Syntheses and Characterization of Dinuclear Iron(II, II) and Iron(II, III) Complexes with a Dinucleating Ligand, 2,6-Bis[bis(2-pyridylmethyl)-aminomethyl]-4-methylphenolate (1−)

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(Received March 30, 1987)

Dinuclear iron(II, II) complexes, $[Fe_2(L\text{-}py)(RCOO)_2]BF_4\cdot nH_2O$ (RCOO : CH_3COO (**1a**) and C_6H_5COO (**2a**)), and two types of dinuclear mixed valence iron(II, III) complexes $[Fe_2(L\text{-}py)(RCOO)_2](BF_4)_2\cdot nH_2O$ (RCOO : CH_3COO (**1b**) and C_6H_5COO (**2b**)) and $[Fe_2(L\text{-}py)(CH_3COO)(OH)](BF_4)_2\cdot 2H_2O$ (**3**) were prepared, where L-py represents 2,6-bis[bis(2-pyridylmethyl)aminomethyl]-4-methyl-phenolate(1−). Only one of the two iron(II) ions in the iron(II, II) complexes is easily oxidized with molecular oxygen in methanol to form the mixed valence complexes, $[Fe_2(L\text{-}py)(RCOO)_2](BF_4)_2\cdot nH_2O$, which were characterized by chemical analyses and Mössbauer measurements. Magnetic susceptibility measurements over the temperature range 80—300 K revealed that high-spin iron(II) and iron(III) ions are antiferromagnetically coupled with the spin-exchange coupling constants $J=-3$—$-8\,\mathrm{cm^{-1}}$. The complexes exhibited an ESR signal of $g_{av}\approx 1.7$ near liquid helium temperature. Such an ESR signal arises from an antiferromagnetically spin-coupled high-spin iron(II, III) dimer. An inter-valence charge-transfer transition was observed in the region 7000—8500 $\mathrm{cm^{-1}}$. The electron delocalization parameter α is estimated to be ca. 0.08, which corresponds to the class II mixed valence type in the classification of Robin and Day. Cyclic voltammogram of the complex **2b** in acetonitrile showed two reversible couples at +0.05 and +0.73 V (vs. SCE), which were assigned to the redox reactions of Fe(II, III)/Fe(II, II) and Fe(III, III)/Fe(II, III), respectively. The comproportionation constants of **1b** and **2b** at 20 °C are 1.6×10^{12} and 5.0×10^{11}, respectively, implying that the present mixed valence complexes are significantly stabilized.

Dinuclear iron(II, III) mixed valence centers have been found to exist in iron proteins such as *semi-met*hemerythrin,[1–3] pink uteroferrin,[4–8] and the reduced form of bovine spleen acid phosphatase.[4,5,9] They exhibited an ESR signal with $g_{av}<2.0$ observable only near liquid helium temperature. Such an ESR signal has been interpreted in terms of antiferromagnetic superexchange interaction between high-spin iron(II) and high-spin iron(III) ions.[10] Spin-exchange coupling constants for pink uteroferrin[6,7] and the reduced form of bovine spleen acid phosphatase[9] are ≈ -10 and $\approx -50\,\mathrm{cm^{-1}}$, respectively. From these data, it was suggested that the former protein had μ-hydroxo bridge[6] and the latter μ-oxo bridge[9]. Recent EXAFS study of the latter protein also suggested the presence of additional bridges such as carboxylato group.[11] For these proteins, phenolato and imidazole groups of tyrosine and histidine residues were proposed as additional coordinating groups;[6,12] possible ligating groups for irons in *semi-met*hemerythrin are imidazole group of histidine residue, and carboxylato groups of aspartic and glutamic acid residues. However, details of structure and function of metal center of these proteins still remain ambiguous.

Synthetic dinuclear mixed valence iron(II, III) complexes with biologically relevant ligands such as imidazole group, carboxylato, and phenolato groups are useful for further elucidation of structure and function of the iron(II, III) centers in the above proteins. In the previous communication, we reported the synthesis and characterization of a mixed valence complex $[Fe_2(L\text{-}Bzim)(C_6H_5COO)_2](BF_4)_2\cdot 2H_2O$ (L-Bzim=2,6-bis[bis(2-benzimidazolylmethyl)aminomethyl]-4-methylphenolate (1-)) and proposed a dinuclear structure of iron(II) and iron(III) bridged triply by a phenolate and a couple of carboxylato groups.[13] Recently we found a similar triply bridging unit in an analogous dinuclear mixed valence manganese(II, III) complex $[Mn_2(L\text{-}py)(C_6H_5COO)_2](ClO_4)_2\cdot H_2O$,[14] where L-py is 2,6-bis[bis(2-pyridylmethyl)aminomethyl]-4-methyl-phenolate(1−) (Fig. 1). Reported herein are the syntheses and various physicochemical properties of the two types of dinuclear mixed valence complexes with the dinucleating ligand, L-py, and carboxylate ion(s), $[Fe_2(L\text{-}py)(RCOO)_2](BF_4)_2\cdot nH_2O$ (RCOO=CH_3COO or C_6H_5COO) and $[Fe_2(L\text{-}py)(CH_3COO)(OH)](BF_4)_2\cdot 2H_2O$. The L-Bzim and L-py complexes are the first examples of synthetic dinuclear mixed valence high-spin iron(II, III) complexes.

Dinuclear metal complexes with metal ions in sterically and electronically controlled environment are expected to reversibly bind molecular oxygen.

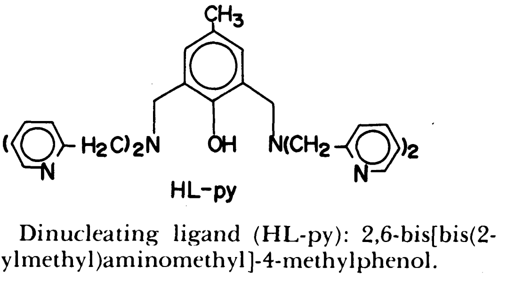

Fig. 1. Dinucleating ligand (HL-py): 2,6-bis[bis(2-pyridylmethyl)aminomethyl]-4-methylphenol.

Recently, we have demonstrated that dinuclear cobalt(II, II) complexes $[Co_2(L\text{-py})(RCOO)_2]^+$ and $[Co_2(L\text{-py})(RCOO)]^{2+}$ react reversibly with molecular oxygen to form μ-peroxo complexes $[Co_2(L\text{-py})(RCOO)(O_2)]^{2+}$.[15] The irreversible oxidation of cobalt ion was much suppressed in the above dioxygen complexes. Such stabilty of the dioxygen complexes must stem from a geometry and donor properties of the ligands. In this study, we also prepared the dinuclear iron(II, II) complexes with L-py and carboxylate ions, $[Fe_2(L\text{-py})(RCOO)_2]BF_4\cdot nH_2O$, and their reaction with molecular oxygen was investigated.

