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Orientation-Dependent ^{1}H and ^{13}C Isotropic Shifts of Low-Spin Tetracyano(1,2-diamine)ferrates(III)

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Paramagnetic ^{1}H and ^{13}C NMR signals of low-spin tetracyanodiamineferrates(III), $[Fe^{III}(CN)_4(diamine)]^-$, containing ethylenediamine, (*R*)-1,2-propanediamine, (1*R*,2*R*)-*trans*-cyclohexanediamine, and *N*,*N*′-dimethylethylenediamine, were assigned by the use of rapid electron exchange between the Fe^{III} complex and the diamagnetic Fe^{II} complex with an identical set of ligands. The C-$\underline{H}$ on the five-membered chelate ring showed isotropic shifts with different signs depending on their orientations: 14—18 ppm downfield and ca. 16—23 ppm upfield for axial and equatorial protons respectively. The isotropic shifts for the ^{13}C nuclei were attenuated, their signs alternating with each separation by one carbon-carbon bond from the metal ion. The isotropic shift is compared with that of the Ni^{II} complex qualitatively in terms of the dipolar and Fermi contact shifts.

The paramagnetic NMR spectra of Fe^{III} complexes are widely used to assign their spin states and stereochemistry for rather complex molecules, such as those with porphyrins[1] and heme proteins.[2-4] There have, however, been few studies on the paramagnetic NMR spectroscopy for the Fe^{III} complexes with simple structures. The analysis of the simple Fe^{III} complexes will provide some insights into the mechanism of the paramagnetic shift.

The Fe^{III} complexes, tetracyano(diamine)ferrates(III) $[Fe^{III}(CN)_4(diamine)]^-$,[5-8] are low spin,[7,8] and their structures are so simple that all the paramagnetic signals can be identified.

The stereochemistry of the five-membered chelate rings formed with various diamines has been investigated by means of a wide range of experimental methods.[9] The present Fe^{III} complexes offer a good opportunity to study their NMR spectra because: 1) They are kinetically inert, and so there is no need to consider complex formation equilibrium; 2) the corresponding Fe^{II} complexes, tetracyano(diamine)ferrates(II) are diamagnetic, and their NMR spectra have been analyzed by conventional methods; 3) the rapid electron exchange between low-spin Fe^{II} and Fe^{III} complexes affords the time-averaged spectra of each complex, depending on the compositions for mixtures of them, and 4) the stereochemistry of the five-membered chelate rings formed with 1,2-diamines has been extensively studied, and so the existing information about them can be utilized for reference.

Reports on the paramagnetic NMR spectra of transition metal complexes with saturated ligands such as 1,2-diamines are relatively few in number. Ni^{II} complexes with diamines have been reported by Reilley and his colleagues,[10,11] while Ni^{II} and Co^{II} complexes with monoamines have been reported by Morishima et al.[12] The former studies have revealed the usefulness of paramagnetic NMR for the analysis of the structures of metal complexes in solution and their dynamics. The latter treated the origin of the paramagnetic shift and the orientation-dependence of spin propagation by considering spin-polarization and direct-spin-delocalization mechanisms. However, the NMR signals of the Ni^{II} complexes are relatively broad, and there is a problem that the chemical species responsible for NMR is really a mixture formed by an equilibrium among several species.

We have now investigated the paramagnetic NMR of these Fe^{III} complexes in order to elucidate the mechanism of the paramagnetic shift. In this paper, the assignments of all the $\underline{C}$-$\underline{H}$ of some 1,2-diamines coordinated to the Fe^{III} center and a qualitative conclusion about the use of the isotropic shift for the analysis of the stereochemistry of chelate rings will be described.

Experimental

Materials. Sodium tetracyano(diamine)ferrates(III), and their corresponding Fe^{II} complexes were isolated according to the methods reported previously, using ethylenediamine (en),[5,13] (*R*)-1,2-propanediamine(*R*-pn),[6,7] (1*R*,2*R*)-*trans*-cyclohexanediamine(*R*-chxn),[6,7] and *N*,*N*′-dimethylethylenediamine(s-Me$_2$en)[5,13] as diamines.

^{1}H and ^{13}C NMR Measurements. A weighed sample (40—50 mg) in a sample tube 5 mm in diameter was dissolved in pD 2.0 DCl-D$_2$O (0.3 cm^3) to prevent a disproportionation reaction with concomitant diamine dehydrogenation[14] in a neutral or basic aqueous solution, from occurring. Sodium 3-trimethylsilylpropionate-2,2,3,3-*d*$_4$ (TSP; 0.00 ppm) and 1,4-dioxane (67.44 ppm) were used as the internal stadards for the ^{1}H and ^{13}C NMR measurements respectively. The chemical shift, δ, is positive for a downfield shift from the standards. The spectra were recorded with JEOL MH-100 and FX-100 spectrometers.

The ^{1}H and ^{13}C NMR spectra of the Fe^{II} complexes were measured in a manner similar to that described above except that D$_2$O was used as the solvent.

