less concentrated solutions generate $P_2Mo_{18}O_{62}^{6-}$ as the principal product.

(3) The electrochemical behavior of **1** in CH_3CN is the least reversible of any polyoxometalate constituted exclusively or primarily of type I MO_6 octahedra (those with one terminal oxo group on the d^0 TM ion) that has been reported to date. All redox couples from +0.4 to -2.4 V vs $Ag/Ag^+(AgNO_3/CH_3CN)$ are completely irreversible.

(4) Treatment of **1** with 1 equiv of OH^- in CH_3CN reversibly generates $H_2PMo_{11}O_{39}^{5-}$, whereas 2 equiv of OH^- rapidly produces A-$PMo_9O_{31}(OH)_3^{6-}$ and, interestingly, the parent Keggin structure, $PMo_{12}O_{40}^{3-}$, in addition to $H_2PMo_{11}O_{39}^{5-}$. Whereas **1** can be reversibly protonated with 1 equiv of H^+ in CH_3CN to $H_4PMo_{11}O_{39}^{3-}$ over a period of several minutes, the latter complex decomposes over a period of hours and days to three other complexes, $P_2Mo_5O_{23}^{6-}$, $PMo_{12}O_{40}^{3-}$, and $P_2Mo_{18}O_{62}^{6-}$. In the presence of 2 equiv of H^+, many products observable in the ^{31}P NMR are produced rapidly which convert more slowly to $PMo_{12}O_{40}^{3-}$ in high yield.

(5) Metalation of **1** by several divalent $3d^n$, $n \neq 0$, transition-metal (TM) ions to form the corresponding TM-substituted polymolybdophosphates, $PMo_{11}(TM)O_{39}^{5-}$, can be readily accomplished by using a homogeneous one-phase procedure (acetonitrile solvent and TM triflate salt) or by a heterogeneous two-phase procedure (treatment of 3:2 acetonitrile-toluene solution of **1** with an aqueous solution of the TM salt). The exception is for Zn^{II} which by either metalation method leads to substantial (as high as 50%) decomposition of **1**.

(6) Reversible loss of the terminal axial ligand, L, of $PMo_{11}(TM^{II}-L)O_{39}^{5-}$ is observed on drying of the solid in vacuo. Several lines of evidence are consistent with the exchange of L, on both $PMo_{11}(TM^{II}-L)O_{39}^{5-}$ and the analogous tungsten compounds in aprotic media, being thermodynamically controlled. However, some kinetic control cannot be ruled out in the complex case of $PMo_{11}(Co^{II}-L)O_{39}^{5-}$ in acetonitrile.

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Supplementary Material Available: Infrared spectra (200-4000 cm^{-1}) of **1** and the parent Keggin ion, α-$Q_3PMo_{12}O_{40}$ (Figure S1), and UV/visible spectrum of **1** in CH_3CN (Figure S2) (2 pages). Ordering information is given on any current masthead page.

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Reduced Rubredoxin Models Containing Z-Cys-Pro-Leu-Cys-Gly-NH-C_6H_4-*p*-X (X = MeO, H, F, CN): Electronic Influence by a Distant Para Substituent through NH---S Hydrogen Bonds

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Model complexes of reduced rubredoxin, $[Fe^{II}(Z\text{-cys-Pro-Leu-cys-Gly-NH-}C_6H_4\text{-}p\text{-}X)_2]^{2-}$ (X = MeO (**4**), H (**5**), F (**6**) and CN (**7**)), were synthesized by a ligand-exchange reaction of $[Fe^{II}(S\text{-}t\text{-}Bu)_4]^{2-}$ with Z-Cys(SH)-Pro-Leu-Cys(SH)-Gly-NH-C_6H_4-*p*-X. These complexes gave positively shifted redox potentials compared to other peptide model complexes such as $[Fe^{II}(Z\text{-cys-Pro-Leu-cys-OMe})_2]^{2-}$ (**2**) and $[Fe^{II}(Z\text{-cys-Pro-Leu-cys-Gly-Val-OMe})_2]^{2-}$ (**3**) in a weakly nonpolar solvent, e.g. 1,2-dimethoxyethane (DME). The most positively shifted redox potential at -0.24 V vs SCE was observed for **7** in DME with the strongest electron-withdrawing *p*-substituent. The strength of the NH---S hydrogen bonds in **4**-**7** in DME was in the order X = OMe < H < F < CN. The observed aromatic substituent effect is explained by an electronic charge flow from sulfur of the coordinated cysteine residue to the benzene ring through an NH---S hydrogen bond.

Introduction

Rubredoxin (Rd), which possesses an iron atom surrounded by four sulfur atoms of cysteine residues, is known to be an electron-transfer metalloprotein using a Fe(II)/Fe(III) redox couple at -0.31 V vs SCE (saturated calomel electrode) in aqueous solution.[1,2] Although many simple alkane- and arenethiolate complexes have been synthesized as model complexes of Rd,[3-5] the redox potentials of Fe(II)/Fe(III) of these model complexes, for example, $[Fe(S\text{-}Et)_4]^{2-/-}$ having a value of -1.08 V vs SCE in CH_3CN[3] and $[Fe(S_2\text{-}o\text{-}xyl)_2]^{2-/-}$ having a value of -0.99 V vs SCE in Me_2SO,[5] were substantially more negative than that of Rd.

In our continued study, we have synthesized Fe(II) complexes containing Cys-oligopeptide ligands having the invariant fragments of the rubredoxin peptide chain.[6-9] $[Fe^{II}(Z\text{-cys-Pro-Leu-cys-OMe})_2]^{2-}$ (**2**) has a redox potential at -0.54 V vs SCE in CH_3CN, which is much more positive than those of simple alkane- or arenethiolate complexes. In particular, in a weakly nonpolar solvent, e.g. 1,2-dimethoxyethane (DME), the redox potential of $[Fe^{II}(Z\text{-cys-Pro-Leu-cys-Gly-Val-OMe})_2]^{2-}$ (**3**) is -0.35 V vs SCE, which is the nearest value to that of native Rd. This positive shift is caused by the formation of NH---S hydrogen bonds from NH of the neighboring peptide residue to S of the cysteine residue as reported in previous paper.[7,8]

Instead of the conserved valine residue in a sequence Cys-Pro-Leu-Cys-Gly-Val, peptides with a para-substituted anilide residue, i.e., Z-Cys-Pro-Leu-Cys-Gly-NH-C_6H_4-*p*-X (X = MeO, H, F, CN), were synthesized. The para-substituent effect on the redox potential was examined in $[Fe(Z\text{-cys-Pro-Leu-cys-Gly-NH-}C_6H_4\text{-}p\text{-}X)_2]^{2-}$ in order to verify the electronic interaction through the NH---S hydrogen bonds. Without the NH---S hydrogen bond, the potential will not be susceptible to the para-substituent effect.

