Correlation between Detrapped Valence States and Molecular Packing of Mixed-Valence Dinuclear Iron(II,III) Complexes of a Septadentate Polypyridine Ligand

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(Received July 21, 1994)

Dinuclear iron(II,III) complexes with dicarboxylic acid $[Fe_2L(B)](BF_4)_2$ were prepared, where HL represents 2,6-bis[di(2-pyridylmethyl)aminomethyl]-4-methyl-phenol, H_2B is dicarboxylic acid($HOOC(CH_2)_nCOOH$). Rapid electron interexchange between iron(II) and iron(III) are observed for the complexes with n=6 or n=12.

Mixed-valence iron(II,III) complexes have been intensively studied in recent years since it is known that dinuclear iron clusters in the active sites of metalloprotein play an important role in biological systems[1] and that there is a hope[2] that dinuclear polymers will be able to donate new electronic materials. Specific attention has been attracted to mixed-valence states in the solid state, especially detrapped valence states in order to clarify the mechanism of the intramolecular electron transfer between the metal atoms through the bridging ligands.

The complexes with L ligand were first prepared by Suzuki et al.[3] and the chemical structure of $[Fe_2L(ena)_2](BF_4)_2$ (Hena: heptanoic acid) for which detrapped valence states are observed above 260 K has been determined.[4] The mixed-valence dinuclear iron complexes were prepared using various dicarboxylic acids $HOOC(CH_2)_nCOOH$; 1,4-butanedicarboxylic acid(n=4, but), 1-6-hexanedicarboxylic acid(n=6, hex), 1,8-octanedicarboxylic acid(n=8, oct), 1,10-decanedicarboxylic acid(n=10, dec), 1,11-undecanedicarboxylic acid(n=11, und), or 1,12-dodecanedicarboxylic acid(n=12, dod) according to the method reported elsewhere.[3,4] The complexes are polymeric and insoluble in normal organic solvent, elemental analysis for the complexes being shown in reference 5. Both of the carboxylic groups in a molecule are observed to be coordinated to iron atoms in the IR spectra and an estimated model structure(with a layer structure) is drawn in Fig. 1 on the basis of the chemical structure of $[Fe_2L(ena)_2](BF_4)_2$.

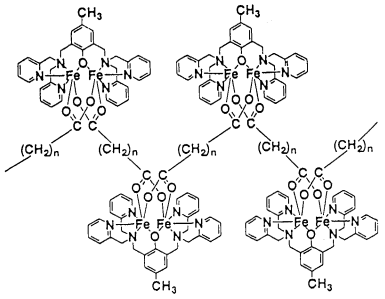

Fig. 1. An estimated structure for the complexes.

The magnetic susceptibility data obtained in the temperature range of 78-300 K for the complexes were fitted by the equation derived from the general isotropic exchange Hamiltonian in a dinuclear system,

$H=-2JS_1 \cdot S_2 \quad (S_1=2,\ S_2=5/2)$

$$H = \frac{N\beta^2 g^2}{4kT} \cdot \frac{x^{24}+10x^{21}+35x^{16}+84x^{9}+165}{x^{24}+2x^{21}+3x^{16}+4x^{9}+5} + N\alpha \quad (x=\exp(-J/kT))$$

The results of the magnetic data obtained from the plots of the magnetic susceptibilities vs. temperature are collected in Table 1.

The values of the magnetic moment for the complexes are similar to those reported for the analogous complexes with monocarboxylic acids[1-3] and support the isotropic magnetic-exchange interaction between high-spin Fe(II) and Fe(III) ions.

The Mössbauer spectra for the complexes were measured at 296 and 78 K, and curve fitting lines are also shown in Fig. 2. A

Table 1. Magnetic data for the complexes

Complexes	ab[a]	J / cm^{-1}	g	μ_B[b]
$[Fe_2(L)(but)](BF_4)_2$	1	-7.9	2.0	6.92
$[Fe_2(L)(hex)](BF_4)_2$	2	-1.4	2.1	8.09
$[Fe_2(L)(oct)](BF_4)_2$	3	-5.1	2.0	7.48
$[Fe_2(L)(dec)](BF_4)_2$	4	-4.2	2.0	7.38
$[Fe_2(L)(und)](BF_4)_2$	5	-2.3	2.1	8.08
$[Fe_2(L)(dod)](BF_4)_2$	6	-1.9	2.0	7.75

a) abbreviation of the complexes.
b) measured at 300 K.

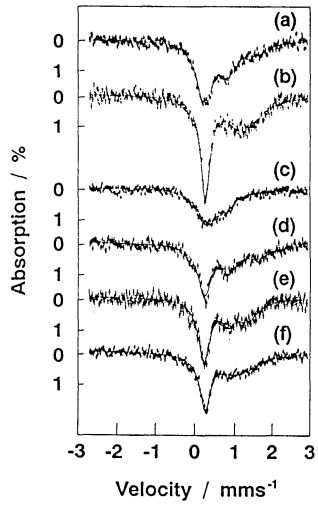

Fig. 2. The Mössbauer spectra for the complexes at 296 K.
a) for 1, b) for 2, c) for 3, d) for 4, e) for 5, f) for 6.