Changes in Chemical Shift by the Variation in the Mixing Ratio of the Fe^{III} and the Corresponding Fe^{II} Complexes (Variation Experiment). In a 5 cm^3 flask, ca. 300 mg (10^{-3} mol) of the Fe^{II} complex was dissolved in pD 2.0 DCl-D$_2$O containing 0.4% sodium 2,2-dimethyl-2-silapentane-5-sulfonate (DSS; 0.00 ppm) and 1,4-dioxane. Weighed amounts of the corresponding Fe^{III} complex were mixed with this solution (0.5 cm^3) to make mixtures in various compositions. The ^{1}H and ^{13}C NMR spectra were measured at 300 K with JEOL MH-100 and FX-100 spectrometers.

Direct Preparation of the Sample Solution of the Fe^{III} s-Me$_2$en Complex. The isolated Fe^{II} s-Me$_2$en complex (50.2 mg) was dissolved in 0.5 cm^3 of D_2O. After standing at room temperature for more than 5 min, the solution was acidified by the addition of 45.1 mg of 37% DCl; $Na_2S_2O_8$ (104.0 mg) was then added at 0 °C. The mixture was allowed to stand at 0 °C for 2 h, and the resulting solution was used for the ^{1}H NMR measurement.

Results and Discussion

^{1}H and ^{13}C NMR Spectra of Fe^{III} Complexes and Assignments of Their Signals. Tetracyano(1,2-diamine)ferrate(III) and tetracyano(1,2-diamine)ferrate(II) complexes are both low-spin;[7,8] their electronic configurations are $(t_{2g})^5$ and $(t_{2g})^6$. The large variation in the chemical shifts and the diminution of the ^{1}H–^{1}H couplings precludes the assignments of the paramagnetic NMR signals by conventional methods. Since no previous examples of this class of Fe^{III} complex are known, we could not use any previously reported information about the chemical shift. The signals have been assigned by the use of the rapid electron exchange between the pair of low-spin Fe^{II} and Fe^{III} complexes (variation experiment). At first, the signals of the Fe^{II} complexes were assigned by conventional methods. Then the signals of the Fe^{III} complexes were correlated with those of the Fe^{II} complexes on the basis of the spectral changes induced by the variation in the ratio of the Fe^{III} complexes to the corresponding Fe^{II} complexes.

The values of the chemical shifts, δ, for the Fe^{III} and Fe^{II} complexes described below are summarized in Table 1. The numbering of the nuclei for each complex is denoted in Fig. 1 and is used throughout this paper.

(*R*)-1,2-Propanediamine Complex. The *R*-pn chelates are well known to have λ *gauche* conformations in the solid state,[15–18] in which the methyl groups are equatorial to the chelate ring. The conformations in solution have been investigated by means of ^{1}H NMR spectroscopy.[19–22] For example, the *R*-pn chelate ring of $[Co^{III}(CN)_4(R\text{-pn})]^-$ is predominantly in a λ *gauche* form in solution.[20,21] The ^{1}H NMR spectrum of $[Fe^{II}(CN)_4(R\text{-pn})]^{2-}$, has been shown to be similar to that of this Co^{III} complex.[6]

Figure 2 shows the ^{1}H NMR spectrum of $[Fe^{III}(CN)_4(R\text{-pn})]^-$. Three signals were observed — at 17.40, 9.31, and −20.05 ppm — with an area ratio of 2:3:1. The signal at 9.31 ppm was assigned to the methyl protons because of its area ratio. Because of an unpaired electron, the signals are distributed over the wide range of ca. 37 ppm.

Figure 3 shows the ^{1}H NMR spectra of the mixtures of Fe^{II} and Fe^{III} complexes obtained by varying the mole fraction of the latter, *f*, at 300 K. The spectrum

Table 1. ^{1}H and ^{13}C NMR Chemical Shifts[a] of $[Fe^{II,III}(CN)_4(\text{diamine})]^{2-,-}$

Diamine	Nucleus	Chemical shift/ppm Fe^{II}	Chemical shift/ppm Fe^{III}	Isotropic shift/ppm	Contact shift of Ni^{II}/ppm[b]
en	H	2.50	−0.91	−3.41	93.8
	C	45.2	251.6	206.4	−328
R-pn	H^{1a}	2.74	17.40	14.66	21.0
	H^{2a}	2.16	17.40	15.24	21.0
	H^{2e}	2.61	−20.05	−22.66	148.3
	H^3	1.22	9.31	8.09	18.0
	C^1	52.7	241.5	188.8	−330
	C^2	50.9	248.0	197.1	−282
	C^3	19.6	−49.2	−68.8	471
R-chxn	H^{1a}	2.04	15.98	13.94	
	H^{2a}	1.16	10.86	9.70	
	H^{2e}	2.04	10.86	8.82	
	H^{3a}	1.16	6.61	5.45	
	H^{3e}	1.65	1.49	−0.16	
	C^1	60.6	258.3	197.7	
	C^2	35.6	−18.9	−54.5	
	C^3	25.3	30.0	4.7	
s-Me$_2$en	H^a	2.12	19.84	17.72	40.0[c]
	H^e	2.78	−12.84	−15.62	156.3[c]
	H^2	2.52	−17.59	−20.11	133.8[c]
	C^1	54.2	301.1	246.9	
	C^2	41.8	156.1	114.3	

a) The positive values indicate downfield shifts. b) Refs. 19 and 28. c) Racemic form.