Experimental

Materials. HL-py was synthesized as previously described.[15] Iron(II) tetrafluoroborate hexahydrate was prepared according to the method of literature.[16] Other chemicals used were of reagent grade.

Preparation of Iron(II, II) Complexes. $[Fe_2(L\text{-py})(RCOO)_2]BF_4\cdot nH_2O$ (RCOO: CH_3COO (1a) or C_6H_5COO (2a)): The complexes were prepared by ordinary Schlenk techniques in an inert atmosphere. A solution of $Fe(BF_4)_2\cdot 6H_2O$ (1 mmol) in 20 cm^3 of ethanol was added to a solution of HL-py (0.5 mmol), RCOOH (1 mmol), and triethylamine (1 mmol) in 20 cm^3 of ethanol with stirring. The reddish yellow solution was concentrated to a half of the original volume by vacuum evaporation and allowed to stand overnight at 0 °C. Orange-yellow crystals formed were collected by filtration, washed with ethanol and ether, and dried in vacuo.

Preparation of Iron(II, III) Complexes. $[Fe_2(L\text{-py})RCOO)_2](BF_4)_2\cdot nH_2O$ (RCOO: CH_3COO (1b) or C_6H_5COO (2b)): A solution of $Fe(BF_4)_2\cdot 6H_2O$ (1 mmol) in 40 cm^3 of ethanol was added to a mixture of HL-py (0.5 mmol), RCOOH (1 mmol), and triethylamine (1 mmol) in 20 cm^3 of methanol with stirring under a nitrogen atmosphere. The reddish yellow solution was then exposed to an oxygen atmosphere at 10 °C with stirring to cause an instanteneous color change to dark green. The solution was kept at 0 °C for several hours. Dark green crystals thus obtained were collected by filtration, washed with ethanol and ether, and dried in vacuo; they were recrystallized from methanol under a nitrogen atmosphere. The crystals are stable in the open atmosphere. Single crystals suitable for X-ray analysis have not yet been obtained.

$[Fe_2(L\text{-py})(CH_3COO)(OH)](BF_4)_2\cdot 2H_2O$ (3): A solution of $Fe(BF_4)_2\cdot 6H_2O$ (1 mmol) in 20 cm^3 of ethanol was added to a solution of HL-py (0.5 mmol), CH_3COOH (0.5 mmol), and triethylamine (1 mmol) in 20 cm^3 of ethanol under a nitrogen atmosphere. The resulting pale yellow solution was exposed to an oxygen atmosphere with stirring at 10 °C to cause an instanteneous color change to dark blue. The dark blue solution was cooled to 0 °C and allowed to stand for one hour to yield dark blue microcrystalline powders. They were collected by filtration, washed with ethanol and ether, and dried in vacuo. The product is stable in the open atmosphere.

Measurements. The electronic spectra in acetonitrile solution were measured on a Jasco UVIDEC 505 UV/VIS recording digital spectrophotometer and a Hitachi 323 recording spectrophotometer. Infrared spectra were obtained by a KBr-disk method and a Nujol mull method with a Jasco A-3 infrared spectrophotometer. Magnetic susceptibilities were measured with a Shimadzu torsion magnetometer MB-2. The apparatus was calibrated by the use of $Hg[Co(NCS)_4]$. Diamagnetic corrections were made by using Pascal's constants.[17] Molar conductivities were measured in *N,N*-dimethylformamide or acetonitrile solution (1×10^{-3} mol dm^{-3}) at 25 °C with a Yokogawa Universal Bridge Type BUZ-10A. Mössbauer spectra were measured at 77 K against a ^{57}Co(Pt) source moving in a mode of constant acceleration at room temperature. Velocity calibration was carried out by the resonance lines of metallic iron, and isomer shifts were given relative to iron metal at room temperature. Cyclic voltammograms were measured with a Yanagimoto P-900 in a cell containing a glassy carbon working electrode, auxiliary electrode, and a saturated calomel electrode. Applied voltage was measured with a Takeda Riken TR-8651 electrometer. Acetonitrile was used as the solvent and tetrabutylammonium perchlorate as the supporting electrolyte. Ferrocene was added for an internal check on redox potential and reversibility. $E_{1/2}$ of ferrocene was 0.39 V (vs. SCE) with a peak-to-peak separation of 70 mV. ESR spectra above 10 K were measured on a JEOL JES-FE2XG ESR spectrometer (X-band microwave unit, 100 kHz field modulation) equipped with an Air Product LTD-3-110 liquid helium transfer system. The microwave frequency was measured with a Takeda Riken TR5212 microwave counter, and the resonance magnetic field values of the signals were measured with an NMR field meter (ECHO Electronics Co., Ltd.). ESR spectra at 6 K were recorded on a Varian E-112 spectrometer (X-band microwave unit, 100 kHz modulation) equipped with an Oxford cryostat.

Analyses of Iron(II) and Iron(III) Ions. The contents of iron(II) and iron(III) ions in the mixed valence complexes were determined colorimetrically.[18] A weighted quantity of the complex (ca. 40 mg) was dissolved into a solution of 1,10-phenanthroline (200 mg) in 20 cm^3 *N,N*-dimethylformamide under nitrogen atmosphere. The solution was stirred for 1 min and treated with an aqueous suspension (20 cm^3) of excess H_4edta (ca. 100 mg) for preventing the reduction of the iron(III) and masking iron(III)-phenolato complexes.[19] The mixture was diluted to ca. 250 cm^3 with water and the pH of the solution was adjusted to ca. 4 with acetic acid. The volume of the resulting solution was adjusted to 500 cm^3. After filtration, the iron(II) content was determined spectrophotometrically at 510 nm as $[Fe(phen)_3]^{2+}$ ($\varepsilon=11300$ mol^{-1} dm^3 cm^{-1}). Total content of iron(II) and iron(III) ions was determined in a similar way after the iron(III) ion had been reduced to divalent state. The iron(III) content was known from the difference. The analytical data are given in Table 1 together with the magnetic moments.

Results and Discussion

Characterization of Complexes. The effective magnetic moments of **1b** and **2b** are 7.7 and 7.3 B.M./Fe$_2$, respectively, indicating that both iron(II) and iron(III) ions are in high-spin state. The infrared spectra of the complexes in the region of 600—4000 cm^{-1} are almost the same as those of the corresponding manganese(II,III) complexes $[Mn_2(L\text{-py})(RCOO)_2](ClO_4)_2\cdot nH_2O$,[14] except for the stretching vibration region of perchlorate and tetrafluoroborate ions.