Table 2. ^{57}Fe Mössbauer parameters for the complexes

Complexes	T / K	ΔE / mm s^{-1} Fe^{2+}	ΔE / mm s^{-1} Fe^{3+}	δ / mm s^{-1} Fe^{2+}	δ / mm s^{-1} Fe^{3+}
1	296	1.42±0.03	0.60±0.01	0.85±0.05	0.44±0.02
2	78	2.59±0.01	0.53±0.01	1.10±0.01	0.47±0.01
	296	0.98±0.01		0.66±0.02	
3	296	1.42±0.03	0.60±0.01	0.85±0.04	0.44±0.02
4	78	2.77±0.01	0.63±0.01	1.13±0.01	0.48±0.01
	296	1.64±0.03	0.60±0.01	0.74±0.04	0.46±0.02
5	78	2.78±0.01	0.56±0.01	1.12±0.01	0.48±0.01
	296	1.12±0.02	0.64±0.01	0.71±0.03	0.46±0.02
6	78	2.62±0.01	0.58±0.01	1.11±0.01	0.48±0.01
	296	0.85±0.02		0.60±0.03	

similar spectral asymmetry with the spectra (b) and (f) has also been observed for $[Fe_2L(ena)_2](BF_4)_2$ and the reason is described there.[4] The Mössbauer parameters observed are collected in Table 2.

The valence states of the complexes 2 and 6 are detrapped in the Mössbauer time scale($1x10^{-7}$s) at 296 K and trapped at 78 K, while the valence states of the complexes 1, 3, 4 and 5 are trapped even at 296 K in the Mössbauer time scale; the rates of electron interexchange between Fe^{2+} and Fe^{3+} for the latter complexes are slower than 10^7/s.

The X-ray powder diffraction patterns (Fig. 3) support possibilities that the complexes have layered structures and that the distances between the layers are similar to one another, because any considerable shifts of the diffraction positions are not observed(Fig. 3). Therefore, the stacking phases of molecular packing between the layers at solid state are slid on the layers according to the length of the chains of dicarboxylic acids, stacking phase for the complexes with n=6 and n=12 being supposed to be in accordance(on 1 or 1/2) with that of the adjacent layers as shown in Fig. 4. $[Fe_2L(O_2CCR)_2](BF_4)_2$ with carboxylic acid of a short chain shows trapped valence states of iron atoms and the complexes with long ethylene chains(n ≥ 4) of carboxylic acid show detrapped valence state. The

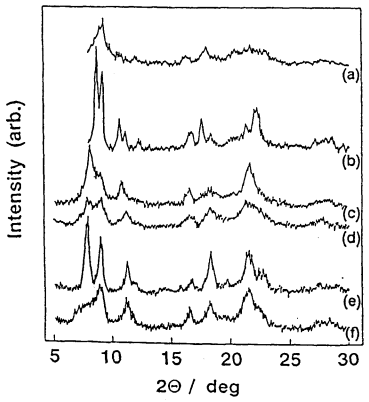

Fig. 3. The X-ray powder diffraction patterns for the complexes. a) for 1, b) for 2, c) for 3, d) for 4, e) for 5, f) for 6.

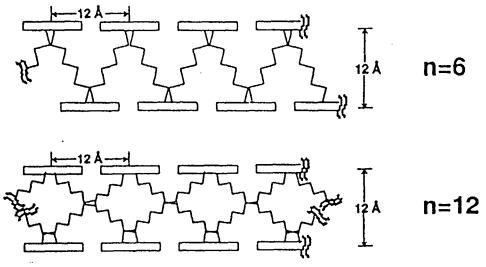

Fig. 4. Estimated models of molecular packing for the complexes with n=6 and n=12.

softness of lattice(rotation of a methylene chain) resulted in the steric flexibility of the ligands and/or new ordering structure made up of molecular packing may play an important role for electron delocalization and the rate.

This work was partly supported by a Grant-in-Aid for Scientific Research No. 06453052 from the Ministry of Education, Science, and Culture, which is greatly acknowledged.

References and Notes

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4 Y. Maeda, Y. Tanigawa, N. Matsumoto, H. Oshio, M. Suzuki, and Y. Takashima, Bull. Chem. Soc. Jpn., **67**, 125(1994).
5 Found: C,47.19;H,4.26;N,8.44;Fe,11.16%. Calcd. for $C_{39}H_{41}N_6O_5Fe_2B_2F_8$(1): C,48.84;H,4.31;N,8.76;Fe,11.65%. Found: C,49.17;H,4.61;N,8.33;Fe,11.11%. Calcd. for $C_{41}H_{45}N_6O_5Fe_2B_2F_8$(2): C,49.88;H,4.60;N,8.52;Fe,11.32%. Found: C,49.14;H,4.70;8.52;Fe,11.32%. Found: C,49.14;H,4.70;N,7.87;Fe,10.80%. Calcd. for $C_{43}H_{49}N_6O_5Fe_2B_2F_8$(3): C,50.87;H,4.87;N,8.28;Fe,11.00%. Found: C,50.52;H,5.06;N,7.96;Fe,10.57%. Calcd. for $C_{45}H_{53}N_6O_5Fe_2B_2F_8$(4): C,51.81;H,5.12;N,8.06;Fe,10.71%. Found: C,51.05;H,5.24;N,7.53;Fe,10.39%. Calcd. for $C_{46}H_{55}N_6O_5Fe_2B_2F_8$(5): C,52.25;H,5.24;N,7.95;Fe,10.57%. Found: C,51.82;H,5.45;N,7.71;Fe,10.25%. Calcd. for $C_{47}H_{57}N_6O_5Fe_2B_2F_8$(6): C,52.69;H,5.36;N,7.85;Fe,10.43%.