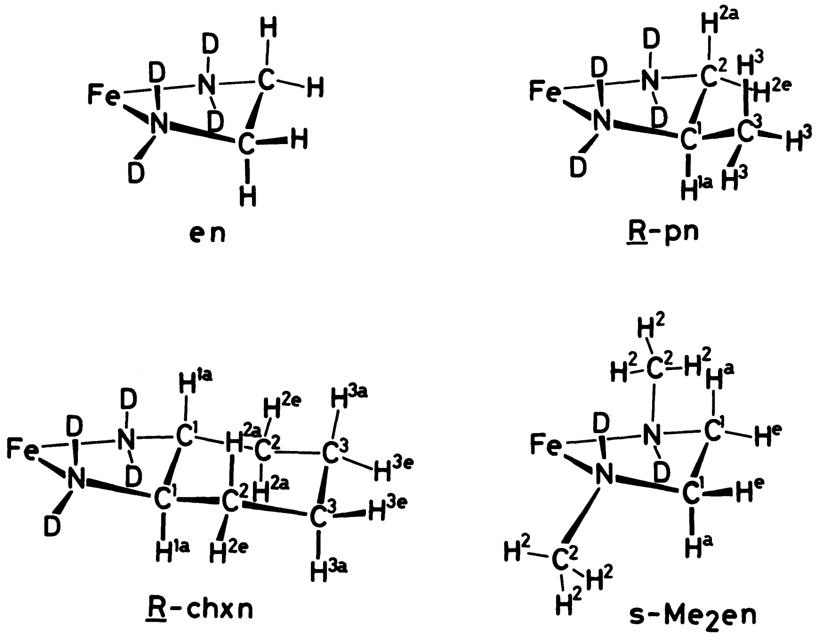

Fig. 1. Schematic structures of the chelates and the numbering of protons and carbons. Fe=Fe(CN)$_4$

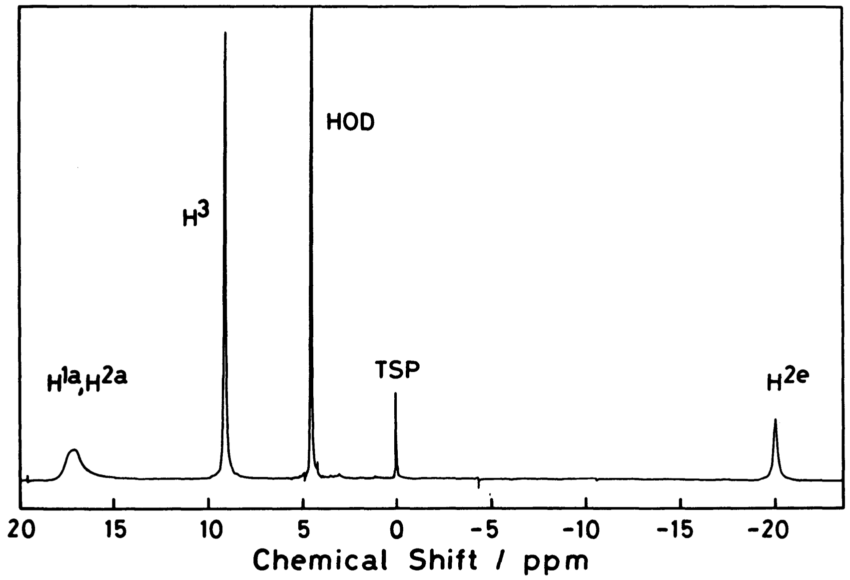

Fig. 2. ^{1}H NMR spectrum of $[Fe(CN)_4(R\text{-pn})]^-$ in 10^{-2} mol dm^{-3} DCl.

shown at the top is that of $[Fe^{II}(CN)_4(R\text{-pn})]^{2-}$; the signals at 2.74, 2.61, 2.16, and 1.22 ppm have been assigned to H^{1a}, H^{2e}, H^{2a}, and H^3 respectively.[6] When small amounts of the Fe^{III} complex were added to the Fe^{II} complex, the ^{1}H NMR spectra changed in shape depending on f: The signal of H^{2e} shifted to an upper field, but the other proton signals shifted downfield. The ^{1}H–^{1}H couplings ($^{3}J_{HCCH}$) could be observed in the region of small f values: the apparent doublet and triplet of H^{2e} and H^{2a} were observed clearly until f reached 0.055.

The δ values vary in proportion to f, as is shown in Fig. 4. This linear relationship shows that the signals for the mixtures are averaged by the rapid electron exchange between the Fe^{II} and Fe^{III} complexes.[23–25] The rate is in the region of fast-limit on the NMR time scale. By the extrapolation of f to 1.0, the Fe^{III} complex signals are assigned as listed in Table 1.