Table 1. Analytical Data and Effective Magnetic Moments of Complexes

No.	Complex	Found (Calcd)/%					μ_{eff}/B.M.[a]
		C	H	N	Fe(II)	Fe(III)	
1a	$[Fe_2(L\text{-}py)(CH_3COO)_2]$-$BF_4\cdot0.5H_2O$	52.02 (51.92)	4.62 (4.71)	9.65 (9.82)			7.4
2a	$[Fe_2(L\text{-}py)(C_6H_5COO)_2]$-$BF_4\cdot3H_2O$	54.99 (55.10)	4.47 (4.82)	8.20 (8.20)			7.2
1b	$[Fe_2(L\text{-}py)(CH_3COO)_2]$-$(BF_4)_2\cdot H_2O$	47.10 (46.70)	4.32 (4.34)	8.90 (8.84)	5.6 (5.87)	5.9 (5.87)	7.7
2b	$[Fe_2(L\text{-}py)(C_6H_5COO)_2]$-$(BF_4)_2\cdot2H_2O$	51.73 (52.07)	4.13 (4.28)	7.60 (7.75)	4.9 (5.11)	5.2 (5.11)	7.3
3	$[Fe_2(L\text{-}py)(CH_3COO)(OH)]$-$(BF_4)_2\cdot2H_2O$	44.89 (45.35)	4.22 (4.46)	9.16 (9.07)	5.9 (6.03)	6.0 (6.03)	7.4

a) At room temperature.

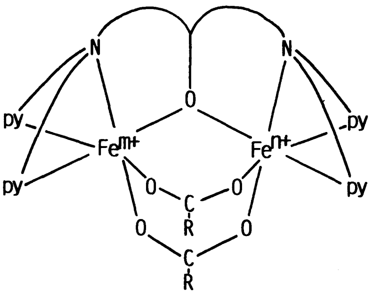

Fig. 2. Possible structure of $[Fe_2(L\text{-}py)(RCOO)_2]^+$ (m=2 and n=2) and $[Fe_2(L\text{-}py)(RCOO)_2]^{2+}$ (m=2 and n=3).

From the IR spectral data, both the mixed valence iron and manganese complexes seem to have the same structure. The crystal structure of $[Mn_2(L\text{-}py)(C_6H_5COO)_2](ClO_4)_2\cdot H_2O$[14b)] showed that manganese(II) and (III) ions are bridged by phenolate and two carboxylate oxygens to form a cofacial bi-octahedral structure. Such triply bridging structure has been found for some dinuclear manganese and iron complexes with bridging groups composed of two carboxylato groups and oxo, hydroxo, or phenolato group.[20–23)] A possible structure of **1b** and **2b** is shown in Fig. 2.

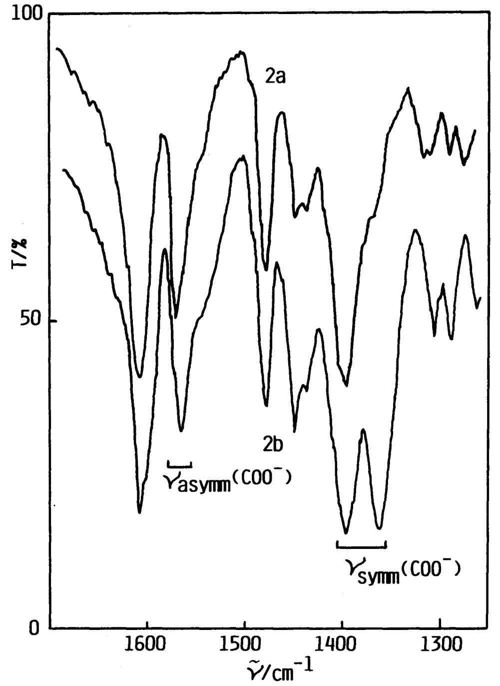

Fig. 3. Infrared spectra of $[Fe_2(L\text{-}py)(C_6H_5COO)_2]$-$BF_4\cdot3H_2O$ (**2a**) and $[Fe_2(L\text{-}py)(C_6H_5COO)_2](BF_4)_2\cdot2H_2O$ (**2b**).

Infrared spectra of **2a** and **2b** in the $\nu(COO^-)$ stretching vibration region (Fig. 3) showed that the $\nu_{\mathrm{symm}}(COO^-)$ of **2b** splits into two bands at 1395 and 1362 cm^{-1}, suggesting the presence of two types of carboxylato groups. A similar splitting of $\nu_{\mathrm{symm}}(COO^-)$ was also observed in manganese(II,III) complex $[Mn_2(L\text{-}py)(C_6H_5COO)_2](ClO_4)_2\cdot H_2O$[14b)] in which two bridging benzoato groups are not equivalent: one symmetrically bridges manganese(II) and (III) ions, and the other unsymmetrically. The Mn(III)-O and Mn(II)-O bond distances, and two C-O bond distances of unsymmetrically bridging benzoato group considerably differ from each other. It has been suggested that $\Delta\tilde{\nu}(COO^-)$ value ($\tilde{\nu}_{\mathrm{asymm}}(COO^-) - \tilde{\nu}_{\mathrm{symm}}(COO^-)$) is diagnostically useful for elucidating coordination mode of carboxylato group; a symmetrically bridging carboxylato group gives $\Delta\tilde{\nu}$ smaller than 200 cm^{-1}, whereas an unsymmetrically bridging group a larger $\Delta\tilde{\nu}$.[24)] The $\Delta\tilde{\nu}$ values are 150 and 200 cm^{-1} for **1b**, and 173 and 206 cm^{-1} for **2b**. Thus the larger $\Delta\tilde{\nu}$ values correspond to an unsymmetrically bridging carboxylato group and the smaller values to a symmetrically bridging one.

The complex **3** is air-stable in the solid state, but easily oxidized with molecular oxygen in various solvents at room temperature. Its effective magnetic moment is 7.4 B.M./Fe_2 at room temperature, indicating that iron(II) and iron(III) ions are in high-spin state. The molar conductivity (137 $\Omega^{-1}\,\mathrm{cm}^2\,\mathrm{mol}^{-1}$) in DMF indicates that the complex is a 2:1 electrolyte. From the molar conductivity measurement and elemental analysis, the coordination of hydroxide ion is

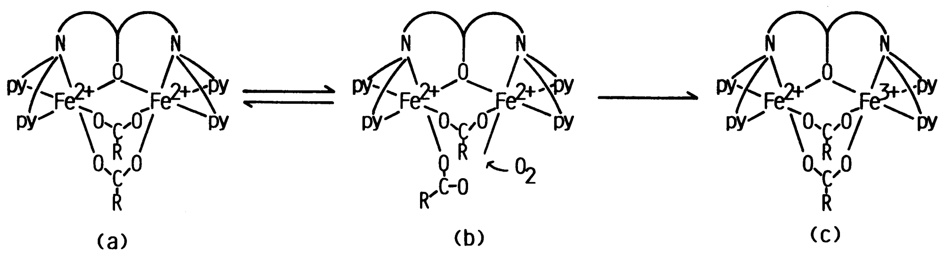

Fig. 4. A possible reaction scheme of oxidation of $[Fe_2(L\text{-}py)(RCOO)_2]^+$ (**1a** and **2a**).

plausible and the complex **3** may be formulated as $[Fe_2(L\text{-}py)(CH_3COO)(OH)](BF_4)_2\cdot 2H_2O$.

