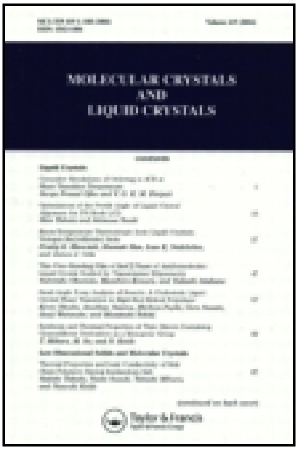

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CORRELATION BETWEEN THE RATE OF INTRAMOLECULAR ELECTRON TRANSFER OF DINUCLEAR IRON COMPLEXES(II,III) AND THE PHASES OF THE MOLECULAR STRUCTURES

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Abstract Dinuclear iron(II, III) complexes with a hexadentate ligand $[Fe_2bpmp(L)_2](BF_4)_2$ were prepared, where Hbpmp represents 2,6-bis[bis(2-pyridylmethyl)aminomethyl]-4-methylphenol and L is $CH_3(CH_2)_nCOO^-$ or $Ph(CH_2)_nCOO^-$. The Mössbauer spectra of the mixed-valence complexes of $L=CH_3(CH_2)_nCOO^-$ with n=0, 1 and 2 consist of two quadrupole doublets due to high-spin iron(II) and high-spin iron(III). However, the complexes with n=3, 4, 5, 6 and 7 show one quadrupole doublet at room temperature, which suggests a delocalized valence state. The complexes of $L=Ph(CH_2)_nCOO^-$ with n=0, 1, 2 and 3 show localized valence states and those with n= 4 and 5 show a delocalized one.

INTRODUCTION

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 metaloprotein play an important role in biological systems such as hemerythrin(Hr),[1,2] and there is a hope that dinuclear polymers will be able to donate new electronic materials. The studies of synthetic dinuclear Fe(II)Fe(II) and Fe(II)Fe(III) units[3] that mimic physicochemical properties found for the above proteins are rare in comparison with their Fe(III)Fe(III) analogues.4) There are some studies about $[Fe_2(bpmp)(O_2CH_3)_2]$5,6) and some of the complexes with long carboxylic acid show an averaged valence states between high-spin Fe(II) and Fe(III).[7,8]

Materials.

Hbpmp was synthesized by the condensation of 2,6-bis(chloromethyl)-4-methylphenol with bis(2-pyridylmethyl)amineaccording to the literature. The iron complexes were prepared in a manner similar to that reported. [5] The crystals of the complexes were recrystallized from a mixture of acetonitrile and ethylalcohol. The The abbreviation of the ligands used are as follows. n= 0; acetic acid(ace), n=1; propionic acid(pro), n=2; butyric acid(but), n=3; n-valeric acid(val), n=4; n-caproic acid(capro), n=5; enantic acid(ena), n=6; n-caprylic acid(capry), n=7; pelargonic acid(pel) for $CH_3(CH_2)_nCOO^-$, and n=0; benzoic acid(bez), n=1; phenylacetic acid(phe), n=2; 3-phenylpropionic acid, n=3; 4-phenyl-n-butyric acid, n=4; 5-phenyl-n-valeric acid, and n=5; 6-phenyl-n-hexanoic acid for $Ph(CH_2)_nCOO^-$.

Measurements.

Mössbauer spectra were measured with a constant acceralation spectrometer. A cobalt-57 source of 10 mCi diffused into palladium foil was used for absorption measurement. The spectra were fitted to a Lorentzian line shape using a least-square method at the Computer Center, Kyushu University, and the velocity scales were normalized to iron foil enriched with ^{57}Fe at room temperature. The absorption and reflection spectra were recorded with a SHIMADZU UV-3100PC self-recording spectrophotometer in the region from 300 to 2600 nm. The magnetic susceptibility measurements were made using an electrobalance and the temperature was controlled over 80-300 K using a digital temperature controller.

RESULTS AND DISCUSSION

The Intensity data of X-ray diffraction for $[Fe_2bpmp(Ph(CH_2)_3COO)_2](BF_4)_2$ were obtained from a single crystal of 0.3x0.3x0.1mm which was placed on a Rigaku AFC four-circled diffractometer equipped with a Mo-K$_a$ (0.71069 Å) source and a graphite monochromater. Preliminary diffractometer routines indicate a monoclinic cell with space group $P2_1/c$, and lattice constants are a=10.7010 Å, b=19.7250 Å, c=25.7370 Å, β=93.428° , z=4, R=0.085, R_w=0.074. The structure of $[Fe_2bpmp(Ph(CH_2)_3COO)_2]^-$ with localized valence states and the packing on the bc plane of the complex , are shown in Fig. 1. The bond lengths of Fe(II)-N are longer then those of Fe(III)-N. The bond length of Fe-Fe 3.4 Å is similar to that of $[Fe_2bpmp(ena)_2](BF_4)_2$,[7] and