Previously, we and Sanders-Loehr and co-workers have reported the existence of similar NH---S hydrogen bonds indirectly by IR or Raman spectroscopy.[10,11] Now, ^2H NMR spectra of the

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N-deuterated peptide–Fe(II) complexes of similar structure were measured to detect contact-shifted resonances through the path N–H···S–Fe. The observation of these shifted peaks will also provide direct evidence for formation of the NH···S hydrogen bonds.

Experimental Section

Materials. L-Cysteine and all other L-amino acids were purchased from Protein Research Foundation, Osaka, Japan, and used without further purification. Para-substituted anilines were obtained from Tokyo Kasei Co. Ltd and purified by distillation. Z-Cys(Acm)-Pro-Leu-OPac was synthesized as described in the previous paper.[8] Boc-Cys(Acm)-Gly-NH-C_6H_4-*p*-X (X = MeO, H, F, CN) were prepared stepwise by the MA (mixed anhydride) method as reported in the literature.[12,13] $(Et_4N)_2[Fe(S\text{-}t\text{-}Bu)_4]$ was prepared by the same method as reported in the previous paper.[8] All the solvents were distilled before use.

Synthesis of Z-Cys(Acm)-Pro-Leu-Cys(Acm)-Gly-NH-C_6H_5 (X = H). The titled peptide was synthesized by condensation of Z-Cys(Acm)-Pro-Leu-OPac with Boc-Cys(Acm)-Gly-NH-C_6H_5 using the DCC (*N,N'*-dicyclohexylcarbodiimide)/HOBt (1-hydroxybenzotriazole) method. To a solution of Z-Cys(Acm)-Pro-Leu-OPac (2.0 g, 3.0 mmol) in 90% acetic acid (90 mL) was added zinc powder (10.0 g). The mixture was stirred for 1 h at 0 °C and was stirred overnight at room temperature. The excess zinc was removed by filtration. The colorless filtrate was concentrated in vacuo. The residue was dissolved in water, acidified by citric acid, and extracted with ethyl acetate. The solvent was removed in vacuo, and a colorless oil, Z-Cys(Acm)-Pro-Leu-OH, was obtained. This oil was dissolved in DMF (4 mL), and a mixture of HCl·Cys-(Acm)-Gly-NH-C_6H_5 (3.0 mmol) and triethylamine (0.42 mL, 3.0 mmol) in DMF (3 mL) was added. After HOBt (609 mg) was added the mixture was cooled to −5 °C by using an ice–salt bath, and DCC (774 mg) was added in the solid state. The mixture was stirred at room temperature for 4 days and purified by the usual procedures to give the desired peptide. The yield was about 20%. Anal. Calcd for $C_{39}H_{54}N_8O_9S_2$ (Z-Cys(Acm)-Pro-Leu-Cys(Acm)-Gly-NH-C_6H_5): C, 55.56, H, 6.46; N, 13.29; S, 7.61. Found: C, 55.57; H, 6.51; N, 13.10; S, 7.67.

The other peptides containing para-substituted anilide, Z-Cys-(Acm)-Pro-Leu-Cys(Acm)-Gly-NH-C_6H_4-*p*-X (X = MeO, F, CN), and *m*-substituted anilide, Z-Cys(Acm)-Pro-Leu-Cys(Acm)-Gly-NH-C_6H_4-*m*-F, were also synthesized by the same method as mentioned above. The purity of these peptides was ensured by their ^1H NMR spectra. For example, the integral ratio of the methylene protons of the benzyloxycarbonyl group and the benzene ring protons of anilide was 0.5 in Z-Cys(Acm)-Pro-Leu-Cys(Acm)-Gly-NH-C_6H_4-*p*-X in $CDCl_3$.

Synthesis of the Silver(I) Complex of Z-Cys-Pro-Leu-Cys-Gly-NH-C_6H_4-*p*-F. To a solution of Z-Cys(Acm)-Pro-Leu-Cys(Acm)-Gly-NH-C_6H_4-*p*-F (27.60 mg, 3.20×10^{-5} mol) in methanol (2 mL) was added a solution of silver trifluoroacetate (35.40 mg, 1.60×10^{-4} mol) in methanol (2 mL). The mixture was stirred overnight. The solvent was removed in vacuo, and the residue was washed with diethyl ether three times to afford the title peptide silver complex. Deprotection of *S*-Acm groups was confirmed by ^1H NMR. The absence of ^1H NMR peaks of methyl protons of Acm at 2.1–2.2 ppm in a solution of the complex in Me_2SO-d_6 indicates the complete deprotection of the Acm groups. Anal. Calcd for $C_{37}H_{41}N_6O_{11}S_2Ag_4F_7$ [Z-Cys(Ag)-Pro-Leu-Cys(Ag)-Gly-NH-C_6H_4-*p*-F][$AgOCOCF_3$]$_2$: C, 32.34; H, 3.01; N, 6.11. Found: C, 32.06; H, 3.32; N, 6.00.

The deprotection of other peptides of Z-Cys(Acm)-Pro-Leu-Cys-(Acm)-Gly-NH-C_6H_4-*p*-X (X = MeO, H, CN) and Z-Cys(Acm)-Pro-Leu-Cys(Acm)-Gly-NH-C_6H_4-*m*-F were carried out in the same manner.

Preparation of SH-Free Peptides. All of the SH-free peptides were prepared from the corresponding Ag(I) complexes by purging with hydrogen sulfide. Black precipitates of Ag_2S were removed by filtration, and the filtrate was concentrated under reduced pressure. The residue was washed with degassed diethyl ether to give a colorless solid, which was used for the synthesis of Fe(II) complexes.

Preparation of N–^2H Peptides. The deuterated peptides were obtained by proton–deuteron exchange of SH-free peptide with methanol-*d*. SH-free peptide (0.05 mmol) was dissolved in CH_3O^2H (1 mL) and stirred for about 15 min at 40 °C. The solvent was removed in vacuo. This procedure was repeated three times to give the desired peptide.