The effective magnetic moments of **1a** and **2a** are 7.4 and 7.2 B.M./Fe_2, respectively, indicating that iron(II) ions are in high-spin state. The infrared spectra of **1a** and **2a** are almost identical to those of the corresponding Co^{II}-Co^{II} complexes, $[Co_2(L\text{-}py)(RCOO)_2]BF_4\cdot nH_2O$,[15] in which cobalt ions were shown to adopt a six-coordinated structure on the basis of their reflectance spectra. On the analogy with the cobalt complexes, the present complexes seem to have six-coordinated structure. This may also be supported by the reactivity of the complexes with molecular oxygen in various solvents (vide infra). A possible structure is shown in Fig. 2.

The complexes **1a** and **2a** are relatively stable for a day in acetonitrile and dichloromethane under an oxygen atmosphere, whereas they rapidly react with molecular oxygen in methanol and *N,N*-dimethylformamide to form dark brown solution. Addition of tetraethylammonium tetrafluoroborate and ethanol to the above dark brown solution gave the mixed valence complexes **1b** and **2b**.

Reactivity of the Iron(II,II) Complexes with Molecular Oxygen. The effect of solvents on the reactivity of the dinuclear iron(II,II) complexes **1a** and **2a** with molecular oxgyen is quite similar to that of the corresponding cobalt(II,II) complexes $[Co_2(L\text{-}py)(RCOO)_2]^+$.[15] Both cobalt and iron complexes readily react with molecular oxygen in methanol and *N,N*-dimethylformamide but to a much lesser extent in acetonitrile and dichloromethane. The cobalt complexes give reversible oxygenation in the former two solvents to give μ-peroxo complexes, whereas the iron complexes form the mixed valence complexes **1b** and **2b** as mentioned in the preceding section. We suggested that the oxygenation of the cobalt complexes proceeds via a five-coordinated species: one of two carboxylato groups dissociates in the former solvents, but not in the latters. In fact, the five-coordinated complexes $[Co_2(L\text{-}py)(RCOO)]^{2+}$ react reversibly with molecular oxygen both in methanol and acetonitrile as well as in the solid state. This is also the case for the oxidation of iron(II,II) complexes: the oxidation of iron complexes seems to take place in a five-coordinated species. A possible reaction scheme is given in Fig. 4. It is probable that one of two bridging carboxylato groups (a in Fig. 4) dissociates to form a species containing five-and six-coordinated irons and then five-coordinated moiety reacts with molecular oxygen to form a hyperoxo complex as a transient intermediate. This hyperoxo complex is unstable and irreversibly oxidized to form mixed valence complex. In the cobalt complex, however, the hyperoxo complex is relatively stable and the coordinated hyperoxide ion displaces the unidentate carboxylate ion to form a μ-peroxo complex.

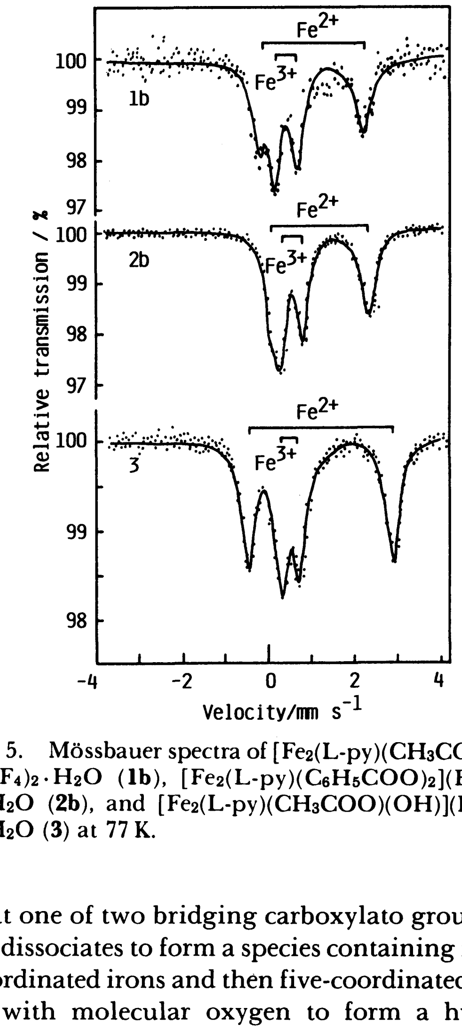

Fig. 5. Mössbauer spectra of $[Fe_2(L\text{-}py)(CH_3COO)_2](BF_4)_2\cdot H_2O$ (**1b**), $[Fe_2(L\text{-}py)(C_6H_5COO)_2](BF_4)_2\cdot 2H_2O$ (**2b**), and $[Fe_2(L\text{-}py)(CH_3COO)(OH)](BF_4)_2\cdot 2H_2O$ (**3**) at 77 K.

Mössbauer Spectra. Mössbauer spectra of the mixed valence complexes are shown in Fig. 5 and their parameters are listed in Table 2. All the spectra were analyzed with a least square fitting program of Lorenztian functions into two sets of quadrupole doublets, each of which was fitted with an equal line width and intensity. The calculated quadrupole splittings ΔE (isomer shifts δ) in mm s^{-1} are 2.06—3.38

Table 2. Mössbauer Parameters of the Mixed Valence Complexes at 77 K[a)]

No.	Complex	Fe(II)			Fe(III)			A(Fe(III)/Fe(II))[c)]
		$\delta^{b)}$	ΔE	Γ_{exp}	$\delta^{b)}$	ΔE	Γ_{exp}	
1b	$[Fe_2(L\text{-}py)(CH_3COO)_2](BF_4)_2\cdot H_2O$	1.16	2.42	0.41	0.47	0.51	0.33	1.03
2b	$[Fe_2(L\text{-}py)(C_6H_5COO)_2](BF_4)_2\cdot 2H_2O$	1.15	2.06	0.56	0.56	0.47	0.28	1.00
3	$[Fe_2(L\text{-}py)(CH_3COO)(OH)](BF_4)_2\cdot 2H_2O$	1.19	3.38	0.34	0.48	0.42	0.43	1.12
	Pink unterrofrin[d)]	1.24	2.68	0.28	0.53	1.84	0.43	

a) All data in mm s^{-1} except for A(Fe(III)/(Fe(II)). b) Isomer shift, δ, relative to iron metal. c) Ratios of areas of Fe(III) to Fe(II). d) Data at 60 K from Ref. 8.

