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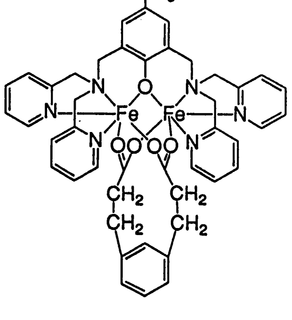
Detrapped Valence State of Iron(II)-Iron(III) Complexes with Carboxylic Acid

Yonezo MAEDA,* Yuichi TANIGAWA, Shinya HAYAMI, and Yoshimasa TAKASHIMA
Department of Chemistry, Faculty of Science, Kyushu University,
Hakozaki, Higashi-ku, Fukuoka 812

Diiron(II)-(III) complexes $[Fe_2L(pa)_2](ClO_4)_2$ and $[Fe_2L(mpdp)](ClO_4)_2$ were prepared, where HL represents 2,6-bis[bis(2-pyridylmethyl)aminomethyl]-4-methylphenol, Hpa is pelargonic acid and H_2mpdp is m-phenylenedipropionic acid. The valences of the irons are localized at low temperature, and delocalized in the Mössbauer time scale($1x10^{-7}$s) above 265 K for both of the complexes.

It is well known that mixed-valence iron clusters in the active sites of metal-oxo proteins play important role in biological system.[1)] Model compounds containing such sites are prepared and characterized by various methods. One of such Fe(II)-Fe(III) complexes is μ-phenoxo carboxylato diiron complexes first reported by Suzuki et al.[2)]

HL was synthesized by the condensation of 2,6-bis(chloromethyl)-4-methylphenol with bis(2-pyridylmethyl)amine according to the literature.[2)] The iron complexes were prepared in a manner similar to that reported. Elemental analysis for $[Fe_2L(pa)_2](ClO_4)_2$, Found C;52.14, H;5.73, N;7.46, Fe;9.70, calc. for $Cl_2C_{51}Fe_2H_{67}N_6O_{13}$, C;53.04, H;5.85, N;7.28, Fe;9.67, and analysis for $[Fe_2L(mpdp)](ClO_4)_2$, Found C;49.75, H;4.19, N;8.21, Fe;10.34, calc. for $Cl_2C_{45}Fe_2H_{45}N_6O_{13}$, C;50.96, H;4.28, N;7.93, Fe;10.53.



A model for 2

The apparatus of a Mössbauer spectrometer is described elsewhere.[3)] All Mössbauer spectra were fitted to Lorentzian line shapes using a least-square method. Isomer shift δ is reported with respect to the centroid of the spectrum of iron foil enriched with ^{57}Fe at 290 K.

Crystal structure of $[FeL(O_2CC_2H_5)_2](BPh_4)_2$ and analogous $[FeL'(O_2CCH_3)_2](ClO_4)_2$ with imidazolyl instead of pyridine ligand arm have

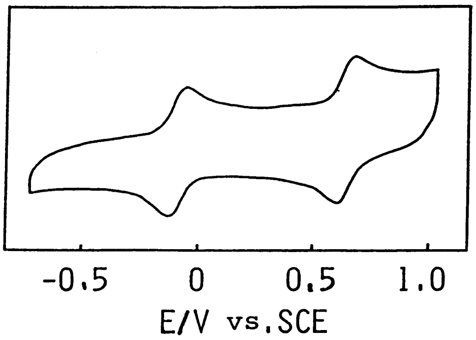


Fig. 1. Cyclic voltammogram of 1.

been communicated.[4)] Carboxylic acid is bridged between two iron atoms in the complex; μ-carboxylate. Electrolytic conductivities at 25 °C on approximately 10^{-3} M acetonitrile are 300 μS/cm for 1 and 320 μS/cm for 2. Such data confirm that the complexes are 1:1 electrolytes. Cyclic voltammetry of 1 in acetonitrile shows reversible waves at -0.09 and 0.64 mV vs. SCE as shown in Fig. 1, which correspond to the Fe(III)Fe(III)/Fe(III)Fe(II) and Fe(III)Fe(II)/Fe(II)Fe(II) couples, respectively, and those of 2 are the same values. These waves are compared with those for $[Fe_2L(O_2CR)_2]X_2$ complex.;[2)] -0.10 and 0.69 mV vs. SCE. The value of μ_{eff} per molecule for 1 varies gradually from 7.64 μ_B at 300 K to 7.50 μ_B at 80 K, and that for 2 from 7.96 to 7.70 μ_B. Both of the IR