Synthesis of $(Et_4N)_2$[Fe(Z-cys-Pro-Leu-cys-Gly-NH-C_6H_4-*p*-X)$_2$] (4–7). All procedures were carried out under argon atmosphere. Solvents were degassed after or during purification either by purging with argon or by the freeze–pump–thaw method. Peptide–Fe(II) complexes were synthesized by ligand-exchange reaction of Z-Cys(SH)-Pro-Leu-Cys(SH)-Gly-NH-C_6H_4-*p*-X (5.00×10^{-5} mol) in CH_3CN (3 mL) with $(Et_4N)_2[Fe(S\text{-}t\text{-}Bu)_4]$ (16.61 mg, 2.47×10^{-5} mol) in tetrahydrofuran (3 mL). After being stirred for about 20 min at room temperature, the reaction mixture was concentrated under reduced pressure and then washed with diethyl ether and dried in vacuo to give a light brown powder. No ^1H NMR signal for the methyl protons of *t*-butanethiolate at 23 ppm indicates a complete exchange of the S-*t*-Bu ligand with the peptide ligand. The Cys-containing Fe(II) complexes are generally hygroscopic and cannot give good analysis data. Therefore, the ^1H NMR method is necessary predominantly to check the purity. The ratio of methyl protons of the countercation and the phenyl protons of the benzyloxycarbonyl group was about 2.4 from the intensity of the peaks due to methyl and phenyl protons in ^1H NMR spectra in CD_3CN. The spectrum also confirms the composition of Fe(II) complexes of Z-Cys-Pro-Leu-Cys-Gly-NH-C_6H_4-*p*-X to be $(Et_4N)_2$[Fe(Z-cys-Pro-Leu-cys-Gly-NH-C_6H_4-*p*-X)$_2$] (X = MeO, H, F, CN).

Synthesis of $(Et_4N)_2$[Fe(Z-cys-Pro-Leu-cys-Gly-NH-C_6H_4-*m*-X)$_2$] (8). This complex was also prepared by the ligand-exchange reaction of $(Et_4N)_2[Fe(S\text{-}t\text{-}Bu)_4]$ (6.23 mg, 9.26×10^{-6} mol) with Z-Cys(SH)-Pro-Leu-Cys(SH)-Gly-NH-C_6H_4-*m*-F (2.07×10^{-5} mol) in THF and CH_3CN. Absorption spectrum (acetonitrile): 312 nm (6500), 330 nm (sh, 5200). CD spectrum (acetonitrile): 302 nm (−8.4), 324 nm (−8.8), 338 nm (+8.9). ^1H NMR spectrum (at lower field in acetonitrile-d_3 at 30 °C): 260, 247, 226, 200, 146 ppm. Redox potentials in acetonitrile, dimethyl sulfoxide and 1,2-dimethoxyethane were −0.36, −0.35, and −0.33 V vs SCE, respectively.

Physical Measurements. Absorption spectra were measured on a JASCO Ubest-30 spectrophotometer using a 1-mm cell. CD spectra were recorded on a JASCO J-40 spectropolarimeter. The 500-MHz ^1H NMR spectra were measured on a JEOL JNM-GX 500 machine. A SGHMG (single-pulse homo-gated decoupling) mode was used for observing contact shifted signals at lower field. The 61-MHz ^2H NMR spectra measurements were carried out in CH_3CN on a JEOL GSX 400 NMR spectrometer. The 470-MHz ^{19}F-NMR spectra were measured on a JEOL JNM-GX 500 NMR spectrometer using a ^{19}F probe. Sample concentrations were about 15 mg/mL. Cyclic voltammograms were recorded on a YANACO P-1100 instrument with a scan rate of 100 mV/s. $[(n\text{-}Bu)_4N][ClO_4]$ (100 mM) was used as a supporting electrolyte. Potentials were calculated vs a saturated calomel electrode (SCE) as a reference.

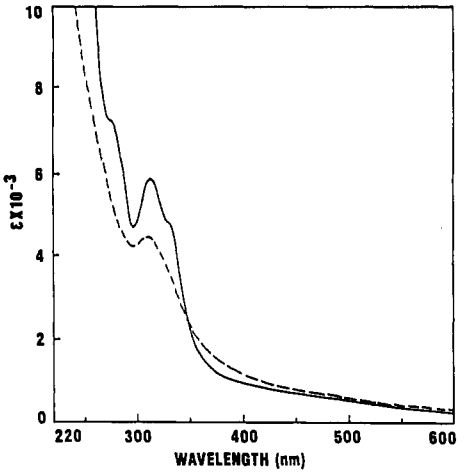

Figure 1. Absorption spectra of (—) [Fe(Z-cys-Pro-Leu-cys-Gly-NH-C_6H_4-*p*-F)$_2$]$^{2-}$ (**6**) and (– –) [Fe(Z-cys-Pro-Leu-cys-Gly-Val-OMe)$_2$]$^{2-}$ (**3**) in acetonitrile.

Results

UV–Vis and CD Spectra. Absorption and CD spectra of **3** and **6** in CH_3CN at ambient temperature are shown in Figure 1 and Figure 2, respectively. Both **3** and **6** have an absorption maximum at 312 nm like that of native Rd, which was assigned to be due to $S^- \rightarrow$ Fe(II) charge transfer.[14] The absorption maxima of **4–7** in CH_3CN were observed at about 312 nm, independent of the para substituents. On the other hand, **6** has a shoulder at 332 nm (sh, 4800) similar to Rd with one at 333 nm (6000). But **3**

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Table I. Spectral Data for Fe(II)–Peptide Complexes in CH_3CN and Rubredoxin in H_2O

complexes	UV–vis[a]		CD[b]		
$[Fe(Z\text{-}cys\text{-}Gly\text{-}Val\text{-}OMe)_4]^{2-}$ (**1**)[c]	316 (5300)		320 (−3.5)		341 (1.2)
$[Fe(Z\text{-}cys\text{-}Pro\text{-}Leu\text{-}cys\text{-}OMe)_2]^{2-}$ (**2**)[c]	314 (5900)		320 (−6.3)		340 (3.3)
$[Fe(Z\text{-}cys\text{-}Pro\text{-}Leu\text{-}cys\text{-}Gly\text{-}Val\text{-}OMe)_2]^{2-}$ (**3**)[c]	312 (4500)		309 (−5.3)		338 (2.8)
$[Fe(Z\text{-}cys\text{-}Pro\text{-}Leu\text{-}cys\text{-}Gly\text{-}NH\text{-}C_6H_4\text{-}p\text{-}OMe)_2]^{2-}$ (**4**)	311 (4250)	331 (3900)	318 (−7.7)		340 (4.2)
$[Fe(Z\text{-}cys\text{-}Pro\text{-}Leu\text{-}cys\text{-}Gly\text{-}NH\text{-}C_6H_5)_2]^{2-}$ (**5**)	312 (5400)	330 (4400)	307 (−10.0)	323 (−10.1)	339 (5.8)
$[Fe(Z\text{-}cys\text{-}Pro\text{-}Leu\text{-}cys\text{-}Gly\text{-}NH\text{-}C_6H_4\text{-}p\text{-}F)_2]^{2-}$ (**6**)	312 (5900)	332 (4800)	308 (−10.2)	322 (−9.6)	339 (6.85)
$[Fe(Z\text{-}cys\text{-}Pro\text{-}Leu\text{-}cys\text{-}Gly\text{-}NH\text{-}C_6H_4\text{-}p\text{-}CN)_2]^{2-}$ (**7**)	312 (5400)	330 (4600)	311 (−9.85)	323 (−10.1)	340 (5.8)
reduced rubredoxin[d]	312 (10900)	333 (6000)	314 (−36)		334 (18)

[a] In nm (ϵ, M^{-1} cm^{-1}). [b] In nm ($\Delta\epsilon$, M^{-1} cm^{-1}). [c] Reference 8. [d] Reference 2.