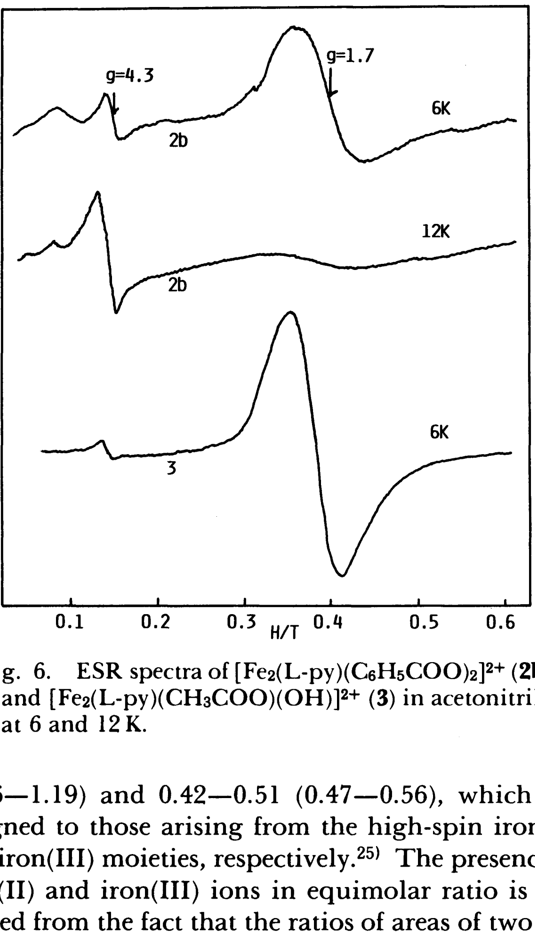

Fig. 6. ESR spectra of $[Fe_2(L\text{-}py)(C_6H_5COO)_2]^{2+}$ (**2b**) and $[Fe_2(L\text{-}py)(CH_3COO)(OH)]^{2+}$ (**3**) in acetonitrile at 6 and 12 K.

(1.16—1.19) and 0.42—0.51 (0.47—0.56), which are assigned to those arising from the high-spin iron(II) and iron(III) moieties, respectively.[25)] The presence of iron(II) and iron(III) ions in equimolar ratio is evidenced from the fact that the ratios of areas of two sets of quadrupole doublets are nearly unity (the last columm in Table 2), which is in good agreement with the results of the chemical analyses as described in the Experimental section.

Pink uteroferrin[8)] also shows two sets of quadrupole doublets. The reported values are listed in Table 2. The quadrupole splitting of the iron(III) moiety in pink uteroferrin is much larger than those of the present complexes. This fact reflects a remarkable structural difference in iron(III) moieties between the protein and the present complexes. It is well-known that μ-oxo dinuclear iron(III,III) complexes tend to exhibit larger quadrupole splittings.[25,26)] However, μ-oxo bridging seems unlikely to occur in pink uteroferrin from its magnetism.[7)] Therefore, iron(III) moiety in pink uteroferrin may have a distorted five-coordinated structure which shows a larger quadrupole splitting because of the larger electric field gradient at nucleus.[25,27)]

ESR Spectra. ESR spectra of **2b** and **3** at 6 and 12 K are shown in Fig. 6. Both complexes exhibit two signals centered at g=1.7 and 4.3, which are quite similar to those observed in the mixed valence iron proteins such as bovine spleen acid phosphatase.[9)] The g=4.3 signal can be assigned to that arising from mononuclear rhombic high-spin iron(III) ion present as impurity which may be produced by a slight decomposition of the complex. The g=1.7 signal is observable only near liquid helium temperature and almost disappears above 12 K as shown in Fig. 6. Such an ESR signal with $g_{av}<2.0$ has been interpreted in terms of antiferromagnetic superexchange interaction between high-spin iron(II) (S=2) and high-spin iron(III) (S=5/2) ions.[10)] In contrast to the iron proteins, the present complexes exhibited only a broad isotropic signal even at 6 K, which suggests a rapid electron spin-lattice relaxation.

Magnetic Susceptibilities. The antiferromagnetic interaction was confirmed by the temperature dependence of magnetic susceptibilities. Magnetic susceptibilities of the mixed valence complexes were measured over the temperature range 80—300 K. The results were analyzed by the usual spin-spin interaction model based on the exchange Hamiltonian $H=-2JS_1\cdot S_2$. The molar susceptibility (χ_A) of $S_1=2-S_2=5/2$ spin exchange coupling dimer is given by Eq. 1,

$$\chi_A=\frac{N\beta^2g^2}{4\kappa T}\times\frac{x^{24}+10x^{21}+35x^{16}+84x^9+165}{x^{24}+2x^{21}+3x^{16}+4x^9+5}+N\alpha \quad (1)$$

where $x=\exp(-J/\kappa T)$ and the symbols have their usual meanings. The magnetic susceptibilities of the complexes were well interpreted in terms of the above equation. Figure 7 shows temperature dependence of magnetic susceptibilities of **2b**. The solid line is the calculated curve by using the parameters listed in Table 3. The g value used in the fit for magnetic susceptibilities is 2.10, which differs significantly from

Table 3. Magnetic Parameters of the Mixed Valence Complexes

No.	Complex	J/cm^{-1}	g	$N\alpha/10^{-6}\,\mathrm{cgs\,mol}^{-1}$
1b	$[Fe_2(L\text{-}py)(CH_3COO)_2](BF_4)_2\cdot H_2O$	−3.2	2.10	0
2b	$[Fe_2(L\text{-}py)(C_6H_5COO)_2](BF_4)_2\cdot 2H_2O$	−8.0	2.10	0
3	$[Fe_2(L\text{-}py)(CH_3COO)(OH)](BF_4)_2\cdot 2H_2O$	−6.5	2.10	0
	Pink uteroferrin[a]	−10		
	Reduced form of bovine spleen acid phosphatase[b]	−50		

a) Refs. 6 and 7. b) Ref. 9.