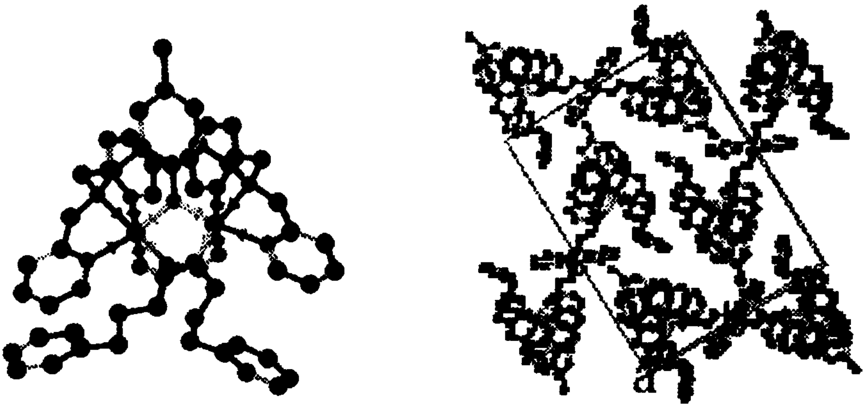

FIGURE 1 Structure of $[Fe_2bpmp(Ph(CH_2)_3COO)_2]^-$ and packing on bc plane for the complex.

$[Fe_2bpmp(O_2CC_2H_5)_2](BPh_4)_2$ and analogous $[Mn_2(L\text{-}Im)(O_2CCH_3)_2](ClO_4)_2$ with imidazolyl instead of pyridine ligand arm.[6] The X-ray powder diffraction patterns for $[Fe_2(bpmp)(CH_3(CH_2)_nCOO)_2](BF_4)_2$ being measured, the data support that the structures of the complexes of n=3-7 are similar to each others, but the complexes of n=0-2 show different structure from the complexes of n=3-7, and the b-axis lengths obtained are estimated under the assumption that the structure of the complexes of n=3-7 are similar to that of $[Fe_2(bpmp)(ena)_2](BF_4)_2$, and the b-lengths become long linearly with the increasing of the alkylchains of methylene groups, as shown in Fig. 2.

It is found that there is a relationship between the rate of intramolecular electron transfer and the phase of molecular packing.[8] Sano et. al have reported recently that the analogous trinuclear iron complexes of carboxylic acid with long chains show the delocalized valence state,[9] and Nakashima et al have reported the mixed-valence state of binuclear ferrocene derivatives with long alkyl substituents.

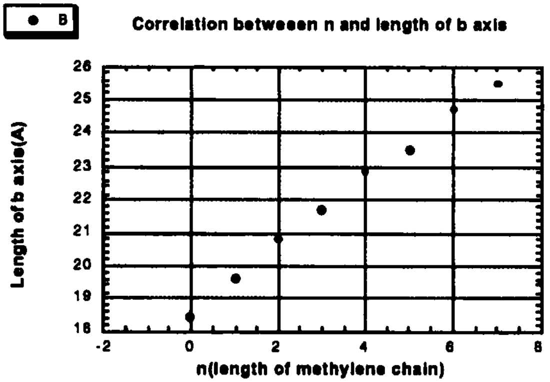

FIGURE 2 Plots of length of b axis for $[Fe_2(bpmp)(CH_3(CH_2)_nCOO)_2](BF_4)_2$

Mössbauer spectra for the complexes were measured at 298 and 80 K, and the spectrum of $[Fe_2(bpmp)(PhCH_2COO)_2](BF_4)_2$ is shown in Fig. 3 and that of $[Fe_2(bpmp)(Ph(CH_2)_5COO)_2](BF_4)_2$ in Fig. 4. The spectrum of the former complex at 298 K comprises two quadrupole doublets Q.S. ; iron(II) of the isomer shift δ of 0.99 mm/s with Q.S. of 1.49 mm/s and iron(III) of δ of 0.42 mm/s with Q.S. of 0.54 mm/s, are consistent with a high-spin with a high-spin Fe(II)-Fe(III) formulation. The area ratio of Mössbauer absorption, iron(III)/iron(II) is larger than 1 in the temperature range measured, which may show the difference of recoilless fractions between iron(II) and iron(III). The spectrum of $[Fe_2(bpmp)(Ph(CH_2)_5COO)_2](BF_4)_2$ collapses into a pair of doublet; with Q.S.=0.98 mm/s and δ =0.67 mm/s at 298 K, and the isomer shift is in average value of about 0.5 mm/s for high-spin iron(III) and about 0.9-1.0 mm/s for high-spin iron(II),