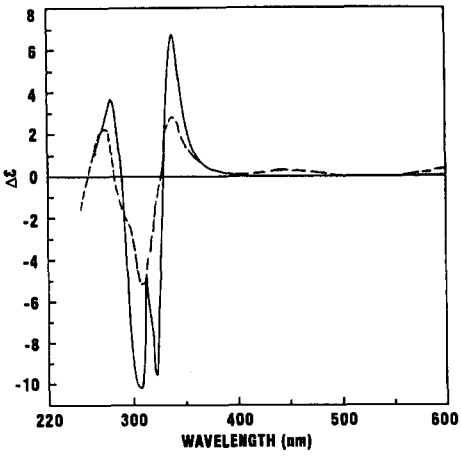

Figure 2. CD spectra of (—) $[Fe(Z\text{-}cys\text{-}Pro\text{-}Leu\text{-}cys\text{-}Gly\text{-}NH\text{-}C_6H_4\text{-}p\text{-}F)_2]^{2-}$ (**6**) and (--) $[Fe(Z\text{-}cys\text{-}Pro\text{-}Leu\text{-}cys\text{-}Gly\text{-}Val\text{-}OMe)_2]^{2-}$ (**3**) in acetonitrile.

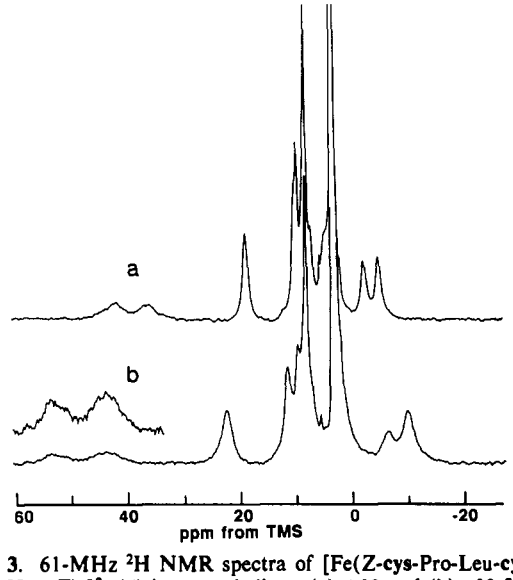

Figure 3. 61-MHz ^2H NMR spectra of $[Fe(Z\text{-}cys\text{-}Pro\text{-}Leu\text{-}cys\text{-}Gly\text{-}NH\text{-}C_6H_4\text{-}p\text{-}F)_2]^{2-}$ (**6**) in acetonitrile at (a) +30 and (b) −30 °C.

has no such absorption, and the same is true for Fe(II) oligopeptide model complexes without an anilide residue. All of these complexes with an anilide residue, $[Fe(Z\text{-}cys\text{-}Pro\text{-}Leu\text{-}cys\text{-}Gly\text{-}NH\text{-}C_6H_4\text{-}p\text{-}X)_2]^{2-}$, exhibited such absorptions: X = MeO, 330 nm (sh, 3900); X = H, 330 nm (sh, 4400); X = CN, 330 nm (sh, 4000) (Table I). Therefore, these absorption maxima at 330–332 nm are caused by the presence of an anilide residue.

A similar distinction can be made by CD spectra as shown in Figure 2 and Table I. **6** has CD extrema at 308 (−10.2), 322 (−9.6), and 339 nm (6.85) while **3** had extrema at 309 (−5.3) and 338 nm (2.8). Native Rd has ones at 314 (−36) and 334 nm (18) in aqueous solution.[2] Two CD troughs were observed in these complexes that have an anilide residue except for X = MeO, while Rd and the other model complexes without anilide residue have only one trough. Thus the additional transition perhaps came from the benzene ring of the anilide. Furthermore, in general, **4–7** exhibited stronger CD extrema than the known Fe(II)–peptide model complexes such as **2** and **3** (Table I). The absorption and CD spectra ensure us that **4–7** have a FeS_4 core and relatively rigid structure around the Cys residues similar to that in the active center of Rd.[15]

^1H NMR and ^2H NMR Spectra. Due to the paramagnetic properties of a high-spin Fe(II) core, the ^1H NMR signals of the Cys CH_2 protons were found to appear at much lower field side just as reported for the native *Desulfovibrio gigas* Rd.[16]

6 gave six resonances at 260, 247, 230, 218, 203, and 150 ppm in CD_3CN at 30 °C, which are reasonably assigned to the Cys CH_2 protons since, for *D. gigas* Rd, four signals at 236, 227, 192, and 150 ppm in D_2O at 55 °C were assigned to Cys CH_2 protons.[16] On the other hand, **4–7** gave almost the same ^1H NMR spectra in CD_3CN at 30 °C whenever X was MeO, H, F, or CN.

Four signals were observed in the ^1H NMR spectrum for *D. gigas* rubredoxin. In our model complexes, there are two isomers as discussed later which should give eight signals for Cys CH_2 protons in total. The intensity of each signal at 203 or 150 ppm was twice that of the other signals (260; 247; 230 or 218 ppm). This indicates that both signals at 203 ppm and at 150 ppm are in fact two overlapped signals.

The presence of NH---S hydrogen bonds was established by the observation of contact-shifted ^2H NMR signals in acetonitrile. The ^2H NMR signals of amide N^2H can be observed at almost the same chemical shift as ^1H NMR signals since the isotope effect is very small in magnitude.[17] The strength of hydrogen bond of N^1H---S and N^2H---S(deuterated) are almost the same because the absorption, CD, and ^1H NMR spectra at the lower field did not change when the peptide amides were deuterated.