Table 4. Electronic Spectral Data of the Mixed Valence Complexes[a]

No.	Complex	$\tilde{\nu}_{max}/\mathrm{cm}^{-1}$ $(\varepsilon/\mathrm{mol}^{-1}\,\mathrm{dm}^3\,\mathrm{cm}^{-1})$ CT band	IT band
1b	$[Fe_2(L\text{-}py)(CH_3COO)_2](BF_4)_2\cdot H_2O$	18000(900)	7700(290)
2b	$[Fe_2(L\text{-}py)(C_6H_5COO)_2](BF_4)_2\cdot 2H_2O$	17400(970)	7400(290)
3	$[Fe_2(L\text{-}py)(CH_3COO)(OH)](BF_4)_2\cdot 2H_2O$	20200(740)	8500(100)

a) In acetonitrile under a nitrogen atmosphere.

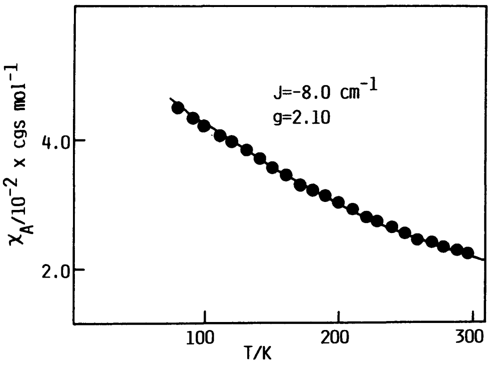

Fig. 7. Temperature dependence of magnetic susceptibilities of $[Fe_2(L\text{-}py)(C_6H_5COO)_2](BF_4)_2\cdot 2H_2O$ (**2b**).

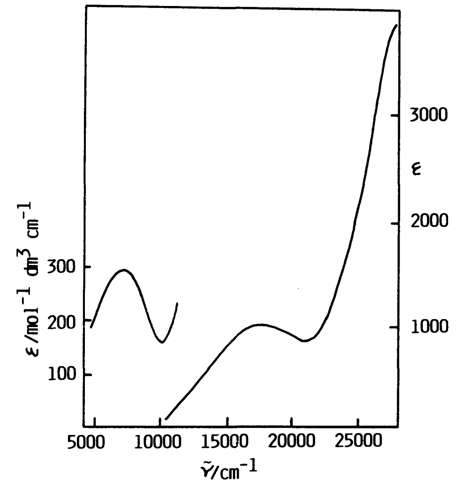

Fig. 8. Electronic spectrum of $[Fe_2(L\text{-}py)(C_6H_5COO)_2](BF_4)_2\cdot 2H_2O$ (**2b**) in acetonitrile under nitrogen atmosphere.

that derived from ESR measurement ($g\approx1.7$). These two g values are not recessarily the same: the former is the average value derived from the energy separations ($g\beta H$) in the five spin states (S=1/2, 3/2, 5/2, 7/2, 9/2), whereas the latter is that in the S=1/2 ground state. The results indicate that high-spin iron(II) and high-spin iron(III) ions are antiferromagnetically coupled to yield the S=1/2 ground state. The corresponding manganese complexes $[Mn_2(L\text{-}py)(RCOO)_2](ClO_4)_2\cdot nH_2O$ also exhibited weak antiferromagnetic interaction ($J\approx-6$ cm^{-1}).[14] Recently such triply bridging units consisting of two carboxylato groups and oxo, hydroxo, or phenolato group have been found for several iron and manganese complexes.[20—23] The magnitude of spin-exchange interaction in dinuclear iron(III,III) complexes having a triply bridging unit is highly dependent on the nature of the bridging groups. In general, μ-oxo bridged complexes exhibit much stronger antiferromagnetic interaction than μ-hydroxo and μ-phenolato bridged ones.[20,22,28]

The J values of the present complexes are comparable to that for pink uteroferrin ($J\approx-10$ cm^{-1}),[6,7] but much smaller than that for the reduced form of bovine spleen acid phosphatase ($J\approx-50$ cm^{-1}).[9] The oxidized forms of both proteins have been suggested to have a μ-oxo bridge on the basis of their strong antiferromagnetic interactions. The presence of μ-oxo bridge is also suggested in the reduced form of bovine spleen acid phosphatase. A much weaker exchange coupling for pink uteroferrin as compared with that for the reduced form of bovine spleen acid phosphatase may reflect a change in the bridging groups. Lauffer et al.[7] proposed a possibility of hydroxo bridge in pink uteroferrin. It is needed to study extensively the dinuclear iron(II,III) complexes with a μ-oxo or μ-hydroxo bridge for further elucidation of the structure of these proteins.

Electronic Spectra. All the mixed valence complexes exhibit absorption band in the near infrared region (ε=300—100 mol^{-1} dm^{3}cm^{-1}/Fe$_2$) in acetonitrile (Fig. 8 and Table 4). Neither iron(II) nor iron(III) complexes in high-spin state has such intense band in this region,[29] and the band is undoubtedly assigned to the intervalence charge transfer transition (IT) of the type

$$[Fe^{II}\text{-}Fe^{III}] \xrightarrow{h\nu} [Fe^{III}\text{-}Fe^{II}]^*$$

The complexes also give an band in the visible region (ε=700—1000 mol^{-1} dm^3 cm^{-1}/Fe^{III}). This is the band characteristic of iron(III)-phenolato complexes[30] and is assigned to charge transfer transition from pπ orbital of bridging phenolato group to half filled dπ^* orbital of iron(III) ion. The ligand field bands may be obscured under the above CT band.

According to Hush,[31] the delocalization coefficient, α^2, a measure of mixing of oxidation states, can be calculated by using Eq. 2

$$\alpha^2 = \frac{(4.24\times10^{-4})\cdot\varepsilon_{max}\cdot\Delta\tilde{\nu}_{1/2}}{\tilde{\nu}_{max}\cdot d^2} \quad (2)$$

The α^2 value calculated for **2b** is 6.8×10^{-3} assuming $\tilde{\nu}_{max}$=7300 cm^{-1}, $\Delta\tilde{\nu}_{1/2}$=5000 cm^{-1}, ε_{max}=290 mol^{-1} dm^3 cm^{-1} and d=3.5 Å. The metal-metal distance (d) is estimated from the corresponding manganese(II, III) complex.[14b] The α^2 value implies that delocalization of electron between iron(II) and iron(III) moieties is relatively small and the complex belongs to so-called class II mixed valence system.[32] This is compatible with the results of Mössbauer spectra: all the mixed valence complexes show two sets of quadrupole doublets arising from iron(II) and iron(III) moieties (Fig. 5 and Table 2), indicating that the thermal electron-transfer rate between iron(II) and iron(III) ions are slower than 10^7 s^{-1} (Mössbauer life time).