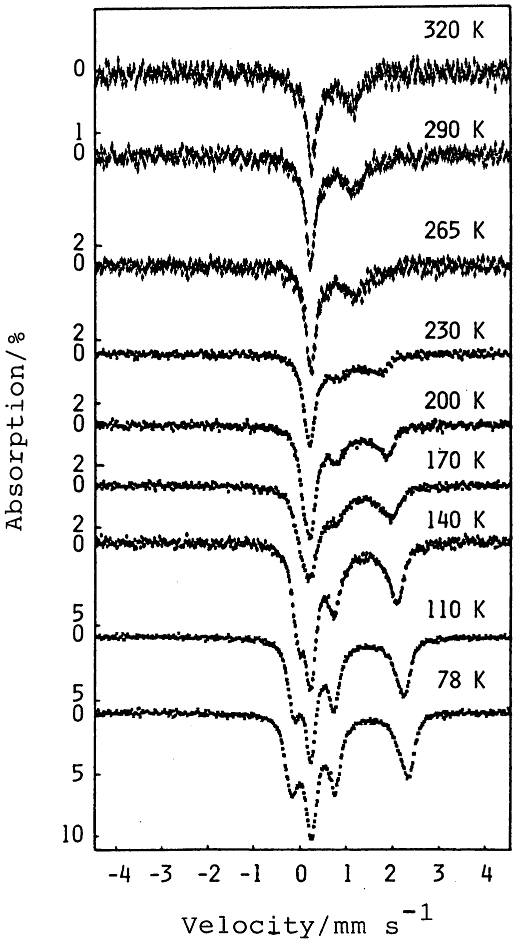


Fig. 2. Mössbauer spectra of 1 at various temperatures.

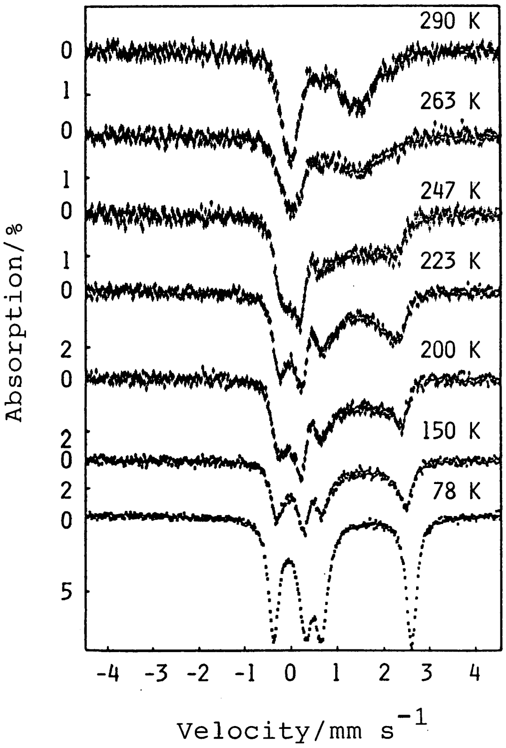


Fig. 3. Mössbauer spectra of 2 at various temperatures.

spectra of **1** and **2** show intense bands at 1410, 1425, 1477, and 1605 cm^{-1} due to coordinating acetate. Above results support that acetate ions coordinate to iron ions as a bridging bidentate ligand.