Fe(II) complexes of an N-deuterated peptide were also synthesized by the reaction of $(Et_4N)_2[Fe(S\text{-}t\text{-}Bu)_4]$ with Z-Cys-(SH)-Pro-Leu-Cys(SH)-Gly-N^2H-C_6H_4-*p*-X, and ^2H NMR spectra were measured in CH_3CN to confirm the formation of N^2H---S hydrogen bonds between S of the cysteine residue and N^2H of the amide residue. The 61-MHz ^2H NMR spectra of **6** in CH_3CN are shown in Figure 3. Contact-shifted signals of **6** at 41.7, 35.9, 18.6, 9.5, −2.3, and −4.9 ppm at 30 °C (Figure 3a) were similar to those of **3**. The peak due to D_2O at 4.7 ppm was used as external reference. However, no signal was found at about −20 ppm, which was assigned to Val-N^2H in **3**.[8] No apparent difference in ^2H NMR spectra was observed among those of **4–7** just as was observed for the ^1H NMR spectra of **4–7**.

In order to locate the anilide N^2H signal, the ^2H NMR spectrum of **6** was measured at a lower temperature. Signals between 8.0 and 10.0 ppm in the ^2H NMR spectra were considered to be due to uncoordinated free peptide. A ^2H NMR peak assignable to N^2H of Gly, which was not involved in the NH---S hydrogen bond, also appeared in this region. Usually, peptide NH signals between 8.0 and 10.0 ppm remain practically unchanged even if

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Table II. Redox Potentials of Fe(II)–Peptide Complexes in CH_3CN, Me_2SO, and DME and σ_p Values

complexes	σ_p	redox potential, V vs SCE		
		CH_3CN	Me_2SO	DME
$[Fe(Z\text{-cys-Pro-Leu-cys-OMe})_2]^{2-}$ (**2**)[a]		−0.54	−0.47	−0.59
$[Fe(Z\text{-cys-Pro-Leu-cys-Gly-Val-OMe})_2]^{2-}$ (**3**)[a]		−0.46	−0.41	−0.35
$[Fe(Z\text{-cys-Pro-Leu-cys-Gly-NH-C}_6H_4\text{-}p\text{-OMe})_2]^{2-}$ (**4**)	−0.27	−0.36	−0.35	−0.33
$[Fe(Z\text{-cys-Pro-Leu-cys-Gly-NH-C}_6H_5)_2]^{2-}$ (**5**)	0	−0.38	−0.37	−0.33
$[Fe(Z\text{-cys-Pro-Leu-cys-Gly-NH-C}_6H_4\text{-}p\text{-F})_2]^{2-}$ (**6**)	0.06	−0.39	−0.36	−0.31
$[Fe(Z\text{-cys-Pro-Leu-cys-Gly-NH-C}_6H_4\text{-}p\text{-CN})_2]^{2-}$ (**7**)	0.66	−0.30	−0.27	−0.24

[a] Reference 8.

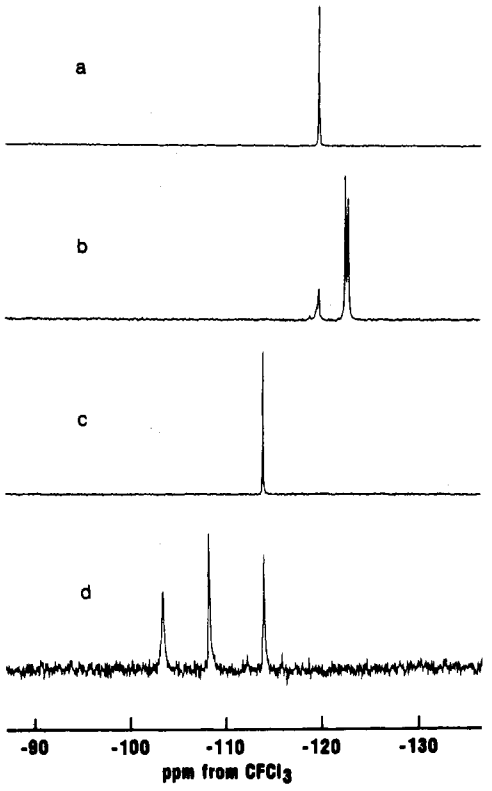

Figure 4. 470-MHz ^{19}F NMR spectra of (a) Z-Cys(SH)-Pro-Leu-Cys-(SH)-Gly-NH-C_6H_4-*p*-F, (b) $[Fe(Z\text{-cys-Pro-Leu-cys-Gly-NH-C}_6H_4\text{-}p\text{-F})^2]^{2-}$ (**6**), (c) Z-Cys(SH)-Pro-Leu-Cys(SH)-Gly-NH-C_6H_4-*m*-F, and (d) $[Fe(Z\text{-cys-Pro-Leu-cys-Gly-NH-C}_6H_4\text{-}m\text{-F})_2]^{2-}$ (**8**) in acetonitrile-d_3 at 30 °c.

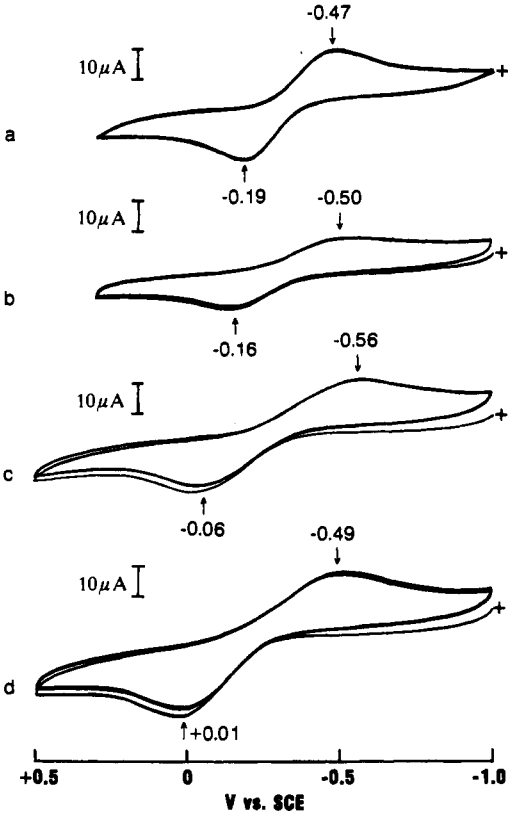

Figure 5. Cyclic voltammograms of (a) $[Fe(Z\text{-cys-Pro-Leu-cys-Gly-NH-C}_6H_4\text{-}p\text{-OMe})_2]^{2-}$ (**4**), (b) $[Fe(Z\text{-cys-Pro-Leu-cys-Gly-NH-C}_6H_5)_2]^{2-}$ (**5**), (c) $[Fe(Z\text{-cys-Pro-Leu-cys-Gly-NH-C}_6H_4\text{-}p\text{-F})_2]^{2-}$ (**6**), and (d) $[Fe(Z\text{-cys-Pro-Leu-cys-Gly-NH-C}_6H_4\text{-}p\text{-CN})_2]^{2-}$ (**7**) in DME.

the temperature is lowered. A signal assignable to anilide N^2H in the 8–10 ppm region shifted from 9.5 ppm at +30 °C to 11.5 ppm at −30 °C. But such a shift was not observed in the temperature-variant ^2H NMR spectra of **2** and **3**. Thus, the signal at 9.5 ppm is correctly assigned to the anilide N^2H group.