Loehr et al.[29] reported the electronic spectrum of *semi-met*hemerythrin (*semi-met*)$_R$Hr, where no IT band is detected in the visible and near infrared regions. The absence of IT band in the visible and near infrared regions implies that delocalization of electron in (*semi-met*)$_R$Hr is less than that in the present complexes, and that iron(II) and iron(III) valences in (*semi-met*)$_R$Hr are firmly trapped. It has been suggested that two iron moeities are not equivalent in *deoxy*- and *met*Hr.[33] Such an unsymmetry of two coordination moieties may be responsible for this trapped valence state.

Cyclic Voltammograms. Cyclic voltammograms of the mixed valence complexes **2b** and **3** in acetonitrile at 20 °C are illustrated in Fig. 9 (Table 5). The complex **1b** exhibits two redox couples at 0.68 and −0.03 V (vs. SCE). The constant potential coulometry revealed that these two redox couples correspond to one-electron redox reactions attributable to Fe^{III}-Fe^{III}/Fe^{II}-Fe^{III} (+0.68 V) and Fe^{II}-Fe^{III}/Fe^{II}-Fe^{II} (−0.03 V). Peak-to-peak separations of these two waves are 70 mV at a scan rate of 100 mV s^{-1} and the ratios of the oxidation currents (i_{pa}) for the forward scan to the reduction currents (i_{pc}) for the reverse scan are close to unity for the both couples. These two couples are fairly reversible since ferrocene present in this system as an internal standard showed a peak-to-peak separation of 70 mV. A similar cyclic voltammogram was observed for **1b**. The complex **3** also exhibits two redox couples at ca. +0.7 and −0.1 V (vs. SCE). However, these two couples are not reversible (Fig. 9). This irreversibility suggests a significant structural change upon electron transfer.

Stability of Mixed Valence Complexes. From the separation of the redox potentials of E_1([II, III]/[II, II])

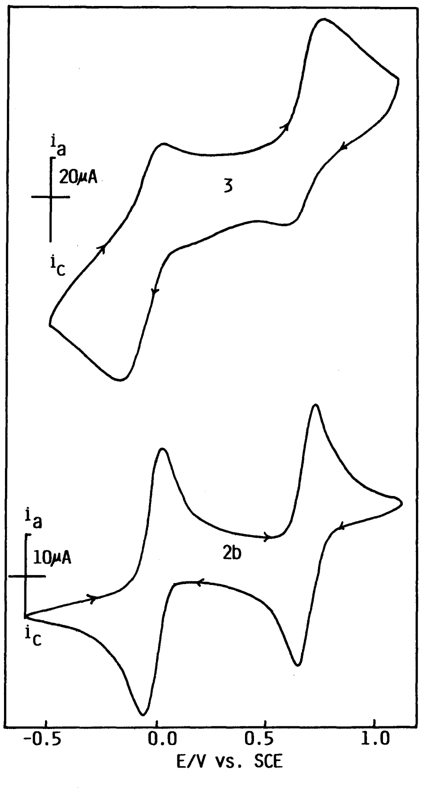

Fig. 9. Cyclic voltammograms of [Fe$_2$(L-py)(CH$_3$COO)$_2$](BF$_4$)$_2$·H$_2$O (**1b**) and [Fe$_2$(L-py)(CH$_3$COO)(OH)](BF$_4$)$_2$·2H$_2$O (**3**) in acetonitrile. The scan rate is 100 mV s^{-1}.

Table 5. Cyclic Voltammetric Data of the Mixed Valence Complexes

No.	Complex	$E_{1/2}$$^{a)}$ E/V (vs. SCE)	$E_{1/2}$$^{b)}$ E/V (vs. SCE)	$(i_{pa}/i_{pc})^{a)}$	$(i_{pa}/i_{pc})^{b)}$	$K_c$$^{c)}$
1b	[Fe$_2$(L-py)(CH$_3$COO)$_2$](BF$_4$)$_2$·H$_2$O	−0.03	+0.68	1.0	1.0	1.6×10^{12}
2b	[Fe$_2$(L-py)(C$_6$H$_5$COO)$_2$](BF$_4$)$_2$·2H$_2$O	+0.05	+0.73	1.0	1.0	5.0×10^{11}
3	[Fe$_2$(L-py)(CH$_3$COO)(OH)](BF$_4$)$_2$·2H$_2$O	−0.08$^{d)}$	+0.67$^{d)}$			

a) For Fe(II, III)/Fe(II, II) redox couple. b) For Fe(III, III)/Fe(II, III) redox couple. c) Comproportionation constant at 20 °C. d) Irreversible.

and E_2([III, III])/[II, III]), comproportionation constants (K at 20 °C) of the following reaction are calculated by Eq. 3.

$$(\mathrm{Fe^{III}}\text{-}\mathrm{Fe^{III}})+(\mathrm{Fe^{II}}\text{-}\mathrm{Fe^{II}}) \rightleftharpoons 2(\mathrm{Fe^{III}}\text{-}\mathrm{Fe^{II}})$$

$$E_2-E_1=RT/F\cdot\ln K \qquad (3)$$

The values obtained for **1b** and **2b** are 1.6×10^{12} and 5.0×10^{11} ($\Delta G=-68$ and -66 kJ mol^{-1}) respectively, indicating that the present mixed valence complexes are highly stabilized. Others have suggested that factors such as electron delocalization, electrostatic interaction, and steric interaction can contribute to the magnitude of K.[34] The electron delocalization energy (E_e) can be estimated by an analysis of the IT band. The value was calculated to be 600 J mol^{-1} for **2b** by using Eq. 4.

$$E_e=\alpha^2\cdot\tilde{\nu}_{\mathrm{IT}}.^{34a)} \qquad (4)$$

Thus the electron delocalization energy for the present system is too small to contribute significantly to its stability. When the metal ions are in close proximity, electrostatic interaction may play an important role. A dinuclear metal(II, II) complex will be more readily oxidized than a metal(II, III) species from electrostatic point of view. This will lead to a greater separation of redox potentials and increase of stability of the mixed valence state. In addition, a steric requirement arising from binucleating ligand L-py and two bridging carboxylato groups seems to be important.

Very recently we found that the reaction of an equimolar mixture of iron(III) and manganese(II) ions with L-py and carboxylate ions yields a dinuclear heterometal manganese(II)-iron(III) complex $[\mathrm{MnFe(L\text{-}py)(RCOO)_2}]^{2+}$ in more than 70% yieid.[35] The reaction of iron(III) ion with a dinuclear manganese(II, II) complex $[\mathrm{Mn_2(L\text{-}py)(RCOO)_2}]^{+}$ also resulted in the formation of the above dinuclear heterometal complex with a slight contamination of dinuclear homometal complexes.[35] Thus the present ligand system affords a favorable coordination sites for dinuclear metal(II, III) complexes.

