw (all data) = 0.183, R_1 ($I > 2\sigma$) = 0.062, G.O.F = 1.14. Crystallographic data has been deposited with Cambridge Crystallographic Data Centre as supplementary publication no. CCDC-656660. Copy of the data can be obtained free of charge via www.ccdc.cam.ac.uk/conts/retrieving.html.
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