The small changes in N^2H ^2H NMR spectra resulted from the NH---S hydrogen bond counterbalanced by any unisotropic magnetic influence by the phenyl ring of anilide. If there is such an NH---S hydrogen bond without interaction of a phenyl group on the Fe–S center, ^2H NMR signals of the amide N^2H should be observed with large chemical shift changes.

^{19}F NMR Spectra. The ^{19}F NMR spectrum was measured for **6** in CD_3CN at 30 °C in order to investigate the influence of Fe(II) ion on the para-substituted F group through the NH---S bond. **6** gave two signals at −122.6 and −122.9 ppm from a reference peak of $CFCl_3$. These are assigned to the coordinated peptide. A peak at −119.9 ppm is assignable to the SH-free peptide (uncoordinated peptide), Z-Cys(SH)-Pro-Leu-Cys(SH)-Gly-NH-C_6H_4-*p*-F (Figure 4a,b). For comparison, $[Fe(Z\text{-cys-Pro-Leu-cys-Gly-NH-C}_6H_4\text{-}m\text{-F})_2]^{2-}$ (**8**) was also synthesized by the same reaction as used in the preparation of **6**. Two contact-shifted signals at −103.5 and −108.3 ppm were observed in **8** while the SH-free peptide, Z-Cys(SH)-Pro-Leu-Cys(SH)-Gly-NH-C_6H_4-*m*-F, showed one peak at −114.0 ppm (Figure 4c,d). The presence of two contact-shifted signals in **6** and **8** may indicate two isomers existing for these complexes (vide post).

Electrochemical Properties. The redox potentials of **4**–**7** were obtained by cyclic voltammetry. **7** exhibits a redox couple with good reversibility at −0.30, −0.27, and −0.24 V vs SCE in acetonitrile, dimethyl sulfoxide and 1,2-dimethoxyethane, respectively. These values were far more positive than those for **6** and **3** (Table II) and also than that for native Rd (−0.31 V vs SCE in aqueous solution). The shift is ascribed to the strong electron-withdrawing property of the cyano group. The redox potentials were unchanged with scanning rates of 50–500 mV/s. Furthermore, the redox potentials were positively shifted with each complex in a nonpolar solvent. For example, the peptide complexes **4**–**7** in DME gave redox potentials −0.33 V, −0.33 V, −0.31 V and −0.24 V vs SCE, respectively (Figure 5), which were more positive than those in CH_3CN and Me_2SO (see Table II).

Discussion

Chelation of Cys-Pro-Leu-Cys-Gly-NH-C_6H_4-*p*-X Ligands in High-Spin Mononuclear Fe(II) Complexes. From the UV and CD spectra of the Fe(II) complexes of Z-Cys-Pro-Leu-Cys-Gly-NH-C_6H_4-*p*-X, retention of the FeS_4 core during the reactions of $[Fe(S\text{-}t\text{-Bu})_4]^{2-}$ with the peptide ligand was confirmed. A chelating structure was confirmed by the strong CD extrema.[6]

The blue shift of LMCT band was also observed in **3**. **3** did not give any absorption near 330 nm although an specific shoulder

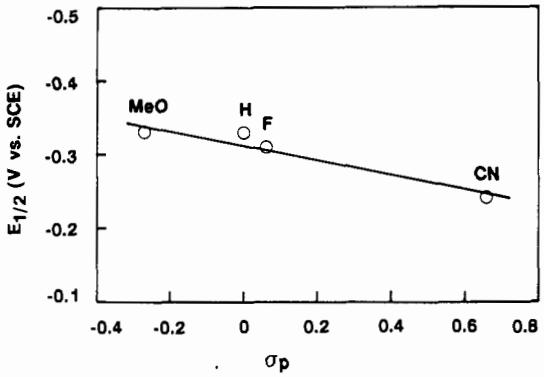

Figure 6. Correlation of redox potentials of $[Fe(Z\text{-cys-Pro-Leu-cys-Gly-NH-}C_6H_4\text{-}p\text{-}X)_2]^{2-}$ with the Hammett σ_p constant in DME.

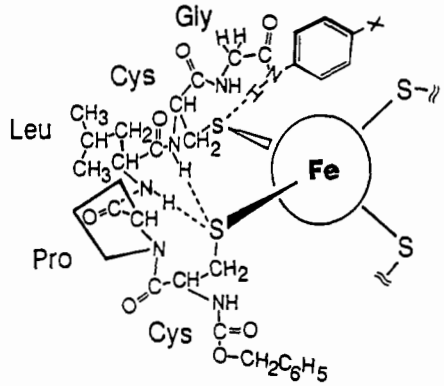

Figure 7. Schematic structure of $[Fe(Z\text{-cys-Pro-Leu-cys-Gly-NH-}C_6H_4\text{-}p\text{-}X)_2]^{2-}$.

is observed around 330 nm with molar extinction coefficients of 3900–4800 in **4–7** like that of Rd.[1]

6 exhibited six Cys CH_2 signals in the ^1H NMR spectrum between 150 and 260 ppm in acetonitrile-d_3 at 30 °C. The intensities of signals at 260 and 247 ppm, 230 and 218 ppm, 203 ppm, and 150 ppm are nearly equal and may be assigned to the four Cys CH_2 protons, respectively. On the other hand, the temperature dependence of resonances at the lower field, between 260 and 150 ppm, were investigated at +30, +10, −10, and −30 °C in acetonitrile-d_3. The plot of Fermi contact shifts ($\Delta H/H_0$) and reciprocal temperature ($1/T$) were nearly linear and obeyed the Curie–Weiss law. The result indicates that these complexes are mononuclear complexes with a high-spin Fe(II) ion and have no significant magnetic interactions among Fe(II) ions.[18]

Fe(II)–thiolato complexes are known to have variable structure depending on the Fe(II)/RS^- ratio. Mono- and polynuclear complexes gave ^1H NMR signals in different regions. For example, CH_2 protons of $[Fe(SCH_2CH_3)_4]^{2-}$ appeared at 196 ppm in CD_3CN at 27 °C,[3] while $[Fe_2(SCH_2CH_3)_6]^{2-}$ and $[Fe_4(SCH_2CH_3)_{10}]^{2-}$ gave signals at 69 ppm and 113 (terminal) and 133 ppm (bridging) in CD_3CN at 27 °C, respectively.[19] Therefore, the signals between 150 and 260 ppm for **6** were all from the mononuclear complex. Furthermore, the polynuclear bridging causes a red shift of LMCT absorption.[6] Such a shift was not observed in our model complexes. A polynuclear structure by bridging coordination of the peptide is thus excluded.