Mössbauer spectra for **1** and **2** were measured at various temperatures, and the spectra for **1** and **2** are shown in Figs. 2 and 3, respectively. The spectrum of **1** at 78 K comprises two quadrupole doublets; iron(II) of isomer shifts of 1.08 mm/s with quadrupole splitting of 2.67 mm/s and iron(III) of isomer shift of 0.47 mm/s with that of 0.54 mm/s, are consistent with a high-spin Fe(II)-Fe(III) formulation. Area ratio of Mössbauer absorption, iron(III)/iron(II) is larger than 1 in the temperature range measured, and the result may show the difference of recoilless fractions between iron(II) and iron(III). As the temperature is raised, the spectra collapse into a pair of doublet; a pair of doublet with Q.S.=0.99 mm/s(at 265 K) for **1** and 1.55 mm/s(at 265 K) for **2**, which are resulted in detrapped valence states. Isomer shift values, 0.68 mm/s for **1** and 0.73 mm/s for **2** are in average one of about 0.5 mm/s for high-spin iron(III) and about 0.9-1.0 mm/s for high-spin iron(II). Mössbauer spectral data obtained are summarized in Table 1. The natural logarithm of ratio of total absorption area at various temperatures to the total absorption area at 78 K, lnA(T)/A(78) is plotted vs. temperature in Fig. 4. The deviation from the linear is found in both the complexes because of the increasing motions of the alkylchains or methylene group in a solid. It has been communicated that in the case of trinuclear mixed valence iron acetate complexes the onset of motion of a

Table 1. Mössbauer parameters for $[FeL(pa)_2](ClO_4)_2$ and $[FeL(mpdp)](ClO_4)_2$

Complex **1**						Complex **2**							
Temp	I.S.		Q.S.		AR[a)]	Temp	I.S.			Q.S.			AR[a)]
K	mm s^{-1}		mm s^{-1}			K	mm s^{-1}			mm s^{-1}			
	Fe^{2+}	Fe^{3+}	Fe^{2+}	Fe^{3+}			Fe^{2+}		Fe^{3+}	Fe^{2+}		Fe^{3+}	
78	1.08	0.47	2.67	0.54	1.26	78	1.16		0.46	3.24		0.38	1.08
110	1.08	0.46	2.50	0.54	1.26								
140	1.03	0.46	2.25	0.55	1.35	150	1.10		0.44	2.98		0.47	1.17
170	0.98	0.46	2.04	0.57	1.82								
200	0.96	0.48	1.88	0.60	1.87	200	1.05		0.52	2.71		0.73	1.48
230	0.88	0.51	1.68	0.67	2.83	225	1.00		0.47	2.62		0.65	1.08
265	0.68[b)]		0.99[c)]			250	1.02	0.67[b)]	0.42	2.66	1.58[c)]	0.65	
290	0.67		0.97			265		0.73			1.55		
320	0.67		0.92			290		0.72			1.56		

a) Absorption area ratio of Fe(III)/Fe(II). b) Isomer shift for detrapped valence. c) Quadrupole splitting for detrapped valence.

ligand or solvent molecule affects the rate of electron transfer and that electron delocalization for biferrocenium triiodide accompanies motion of counter ions.$^{5)}$ Sano et al have reported very recently that analogous trinuclear iron complex of carboxylic acid with long chain shows delocalized valence state and non-linearity of lnA(T)/A(78).$^{6)}$ The synthetic utility of the bridging dicarboxylate ligand H_2mpdp is reported by Beer et al who point out the conformational flexibility of mpdp^{2-} phenyl ring and its methylene linkers.$^{7)}$ Softness of lattice(rotation of methylene chain) brought by the steric flexibility of ligand may play important role for electron delocalization.

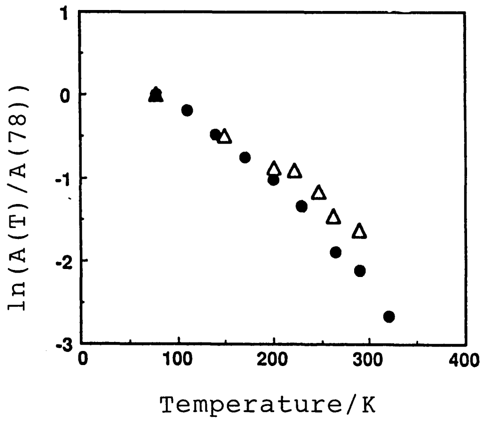


Fig. 4. Temperature dependence of ln(A(T)/A(78)) for **1**(●) and **2**(△).

We are currently investigating the properties of the Fe(II)-Fe(III) complexes and crystal structure to understand the effect of ligand environment on the rate of electron transfer.

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