The ^{13}C NMR spectra of both $[Fe^{II}(CN)_4(R\text{-pn})]^{2-}$ and $[Fe^{III}(CN)_4(R\text{-pn})]^-$ showed three signals coupled with adjacent protons in off-resonance measurements. The signals at 241.5, 248.0, and −49.2 ppm for the Fe^{III} complex and those at 52.7, 50.9, and 19.6 ppm for the Fe^{II} complex are assigned to C^1, C^2, and C^3

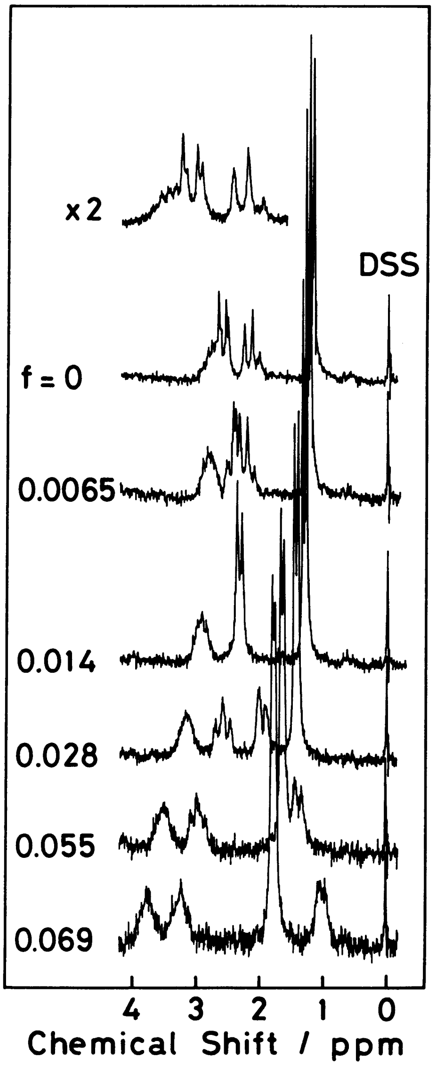

Fig. 3. ^{1}H NMR spectral changes of [Fe(CN)$_4$(*R*-pn)]$^{2-}$ on addition of [Fe(CN)$_4$(*R*-pn)]$^-$ in 10^{-2} mol dm^{-3} DCl. *f*: Mole fraction of the Fe$^{\mathrm{III}}$ chelate.

respectively.

Ethylenediamine Complex. As is shown in Table 1, only one signal is observed for each of the Fe$^{\mathrm{III}}$ and Fe$^{\mathrm{II}}$ complexes. The methylene proton signals appeared at 2.50 and −0.91 ppm for the Fe$^{\mathrm{II}}$ and Fe$^{\mathrm{III}}$ complexes respectively. Each value is in good agreement with the mean of the δ's for H^{2a} and H^{2e} of the *R*-pn chelate: 2.39 and −1.33 ppm for the Fe$^{\mathrm{II}}$ and Fe$^{\mathrm{III}}$ complexes respectively. This agreement indicates that the axial and equatorial methylene protons are averaged by the rapid interconversion of the chelate ring between δ and λ conformations.[11,19]

(1*R*,2*R*)-*trans*-Cyclohexanediamine Complex. The Fe$^{\mathrm{II}}$ complex, [Fe(CN)$_4$(*R*-chxn)]$^{2-}$, shows three ^{13}C signals in the usual region: C^1, 60.6; C^2, 35.6; C^3, 25.3 ppm. This assignment is based on the multiplicity in the off-resonance experiment (a doublet, a triplet, and a triplet) and the electron withdrawing effect of the amino groups.

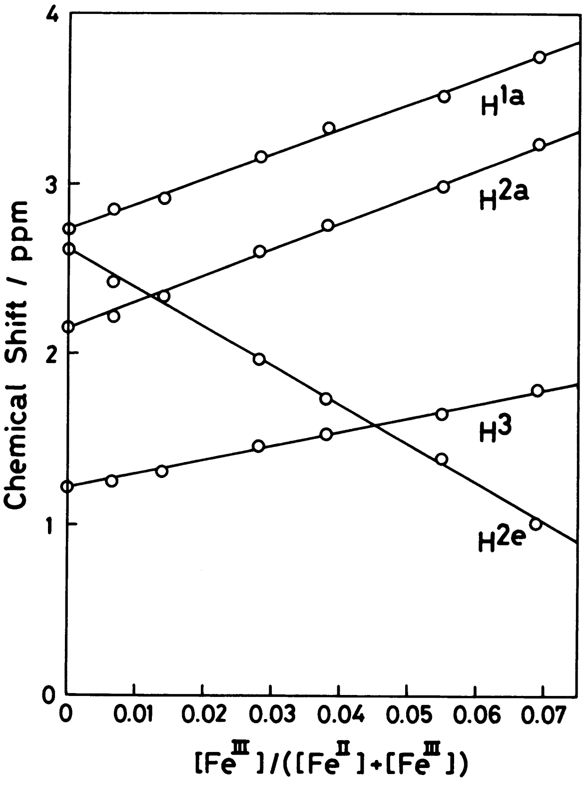

Fig. 4. Plots of chemical shifts of ^{1}H resonances of the mixture of [Fe(CN)$_4$(*R*-pn)]$^{2-}$ and [Fe(CN)$_4$(*R*-pn)]$^-$ vs. mole fractions of the Fe$^{\mathrm{III}}$ chelate.