The present work was supported by a Grant-in-Aid for Scientific Research No. 61540443 from the Ministry of Education, Science and Culture.

References

1) R. G Wilkins and P. C. Harrington, *Adv. Inorg. Biochem.*, **5**, 51 (1983).

2) B. B. Muhoberac, D. C. Wharton, L. M. Babcock, P. C. Harrington, and R. G. Wilkins, *Biochim. Biophys. Acta*, **626**, 337 (1980).

3) D. M. Kurtz,Jr., J. T. Sage, M. Hendrich, P. G. Debrunner, and G. S. Lukat, *J. Biol. Chem.*, **258**, 2115 (1983).

4) L. Que, Jr., *Coord. Chem. Rev.*, **50**, 73 (1983).

5) B. C. Antanaitis and P. Aisen, *Adv. Inorg. Biochem.*. **5**, 111 (1983).

6) B. C. Antanaitis, P. Aisen, and H. E. Lilienthal, *J. Biol. Chem.*, **258**, 3166 (1983).

7) R. B. Lauffer, B. C. Antanaitis, P. Aisen, and L. Que, Jr., *J. Biol. Chem.*, **258**, 14212 (1983).

8) P. G. Debrunner, M. P. Hendrich, J. D. Jersey, D. T. Keough, J. T. Sage, and B. Zerner, *Biochim. Biophys. Acta*, **745**, 103 (1983).

9) J. C. Davis and B. A. Averill, *Proc. Natl. Acad. Sci. U.S.A.*, **79**, 4623 (1982).

10) J. F. Gibson, D. O. Hall, J. H, M. Thornley, and F. R. Whatley, *Proc. Natl. Acad. Sci. U.S.A.*, **56**, 987 (1966).

11) S. M. Kauzlarich, B. K. Teo, T. Zirino, S. Burman, J. C. Davis, and B. A. Averill, *Inorg. Chem.*, **25**, 2781 (1986).

12) a) B. P. Gaber, J. P. Sheridan, F. W. Bazer, and R. M. Robert, *J. Biol. Chem.*, **254**, 8340 (1979); b) B. C. Antanaitis, T. Strekas, and P. Aisen, *J. Biol. Chem.*, **257**, 3766 (1982).

13) M. Suzuki. A. Uehara, and K. Endo, *Inorg. Chim. Acta*, **123**, L9 (1986).

14) a) M. Suzuki, S. Murata, A. Uehara, and S. Kida, *Chem. Lett.*, **1987**, 281; b) M. Suzuki, M. Mikuriya, S. Murata, A. Uehara. H. Oshio, S. Kida, and K. Saito, to be submitted.

15) a) M. Suzuki, H. Kanatomi, and I. Murase, *Chem. Lett.*, **1981**, 1745; b) M. Suzuki, I. Ueda, H. Kanatomi, and I. Murase, *Chem, Lett.*, **1983**, 185; c) M. Suzuki, H. Kanatomi, and I. Murase, *Bull. Chem. Soc. Jpn.*, **57**, 36 (1984).

16) C. L. Spiro, S. L. Lambert, T. J. Smith, E. N. Duesler, R, R, Gagne, D. N. Hendrickson, *Inorg. Chem.*, **20**, 1229 (1981).

17) F. E. Mabbs and D. J. Marchin "Magnetisms and Transition Metal Complexes," Chapman and Hall, London, (1973), p. 5.

18) F. D. Snell and C. T. Snell, "Colorimetric Method of Analysis," 3rd ed, D. Van Nostrand; (1957), Vol. 12, p. 316.

19) A slight reduction of iron(III) ion by phenolate of L-py was observed when iron(III) ion, phenanthroline, HL-py, $\mathrm{CH_3COONa}$, and $\mathrm{CH_3ONa}$ coexist in molar ratio of 2 : 10 : 1 : 2 : 1 in *N,N*-dimethylformamide. However, the addition of aqueous suspension of $\mathrm{H_4edta}$ prevented the reduction of iron(III) in the above mixture.

20) W. H. Armstrong, A. Spool, G. C. Papaefthymiou, R. B. Frankel, and S. J. Lippard, *J. Am. Chem. Soc.*, **106**, 3653 (1984) and references therein.

21) K. Wieghardt, U. Bossek, D. Ventur, and J. Weiss, *J. Chem. Soc., Chem. Commun.*, **1985**, 347.

22) W. H. Armstrong and S. J. Lippard, *J. Am. Chem. Soc.*, **106**, 4632 (1984).

23) B. P. Murch, F. C. Bradley, and L. Que, Jr., *J. Am. Chem. Soc.*, **108**, 5027 (1986).

24) G. B. Deacon and R. J. Phillips, *Coord. Chem. Rev.*, **23**, 227 (1980).

25) N. N. Greenwood and G. T. Gibbs, "Mössbauer Spectroscopy," Chapman and Hall, London (1971), p. 148.

26) K. S. Murray, *Coord. Chem. Rev.*, **12**, 1 (1974).

27) G. J. Long, J. T. Wrubleski, R. V. Thundathil, D. M. Sparlin, and E. O. Schlemper, *J. Am. Chem. Soc.*, **102**, 6040 (1980).

28) M. Suzuki and A. Uehara, unpublished results.

29) J. S. Loehr, T. M. Loehr, A. G. Mauk, and H. B. Gray, *J. Am. Chem. Soc.*, **102**, 6992 (1980).

30) a) E. W. Aniscough, A. M. Brodie, J. E. Plowman, K. L. Brown, A. W. Addison, and A. R. Gainsford, *Inorg. Chem.*, **19**, 3655(1980); b) J. W. Pyrz, A. L. Roe, L. J. Stern, and L. Que, Jr., *J. Am. Chem. Soc.*, **107**, 614 (1985).

31) N. S. Hush, *Prog. Inorg. Chem.*, **8**, 391 (1967).

32) M. B. Robin and P. Day. *Adv. Inorg. Chem. Radiochem.*, **10**, 247 (1967).

33) a) W. T. Elam, E. A. Stern. J. D. McCallum, and J. S. Loehr, *J. Am. Chem. Soc.*, **105**, 1919 (1983); b) R. E. Stenkamp, L. C. Sieker, and L. H. Jensen, *J. Am. Chem. Soc.*, **106**, 618 (1984).

34) a) J. E. Sutton and H. Taube, *Inorg. Chem.*, **20**, 3129 (1981); b) R. R. Gagne, C. L. Spiro, T. J. Smith, C. A. Hamann, W. R. Thies, and A. K. Shiemke, *J. Am. Chem. Soc.*, **103**, 4073 (1981).

35) M. Suzuki, S. Murata, and A. Uehara, unpublished results.