NH---S Hydrogen Bonds of $[Fe(Z\text{-cys-Pro-Leu-cys-Gly-NH-}C_6H_4\text{-}p\text{-}X)_2]^{2-}$. The complexes of $[Fe(Z\text{-cys-Gly-Val-OMe})_4]^{2-}$ (**1**) and **2** have absorption maxima in the near-UV region at 316 nm (5300) and 314 nm (5900) in acetonitrile, respectively (Table I). A slight blue shift of the ligand–metal charge-transfer absorption of **6** at 312 nm (5900) is ascribed to the variation of the Fe–S bond character by the formation of an NH---S hydrogen bond between the NH of the anilide residue and the S of the second cysteine residue. Otherwise, the absorption maxima are nearly unchanged whenever X is MeO, H, F, or CN. This indicates that if there are three NH---S hydrogen bonds in each Fe(II)–oligopeptide model complex, the absorption maximum will approach that of native Rd at 312 nm and is independent of the aromatic substituents. The presence of three NH---S hydrogen bonds, i.e. Leu–NH---S–Cys(1), Cys(2)–NH---S–Cys(1), and p-X-C_6H_4–NH---S–Cys(2), in the complexes of $[Fe(Z\text{-cys-(1)-Pro-Leu-cys(2)-Gly-NH-}C_6H_4\text{-}p\text{-}X)_2]^{2-}$ is similar to that in the *Clostridium pasteurianum* Rd for which the third one is Val(44)–NH---S–Cys(42) instead of p-X-C_6H_4–NH---S–Cys.[20]

6 gave three amide N^2H signals at about 40, 19, and −4 ppm with almost equal intensity in the ^2H NMR spectrum (see Figure 3a). Splitting of the signals at 40 and −4 ppm into two may indicate the existence of two isomers (nearly 1:1) in the case of **2** as discussed in the previous paper.[8] The macrocyclic chelation by the two Cys thiolate ligands of a Cys(1)-Pro-Leu-Cys(2) fragment to Fe(II) provides for the formation of two strong NH---S hydrogen bonds, Leu-NH---S-Cys(1) and Cys(2)-NH---S-Cys(1), which are shielded from solvent. Figure 7 shows the proposed structure of $[Fe(Z\text{-cys-Pro-Leu-cys-Gly-NH-}C_6H_4\text{-}p\text{-}X)_2]^{2-}$.

The formation of an NH---S hydrogen bond between anilide NH and cysteinyl S was further established by the ^{19}F NMR spectra of **8**. ^{19}F signal of the coordinated peptide of **8** shifts to lower field compared with the uncoordinated peptide ligand, i.e. Z-Cys(SH)-Pro-Leu-Cys(SH)-Gly-NH-C_6H_4-m-F, in contrast to that of **6**, which shifts to higher field compared with Z-Cys-(SH)-Pro-Leu-Cys(SH)-Gly-NH-C_6H_4-p-F. The attenuation of the shifts of contact-shifted peaks by distance from the metal atom with sign alternation are the behaviors expected for dominant contact interactions, assuming π-spin transfer.[21,22] The ^1H NMR signals of m-H and p-H have been reported to be observed at 22.3 and −23.5 ppm in the ^1H NMR spectrum of $[Fe(SPh)_4]^{2-}$ in acetonitrile-d_3 at 27 °C, respectively.[4] The peak due to the meta proton shifts to lower field and the one due to the para proton shifts to higher field. Thus, it is clear from these results that some charges flow from the metal center to the benzene ring of anilide through the NH---S hydrogen bond.

Redox Potentials of the Fe(II) Complexes of Peptide with Para-Substituted Anilide. The X-ray analysis of *C. pasteurianum* Rd has suggested that the Cys(39)-Pro-Leu-Cys(42)-Gly-Val chelating segment has three NH---S hydrogen bonds, Leu-(41)–NH---S–Cys(39) (3.55 Å); Cys(42)–NH---S–Cys(39) (3.71 Å) and Val(44)–NH---S–Cys(42) (3.88 Å).[20] The study of the Rd model complexes of Z-Cys-X-Y-Cys-OMe has revealed that the NH---S hydrogen bonds contribute to the positive shift of the Fe(II)/Fe(III) redox potential.[6] Another type of NH---S hydrogen bond occurs between Cys(2)–S and Val–NH in the complex $[Fe(Z\text{-cys(1)-Pro-Leu-cys(2)-Gly-Val-OMe})_2]^{2-}$ in a nonpolar solvent and further contributes to the positive shift.[8] These hydrogen bonds have been considered to be crucial for regulating the redox potential of iron-sulfur proteins, not only for the **1Fe** model complexes but also the **4Fe** ones.[10]

The para-substituent effect of the anilide residue can be estimated by the Hammett constant. The correlation of the redox potentials of **4–7** in DME with σ_p values is shown in Figure 6. The linear relation is observed between them. **7** has the most positively shifted redox potential at −0.24 V vs SCE in DME. This behavior can be explained by the strength of NH---S hydrogen bonds. It became clear that the stronger the electron-withdrawing para substituent of the anilide residue is, the more positive redox potential the corresponding complex in DME has. The strength

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of the NH---S hydrogen bonds in **4–7** in a weakly nonpolar solvent such as DME is in the order X = OMe < H < F < CN. The electron density on the S atom of the peptide ligand was decreased by the electron-withdrawing substituent through the NH---S hydrogen bond and gave a positive shift of the redox potentials.[6]

Conclusion

Form this study, the NH---S hydrogen bonds were found to play an important role in controlling the redox potentials. The observed positively shifted redox potential in native Rd is thus also interpreted by the formation of the same types of NH---S hydrogen bonds. The observation of the charge flow through the NH---S hydrogen bond makes it possible that the hydrogen bond is one of the candidates for a channel for electron transfer in Rd.

Our model complexes exhibited an absorption maximum around 330 nm similar to that in native Rd. It has been thought that there is some kind of electronic interaction between the coordinated sulfur atom and the phenyl rings.[23,24] Further study is required in order to assign the absorption maximum and to understand the effect of the phenyl rings of tyrosyl and phenylalanyl residues close to the Fe ion in Rd.

