Bull. Chem. Soc. Jpn., 62, 3614—3621 (1989) [Vol. 62, No. 11

Analysis of Isotropic ^1H and ^{13}C NMR Shifts of Low-Spin Fe^{III} Complexes: Tetracyano(1,2-ethanediamine)ferrate(III) and Tetracyano(*N,N'*-dimethyl-1,2-ethanediamine)ferrate(III)

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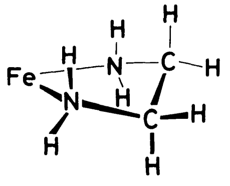
(Received March 31, 1989)

^1H NMR spectra of low-spin d^5 complexes, $[Fe^{III}(CN)_4(en)]^-$ and $[Fe^{III}(CN)_4(s\text{-}Me_2en)]^-$ (en=1,2-ethanediamine, *s*-Me₂en=*N,N'*-dimethyl-1,2-ethanediamine), were measured at 185—323 K. These complexes showed a non-Curie behavior. The spin states of the complexes were determined by an analysis of the *g* values from the ESR spectrum of a polycrystalline sample of $[Fe^{III}(CN)_4(en)]^-$ measured at liquid-helium temperatures. The isotropic shifts for the ^1H and ^{13}C nuclei, δ^{iso}, were separated into Fermi contact shifts, δ^{con}, and dipolar shifts, δ^{dip} and the strong dependence of δ^{iso} on the location of ligand nuclei was found to be due to the different δ^{con} as well as δ^{dip}. A combination of information concerning ESR and NMR enabled the assignment of the *g* values obtained from a polycrystalline sample, i.e. $g_{xx}=3.15$, $g_{yy}=1.99$, and $g_{zz}=0.82$, and determination of spin-orbit coupling constant, $\zeta=160\,cm^{-1}$.

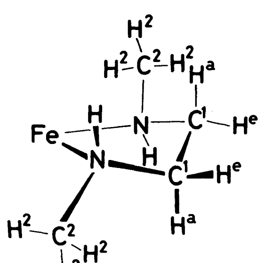
Numerous studies have appeared which applied NMR to investigate the stereochemistry and spin states of paramagnetic complexes, e.g. porphyrins[1] and heme proteins.[2–4] Most of the studies have, however, dealt with the NMR of unsaturated ligands, and little work has been done with saturated compounds coordinated to paramagnetic transition metal ions to investigate the correlations between the NMR shift and stereochemistry.[5]

Tetracyano(1,2-diamine)ferrates, $[Fe(CN)_4(1,2\text{-diamine})]^-$ and $[Fe(CN)_4(1,2\text{-diamine})]^{2-}$, are low-spin complexes with 1,2-diamine as a saturated compound. In a previous paper, we reported that the isotropic ^1H and ^{13}C NMR shifts, δ^{iso}, of the Fe^{III} complexes are strongly dependent on the location of the ligand nuclei and do not follow the Curie law.[6,7]

We have chosen $[Fe^{III}(CN)_4(en)]^-$ and $[Fe^{III}(CN)_4(s\text{-}Me_2en)]^-$ (en=1,2-ethanediamine and *s*-Me₂en=*N,N'*-dimethyl-1,2-ethanediamine) since the five-membered chelate ring formed by en is the simplest one among this class of complexes, and that formed by *s*-Me₂en is practically fixed in either the δ or λ conformation, at least below 323 K.[7] In this paper δ^{iso} for the ^1H and ^{13}C nuclei of the en and *s*-Me₂en complexes[6] were separated into Fermi contact shifts, δ^{con}, and dipolar shifts, δ^{dip}, by using the equations of Kurland and McGarvey.[8,9] Analysis of the ESR spectra of $[Fe^{III}(CN)_4(en)]^-$ at liquid-helium temperatures afforded the information necessary for the separation of δ^{iso} and the clarification of the non-Curie behavior. The distribution of unpaired spin over the chelates is discussed on the basis of the Fermi constants and spin populations in s orbitals for C<u>H</u>, N<u>H</u>, and C nuclei. The present treatment of δ^{iso} is a useful method for assigning the *g* values obtained from ESR measurements of polycrystalline samples, and determining the spin-orbit coupling constant.



en



s-Me₂en

Experimental

Materials. Sodium tetracyano(diamine)ferrate(III) and ferrate(II) (diamine=1,2-ethanediamine (en)[10] and *N,N'*-dimethyl-1,2-ethanediamine (*s*-Me₂en)[11]) and potassium tetracyano(1,2-ethanediamine)cobaltate(III)[12] were prepared as reported previously.