The ^{13}C NMR spectrum of the corresponding Fe$^{\mathrm{III}}$ complex, shown in Fig. 5A, exhibited three signals — at 258.3, −18.9, and 30.0 ppm. These signals were correlated to those of the Fe$^{\mathrm{II}}$ complex as follows by means of the variation experiments: 258.3→60.6; −18.9→35.6; 30.0→25.3 ppm. They were thus assigned to C^1, C^2, and C^3 respectively.

The ^{1}H NMR spectrum of the Fe$^{\mathrm{II}}$ complex, shown at the top of Fig. 6, exhibited only three peaks — at 2.04, 1.65, and 1.16 ppm, with an area ratio of 2:1:2. These peaks have previously been assigned to a composite of H^{1a} and H^{2e}, H^{3e}, and a composite of H^{2a} and H^{3a} respectively.[6]

The Fe$^{\mathrm{III}}$ complex showed four ^{1}H NMR signals, with an area ratio of 1:2:1:1, at 15.98, 10.86, 6.61, and 1.49 ppm. These signals were correlated to those of the Fe$^{\mathrm{II}}$ complex by means of the variation experiments (Fig. 6). The results of the signal correlation are shown in Fig. 7.

The ^{1}H signals of the Fe$^{\mathrm{III}}$ complex were assigned in the following way. The signal at 1.49 ppm was correlated to the signal at 1.65 ppm attributable to H^{3e} for the Fe$^{\mathrm{II}}$ complex, and so it was assigned to H^{3e}. The ^{1}H selective irradiation at 6.61 or 1.49 ppm changed the Fe$^{\mathrm{III}}$ C^3 signal from a double-doublet (Fig. 5B) to a doublet, as is shown in Figs. 5C and D. Thus, the signal at 6.61 ppm was assigned to H^{3a}. Since the H^{1a} and H^{2a} in the Fe$^{\mathrm{III}}$ *R*-pn complex

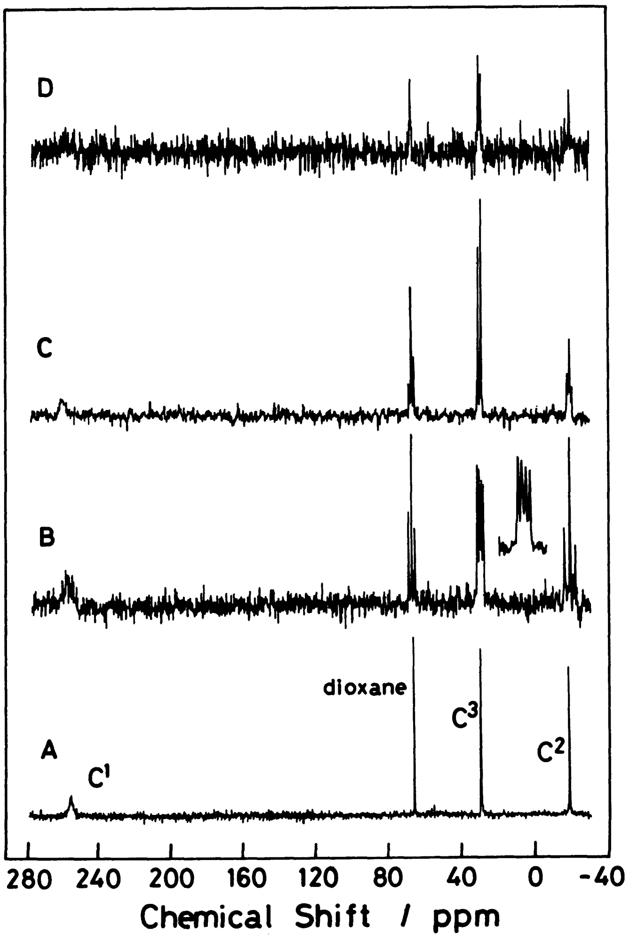

Fig. 5. ^{13}C NMR spectra of $[\mathrm{Fe(CN)_4}(R\text{-chxn})]^-$. A. complete decoupling for ^{1}H; B. off-resonance for ^{1}H; C and D. selective irradiation at $\mathrm{H^{3a}}$ and $\mathrm{H^{3e}}$.