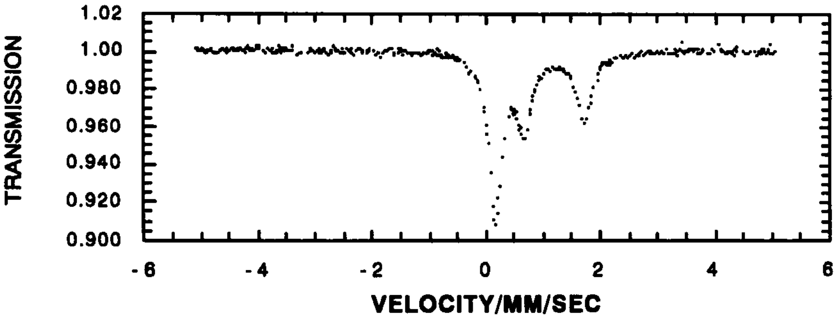

FIGURE 3 Mössbauer spectrum of $[Fe_2(bpmp)(PhCH_2COO)_2](BF_4)_2$.

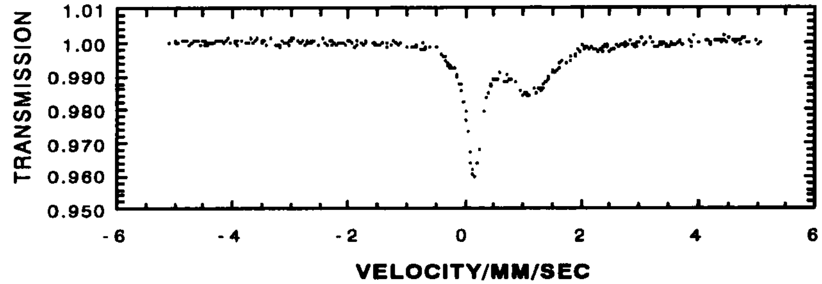

FIGURE 4 Mössbauer spectrum of $[Fe_2(bpmp)(Ph(CH_2)_5COO)_2](BF_4)_2$.

which is resulted in the delocalized valence state. The Mössbauer spectra of these complexes are composed of two pairs of a doublet at 80 K. The magnetic moments of these complexes are 7.57-8.10 BM for two irons and observed antiferromagnetc interactions are weak(J=-0.4 - -9.7cm^{-1}).

TABLE I Length of b-axis and absorption data for the complexes.

Complexes	b(Å)	PP*(nm)	Γ(nm)**	α^2***
$[Fe_2(bpmp)(ace)_2](BF_4)_2$	(18.4)	1, 284	585	3.5
$[Fe_2(bpmp)(pro)_2](BF_4)_2$	(19.6)	1, 308	629	3.7
$[Fe_2(bpmp)(but)_2](BF_4)_2$	20.8	1, 306	635	4.1
$[Fe_2(bpmp)(val)_2](BF_4)_2$	21.7	1, 313	613	4.0
$[Fe_2(bpmp)(capro)_2](BF_4)_2$	22.9	1, 309	634	4.2
$[Fe_2(bpmp)(ena)_2](BF_4)_2$	23.5	1, 318	656	4.5
$[Fe_2(bpmp)(capry)_2](BF_4)_2$	24.7	1, 311	637	4.5
$[Fe_2(bpmp)(pel)_2](BF_4)_2$	25.5	1, 312	622	3.9

*PP is a peak position , **Γ is the width of a absorption line.
*** mixing parameters(10^{-3} mol^{-1})

The reflection spectra for $[Fe_2(bpmp)(CH_3(CH_2)_nCOO)_2](BF_4)_2$ were measured, absorptions due to intervalence electron transition bands(IT) in addition to a charge transfer band from the ligand to the iron being observed. The data collected are shown in Table I. According to Hush,[11] delocalization coefficient, α^2 a measure of mixing of oxidation states, can be calculated by using a following equation.

$$\alpha^2 = \{(4.24\mathrm{x}10^{-4}) \cdot \varepsilon_{\max} \cdot \Delta\nu_{1/2}\} \;/\; \{\nu_{\max} \cdot d^2\}$$

The values calculated under assuming d=3.4Å for the complexes are listed in TABLE I. It is not clear whether the rate of the intervalence electron transfer is correlated with the values of α^2, because Mössbauer spectra are not sensitive to slower rate than 10^{-6} s. However, the values suggest that intramolecular electron exchange happens in these complexes examined here.

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