Registry No. Z-Cys(Acm)-Pro-Leu-OH, 82154-63-0; HCl·Cys(Acm)-Gly-NH-C_6H_5, 135615-70-2; Z-Cys(Acm)-Pro-Leu-Cys(Acm)-Gly-NH-C_6H_5, 135615-71-3; Z-Cys(Acm)-Pro-Leu-Cys(Acm)-Gly-NH-C_6H_4-*p*-OMe, 135615-72-4; Z-Cys(Acm)-Pro-Leu-Cys(Acm)-Gly-NH-C_6H_4-*p*-F, 135615-73-5; Z-Cys(Acm)-Pro-Leu-Cys(Acm)-Gly-NH-C_6H_4-*p*-CN, 135615-74-6; Z-Cys(Acm)-Pro-Leu-Cys(Acm)-Gly-NH-C_6H_4-*m*-F, 135615-75-7; Z-Cys(SH)-Pro-Leu-Cys(SH)-Gly-NH-C_6H_4-*p*-OMe, 135615-77-9; Z-Cys(SH)-Pro-Leu-Cys(SH)-Gly-NH-C_6H_5, 135615-78-0; Z-Cys(SH)-Pro-Leu-Cys(SH)-Gly-NH-C_6H_4-*p*-F, 135615-76-8; Z-Cys(SH)-Pro-Leu-Cys(SH)-Gly-NH-C_6H_4-*p*-CN, 135615-79-1; $(Et_4N)_2$[Fe(Z-Cys-Pro-Leu-Cys-Gly-NH-C_6H_4-*p*-OMe)$_2$], 135619-95-3; $(Et_4N)_2$[Fe(Z-Cys-Pro-Leu-Cys-Gly-NH-C_6H_5)$_2$], 135619-97-5; $(Et_4N)_2$[Fe(Z-Cys-Pro-Leu-Cys-NH-C_6H_4-*p*-F)$_2$], 135619-99-7; $(Et_4N)_2$[Fe(Z-Cys-Pro-Leu-Cys-Gly-NH-C_6H_4-*p*-CN)$_2$], 135620-01-8; Z-Cys(SH)-Pro-Leu-Cys(SH)-Gly-NH-C_6H_4-*m*-F, 135615-80-4; $(Et_4N)_2$[Fe(Z-Cys-Pro-Leu-Cys-Gly-NH-C_6H_4-*m*-F)$_2$], 135638-53-8; Z-Cys(SH)-Pro-Leu-Cys(SH)-Gly-N^{2}H-C_6H_4-*p*-OMe, 135615-81-5; Z-Cys(SH)-Pro-Leu-Cys(SH)-Gly-N^{2}H-C_6H_5, 135615-82-6; Z-Cys(SH)-Pro-Leu-Cys(SH)-Gly-N^{2}H-C_6H_4-*p*-F, 135615-83-7; Z-Cys(SH)-Pro-Leu-Cys(SH)-Gly-N^{2}H-C_6H_4-*p*-CN, 135615-84-8; $[Fe^{II}$(Z-Cys-Pro-Leu-Cys-Gly-NH-C_6H_4-*p*-OMe)$_2]^{2-}$, 135619-94-2; $[Fe^{II}$(Z-Cys-Pro-Leu-Cys-Gly-NH-C_6H_5)$_2]^{2-}$, 135619-96-4; $[Fe^{II}$(Z-Cys-Pro-Leu-Cys-Gly-NH-C_6H_4-*p*-F)$_2]^{2-}$, 135619-98-6; $[Fe^{II}$-(Z-Cys-Pro-Leu-Cys-Gly-NH-C_6H_4-*p*-CN)$_2]^{2-}$, 135620-00-7.

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Mononuclear Manganese(IV) in Tridentate ONO Coordination. Synthesis, Structure, and Redox Regulation via Oxygen Donor Variation

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The aerobic reaction of *N*-(2-hydroxyphenyl)salicylaldimine (H_2amp) and 2,2′-dihydroxyazobenzene (H_2azp) with manganese(II) or manganese(III) affords $Mn^{IV}(amp)_2$ and $Mn^{IV}(azp)_2$, respectively. In a similar reaction, 2-hydroxy-2′-carboxy-5-methylazobenzene (H_2azc) furnishes $KMn^{III}(azc)_2 \cdot 4H_2O$, which can be oxidized to $Mn^{IV}(azc)_2$ by persulfate. The X-ray structures of $Mn(amp)_2$ and $Mn(azp)_2$ are reported. Crystal data for $Mn(amp)_2$: space group $C2/c$, $Z = 4$, $a = 20.163$ (12) Å, $b = 7.921$ (4) Å, $c = 12.994$ (10) Å, $\beta = 97.65$ (5)°, and $V = 2057$ (2) Å^3. Crystal data for $Mn(azp)_2$: space group $P\bar{1}$, $Z = 2$, $a = 7.766$ (5) Å, $b = 10.377$ (5) Å, $c = 12.964$ (5) Å, $\alpha = 92.80$ (3)°, $\beta = 90.33$ (5)°, $\gamma = 102.92$ (4)°, and $V = 1016.8$ (9) Å^3. The ligands act as meridional tridentate ONO donors. The Mn–O distances fall in the range 1.861 (4)–1.893 (6) Å. The Mn–N(azomethine) length, 1.968 (8) Å, is shorter than the average Mn–N(azo) length, 2.007 (10) Å. The MnO_4N_2 coordination spheres deviate considerably from octahedral geometry, and this is reflected in the EPR spectra of the complexes: strong and weak signals near $g = 4$ and $g = 2$, respectively. The manganese(IV)–manganese(III) reduction potentials of $Mn(amp)_2$, $Mn(azp)_2$, and $Mn(azc)_2$ in dimethyl sulfoxide are respectively −0.09, +0.15, and 0.31 V vs SCE. In MnO_4N_2-type salicylaldimine complexes, the potential varies with oxygen donors according to the order alcoholate < phenolate < carboxylate. The total shift can be as large as 600 mV. The trend is correlated with the p*K*'s of the oxygen donor functions. The significance of the results with respect to carboxylate binding of PS II manganese is noted.

Introduction

The coordination environment of the tetramanganese water oxidation site of photosystem II (PS II) consists of O and N donors,probably more of the former.[1-3] The metal oxidation state is generally believed to lie in the range 2+ to 4+. Plausible models of the tetrametal site span a number of alternatives.[2,4-9] Mononuclear manganese(IV) centers have been implicated[10] in the S_2 state of PS II. Synthetic monomanganese(IV) species in biomimetic O, N coordination are thus of interest. Authentic examples of such complexes are sparse, and structural characterization has been achieved in only a few cases.[11-19]

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