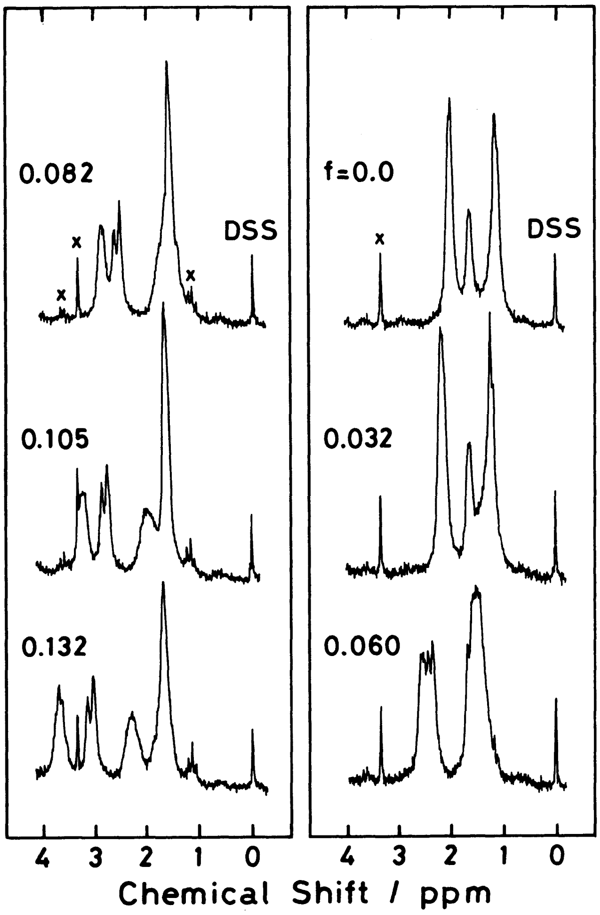

Fig. 6. ^{1}H NMR spectral changes of $[\mathrm{Fe(CN)_4}(R\text{-chxn})]^{2-}$ on addition of $[\mathrm{Fe(CN)_4}(R\text{-chxn})]^-$ in 10^{-2} mol dm^{-3} DCl. *f*: Mole fraction of the $\mathrm{Fe^{III}}$ chelate. X indicates signals due to methyl and ethyl alcohols.

resonated at the most downfield position, the signal at 15.98 ppm was assigned to $\mathrm{H^{1a}}$. The remaining peak at 10.86 ppm corresponds to the two peaks at 1.16 and 2.04 ppm for the $\mathrm{Fe^{II}}$ complex and consists of $\mathrm{H^{2a}}$ and $\mathrm{H^{2e}}$ signals, with, incidentally, the same chemical shift.

***N,N′*-Dimethylethylenediamine Complex.** The s-Me$_2$en complex is able to adopt two kinds of geometrical isomers on coordination to a metal ion. A pair of the racemic form with two pseudoequatorial methyl groups is known to be more stable than the meso form with a pseudoaxial and a pseudoequatorial methyl group.[11,19]

The isolated $[\mathrm{Fe^{III}(CN)_4(s\text{-}Me_2en)}]^-$ showed three ^{1}H NMR signals — at 19.84, −12.84, and −17.59 ppm with an area ratio of 1:1:3. The last signal was assigned to the methyl protons, $\mathrm{H^2}$, on the basis of the area ratio. Since the $\mathrm{Fe^{III}}$ *R*-pn complex showed $\mathrm{H^{2a}}$ and $\mathrm{H^{2e}}$ signals at 17.40 and −20.05 ppm, the former two signals of the $\mathrm{Fe^{III}}$ s-Me$_2$en complex were assigned to $\mathrm{H^a}$ and $\mathrm{H^e}$ respectively. The separation of the $\mathrm{H^a}$ and $\mathrm{H^e}$ shifts by ca. 33 ppm shows that the $\mathrm{Fe^{III}}$ complex is the racemic form. The ^{13}C NMR spectrum

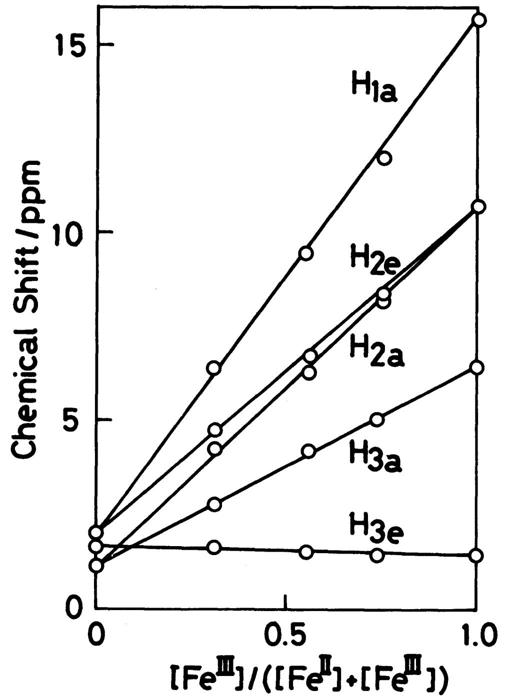

Fig. 7. Plots of chemical shifts of the mixture of $[\mathrm{Fe(CN)_4}(R\text{-chxn})]^{2-}$ and $[\mathrm{Fe(CN)_4}(R\text{-chxn})]^-$ vs. mole fraction of the $\mathrm{Fe^{III}}$ chelate.

of the Fe^{III} complex showed the methyl(C^2) and methylene(C^1) carbon signals at 156.1 and 301.1 ppm respectively.