ESR Measurement. The ESR sample was prepared as follows: $Na[Fe^{III}(CN)_4(en)]\cdot 3H_2O$ (0.0010 g) and $K[Co^{III}(CN)_4(en)]\cdot H_2O$ (0.101 g) were dissolved in a solution (precooled at 0 °C) of acetic acid (0.25 cm³), water (0.25 cm³), methanol (1.0 cm³), and ethanol (1.0 cm³). Ether was added to this solution until it became turbid; the resulting mixture was allowed to stand at −15 °C overnight. Yellow crystals of the Co^{III} complex doped with the Fe^{III} complex were collected on a filter, washed with ether, and dried in vacuo. The obtained crystals were pulverized with an agate mortar and a pestle, placed in an ESR sample tube of 4 mm outer diameter, and sealed in vacuo. The sample was kept at −15 °C while being protected from light until the measurement.

ESR spectra on the polycrystalline sample were recorded with a Varian E-112 spectrometer at X-band frequency at liquid-helium temperatures. The magnetic field was calibrated with 2,2-diphenyl-1-picrylhydrazine (DPPH).

NMR Measurement. ^1H NMR spectra of $[Fe^{III}(CN)_4(diamine)]^-$ in CD_3OD (containing 0.25% DCl) were recorded on a JEOL FX-100 spectrometer at 323—185 K using a sample tube 5 mm in diameter. The concentrations of the complexes were ca. 0.05 mol dm⁻³ in order to prevent the deposition of the complexes below 273 K. Spectra with S/N ratios of ca. 20/1 were obtained by collecting 20—40 transients. Probe temperature were controlled with a JNM-VT-3C temperature-control apparatus and determined based on the chemical shift difference between the methyl and hydroxyl protons of methanol.[13]

The ^1H and ^{13}C NMR spectra (N<u>H</u> and <u>C</u>H) of $[Fe^{III}(CN)_4(diamine)]^-$ were recorded on a JEOL FX-100 spectrometer at 300 K using a sample tube of 5 mm in diameter and 40—50 mg of the complexes dissolved in pD 2.0 DCl–D_2O (0.3 cm³). The ^1H and ^{13}C NMR spectra of $[Fe^{II}(CN)_4(diamine)]^{2-}$ were measured in a manner similar to that described above, except that D_2O was used as the solvent.

Sodium 3-(trimethylsilyl)propionate-2,2,3,3-d_4 (TSP; 0.00 ppm) and 1,4-dioxane (67.44 ppm) were used as internal standards for ^1H and ^{13}C NMR measurements, respectively. Positive chemical shifts indicate downfield shifts.

Theoretical

We set the coordinate axes as shown in Fig. 1 for convenience, where the x axis coincides with the twofold axis of C_2 symmetry, and the other two axes are perpendicular to the twofold axis and are involved in the two symmetry planes defined by the donor atoms.

We assume that (1) the delocalization of 3d electrons into ligand orbitals is represented by the "orbital reduction factor",[14,15] k, and (2) there is no mixing of t_{2g} and e_g states. These assumptions lead to sixfold-degenerate $t_{2g}{}^5$ spin states in the field of O_h symmetry. The $t_{2g}{}^5$ configuration can be treated as being one electron hole in a closed $t_{2g}{}^6$ shell (one-hole notation).[15–18]

One-hole notation simplifies the expressions of the six states as follows:

$$|d_{xz}{}^{\pm}\rangle \equiv -(1/\sqrt{2})(|1^{\pm}\rangle - |-1^{\pm}\rangle),$$
$$|d_{yz}{}^{\pm}\rangle \equiv (i/\sqrt{2})(|1^{\pm}\rangle + |-1^{\pm}\rangle),$$

and

$$|d_{x^2-y^2}{}^{\pm}\rangle \equiv (1/\sqrt{2})(|2^{\pm}\rangle + |-2^{\pm}\rangle),$$

where, for example, $|1^+\rangle$ represents a $+1/2$ spin state with a magnetic quantum number of $+1$.

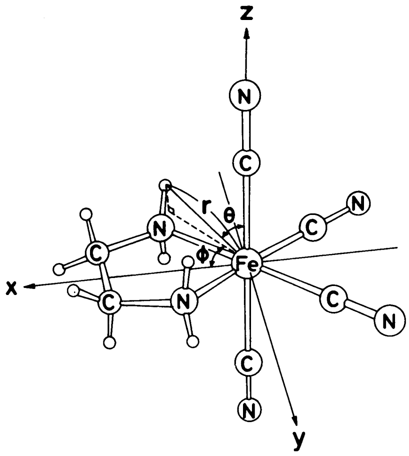


Fig. 1. Schematic representation of the coordinate system for analyzing magnetic resonances of $[Fe^{III}(CN)_4(diamine)]^-$.