The isolated Fe^{II} s-Me_2en complex showed the methyl signal at 2.52 ppm as a singlet and the methylene signals as an A_2B_2 multiplet, the apparent doublets of which at 2.12 and 2.78 ppm were assigned to H^a and H^e respectively, according to the results of Tiethof and Cooke.[26] However, the ^{13}C NMR spectrum of the isolated Fe^{II} complex exhibited two signals for the methylene carbon — at 54.2 and 52.8 ppm, with an intensity ratio of ca. 2:1, along with a single methyl signal at 41.8 ppm.[13] The cobalt complex isostructural to the Fe^{II} complex, $[Co^{III}(CN)_4(s\text{-}Me_2en)]^-$, also exhibited two methylene-carbon signals in a ratio of ca. 2:1.[27]

The results presented above suggest that the isolated Fe^{II} complex contained the racemic and meso isomers, while the isolated Fe^{III} complex consisted of only the racemic isomer. Since the meso isomer of the Fe^{III} complex was expected to have been eliminated during the procedures for isolation, the Fe^{II} complex was oxidized under acidic conditions and the resulting mixture was employed for NMR measurement without undertaking any procedure for separation. The two methylene and one methyl ^1H signals expected for the meso Fe^{III} complex were found at 6.40, 0.36, and −16.75 ppm, with an intensity ratio of 1:1:3, in addition to those for the racemic form. The chemical-shift difference of ca. 6 ppm between the two methylene singals is quite small compared with that of ca. 33 ppm for the racemic form. The s-Me_2en chelate in the meso isomer exists as an equilibrium mixture of the δ and λ forms shown in Fig. 8. Although the four methylene protons in each form are in a different magnetic environment because of the two unsymmetrical methyl groups, the conformational interconversion of the chelate ring between the two forms magnetically replace H^{1a} and H^{1e} with H^{2e} and H^{2a} respectively. Since the interconversion is very rapid in the NMR time scale at room temperature, each couple of the protons shows a mean signal. However, the difference in the chemical shift between the two mean signals can be expected to be much smaller than that for the racemic isomer, firstly because each mean signal is the average of an axial and an equatorial proton signal, and secondly because the difference in chemical shift between them arises only from the difference in position relative to the two methyl groups. Thus, the observation of the two mean signals of the methylene protons with a small separation from each other confirms the assignment of these signals to the meso isomer. The population of these isomers was obtained as racemic:meso=1.7:1 based on the signal intensities. Since the intensity ratio observed for the ^{13}C NMR spectrum of the isolated Fe^{II} complex is almost the same as this population, the signals at 54.2 and 52.8 ppm were assigned to the methylene carbon of the racemic and meso isomers respectively.

The variation experiment using the isolated Fe^{II} and Fe^{III} complexes showed the two sets of methylene and methyl signals. The intensity ratio between them was ca. 2:1. However, the changes in chemical shift observed in the variation experiment were not proportional to the mole fraction of the Fe^{III} complex, for there are electron exchange reactions among the racemic Fe^{II}, meso Fe^{II}, racemic Fe^{III}, and meso Fe^{III} complexes. The major and minor sets of signals, however, were correlated to the signals of the racemic and meso Fe^{III} complexes respectively. The analysis of this system will be described elsewhere.

The following arguments will be restricted to the racemic form.

Isotropic Shifts of the Fe^{III} Complexes and Comparison with Those of Ni^{II} Complexes. Isotropic shift for the Fe^{III} complex, δ^{iso}, is defined as the difference in chemical shift between the Fe^{III} and the corresponding Fe^{II} complexes: $\delta^{iso}=\delta_{Fe^{III}}-\delta_{Fe^{II}}$. The isotropic shifts are summarized in the third column of Table 1. The isotropic shifts of several $[Ni^{II}(H_2O)_{6-2x}(diamine)_x]^{2+}$,[19,28] defined as $\delta^{iso}=\delta_{Ni^{II}}-\delta_{free\ amine}$, are also incorporated in Table 1 for the sake of comparison.

The isotropic shift is the sum of two contributions: the Fermi contact shift (δ^{con}) and the dipolar shift (δ^{dip}). Since the distribution of the two unpaired spins in the $t_{2g}^6e_g^2$ configuration is spherical, δ^{dip} has been regarded as near zero for Ni^{II} complexes. Thus, the δ^{iso}'s for Ni^{II} complexes have been regarded as δ^{con}'s.[29]

A low-spin Fe^{III} complex has, on the other hand, a large magnetic anisotropy, and both terms contribute

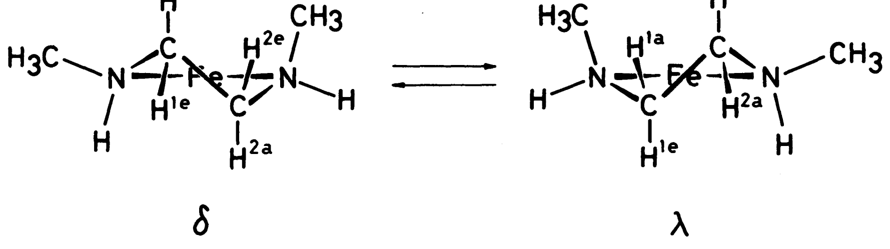

Fig. 8. Schematic structures of the meso s-Me_2en chelate. Fe=$Fe(CN)_4$

to δ^{iso}. If the δ^{iso} for the Fe^{III} complex arises from the Fermi contact interaction, the difference in spin transfer mechanism between low-spin Fe^{III} (L→vacant e_g) and Ni^{II} (L→singly occupied e_g) predicts that the sign of δ^{iso} for Fe^{III} is the opposite of that of Ni^{II}.30) The observed sign of δ^{iso} is not, however, always opposite to that of the Ni^{II} complex, as represented by protons axial to the chelate ring. This confirms that both contributions operate in the Fe^{III} complexes. Qualitatively, however, the δ^{con} for Fe^{III} complex can reasonably be assumed to have the sign opposite to that of the Ni^{II} complex, but the magnitude is not necessarily the same.

Location Dependence of ^{13}C Isotropic Shifts. Carbon atoms bonded to the nitrogen have large positive δ^{iso}'s: 190—250 ppm for members of the chelate ring and 114 ppm for *N*-methyl carbon. The carbon atoms separated by one C–C bond from them, such as C^2 in *R*-chxn and C^3 in *R*-pn, have the smaller negative δ^{iso}'s of −54.5 and −68.8 ppm. The third carbon atom in *R*-chxn, C^3, has, in turn, the small positive δ^{iso} value of 4.7 ppm. ^{13}C δ^{iso} thus alternates in sign with each separation by one C–C bond and attenuates repidly as the number of bonds between the carbon and the Fe^{III} ion increases. This characteristic of ^{13}C δ^{iso} suggests that the Fermi contact shift, δ^{con}, predominates in ^{13}C δ^{iso} for the present Fe^{III} complexes; i.e., the unpaired electron spin is propagated through N–C and/or C–C bonds, mainly by the spin polarization effect.31–33)

The δ^{iso} of the *N*-methyl carbon of the s-Me$_2$en complex is about half the δ^{iso} of the methylene carbon. However, the small difference in δ^{iso} between the methyl C^3 of *R*-pn and the methylene C^2 of *R*-chxn indicates that the spin is propagated more easily to the chelate ring than to the *N*-alkyl groups in the present Fe^{III} complexes.

The isotropic shifts of the relevant Ni^{II} complexes have been reported only for en and pn complexes.28) The ratios of δ^{iso} for the Ni^{II} complexes to δ^{iso} for the Fe^{III} complexes are between −1.4 and −1.8 for the carbons on the chelate rings. This invariance of the ratio shows that Fermi-contact interaction makes the main contribution to the ^{13}C paramagnetic shifts of the Fe^{III} complexes as well as those of the Ni^{II} complexes.

Orientation Dependence of ^{1}H Isotropic Shifts. The axial protons on the five-membered chelate ring have shown positive δ^{iso}'s: 14.66 and 15.24, 13.94, and 17.72 ppm for the *R*-pn, *R*-chxn, and s-Me$_2$en complexes respectively. On the other hand, the equatorial protons have shown negative δ^{iso}'s: −22.66 and −15.62 ppm for the *R*-pn and s-Me$_2$en complexes. The results show that the axial and equatorial protons on the five-membered chelate ring show δ^{iso} values opposite in sign, whereas significant δ^{iso} values have been observed in Ni^{II} complexes only for equatorial protons.11,19)

In the *R*-chxn complex, both protons bound to the carbon atom next to the chelate ring have positive δ^{iso}'s: H^{2a}, 9.70; H^{2e}, 8.82 ppm, but the δ^{iso}'s for protons bonded to the third carbon atom are different in sign and magnitude from each other: H^{3a}, 5.45; H^{3e}, −0.16 ppm. Thus ^{1}H δ^{iso} depends strongly upon the location and orientation of each nucleus within the molecule.

All axial protons have positive δ^{iso} values, which attenuate monotonously with the distance between the axial proton and the paramagnetic center, the Fe^{III} ion. However, the δ^{iso} value for the equatorial proton varies its sign with each separation by one C–C bond and attenuates more rapidly than that for the axial proton. Furthermore, the sign of δ^{iso} for each equatorial proton is opposite to that for the carbon atom to which the proton is bonded. These observations form a striking contrast to the results for the axial protons, which always show positive δ^{iso} values, and suggest the predominance of δ^{con} in δ^{iso} for the equatorial protons, i.e., the predominance of the spin-polarization effect in contributing to the spin propagation from the carbon atom to the equatorial proton. The monotonous behavior of δ^{iso} for the axial protons, on the other hand, seems to be attributable to the dominance of the dipolar shift, δ^{dip}. Thus, the δ^{iso}'s for the axial and equatorial protons are different in magnitude and sign from each other, though they are bonded to the same carbon atom in the present Fe^{III} complexes.

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