ESR. The degeneracy of the $t_{2g}{}^5$ configuration is released to generate three Kramers doublets (Eq. 1) by perturbation arising from crystal-field distortions and spin-orbit coupling:

$$|\psi_i{}^{\pm}\rangle = \pm A_i|d_{xz}{}^{\mp}\rangle - iB_i|d_{yz}{}^{\mp}\rangle + C_i|d_{x^2-y^2}{}^{\pm}\rangle \quad (1)$$
$$i = 1, 2, \text{ and } 3,$$

where $i=1$ represents the ground doublet.

According to the methods reported by Bohan[19] and Taylor,[20] the eigenvalues of the Kramers doublets, E_i, and the axial and rhombic distortions of the crystal field, U and R, are expressed as follows:

$$E_i/\zeta = -(A_i+B_i+C_i)(1/A_i+1/B_i+1/C_i)/6+1/2, \quad (2)$$
$$U/\zeta = -(A_1+B_1+C_1)(1/A_1+1/B_1-2/C_1)/4, \quad (3)$$

and

$$R/\zeta = -(A_1+B_1+C_1)(1/A_1-1/B_1)/2, \quad (4)$$

where ζ (>0) is the spin-orbit coupling constant.

The principal g values are related to the coefficients of the ground Kramers doublet by the following expressions:[21]

$$g_{xx} = 2(-A_1{}^2 + B_1{}^2 + C_1{}^2 + 2kB_1C_1),$$
$$g_{yy} = 2(\ A_1{}^2 - B_1{}^2 + C_1{}^2 + 2kA_1C_1), \quad (5)$$

and

$$g_{zz} = -2(\ A_1{}^2 + B_1{}^2 - C_1{}^2 + 2kA_1B_1),$$

where $A_1{}^2+B_1{}^2+C_1{}^2=1$. For $k=1$, the coefficients are expressed in terms of the principal g values:

$$A_1 = (g_{yy} - g_{zz})/\sqrt{8(g_{xx} + g_{yy} - g_{zz})}\ ,$$
$$B_1 = (g_{xx} - g_{zz})/\sqrt{8(g_{xx} + g_{yy} - g_{zz})}\ , \quad (6)$$

and

$$C_1 = (g_{xx} + g_{yy})/\sqrt{8(g_{xx} + g_{yy} - g_{zz})}\ ,$$

where $g_{xx}+g_{yy}-g_{zz}$ must be positive because Eq. 5 shows

$$g_{xx} + g_{yy} - g_{zz} = 2(A_1 + B_1 + C_1)^2 > 0. \quad (7)$$

The coefficients and eigenvalues for the excited Kramers doublets are obtained by diagonalizing the following perturbation matrix with the U/ζ and R/ζ values calculated from Eqs. 3 and 4:

$$\begin{array}{ccc} |d_{xz}{}^{\mp}\rangle & -i|d_{yz}{}^{\mp}\rangle & |d_{x^2-y^2}{}^{\pm}\rangle \\ \left(\begin{array}{c} -U/(3\zeta)-R/(2\zeta) \\ -1/2 \\ -1/2 \end{array}\right. & \begin{array}{c} -1/2 \\ -U/(3\zeta)+R/(2\zeta) \\ -1/2 \end{array} & \left.\begin{array}{c} -1/2 \\ -1/2 \\ (2U)/(3\zeta) \end{array}\right) \end{array}$$

NMR. The tetracyano(diamine)ferrate(III) complexes are paramagnetic (low-spin),[22] and the corresponding Fe^{II} complexes are diamagnetic.[6] We define isotropic shift, δ^{iso}, for the Fe^{III} complexes as the difference in chemical shift between the Fe^{III}, $\delta_{Fe^{III}}$, and Fe^{II} complexes, $\delta_{Fe^{II}}$: $\delta^{iso}=\delta_{Fe^{III}}-\delta_{Fe^{II}}$. δ^{iso} is composed of three parts,[8,9,23]

$$\delta^{iso} = \delta^{con} + \delta_{L}^{dip} + \delta_{M}^{dip}, \tag{8}$$

where δ^{con} is a Fermi contact shift, δ_{L}^{dip} is a ligand-centered dipolar shift, and δ_{M}^{dip} is a metal-centered dipolar shift. For ^{1}H nuclei δ_{L}^{dip} term is expected to be negligible.

The expressions for δ_{M}^{dip} and δ^{con} reported by Kurland and McGarvey[8,9] can be rewritten with the symbols used in Eqs. 1 and 2 as follows:

$$\delta_{M}^{dip}=(10^{6}/24\pi)[(2\chi_{zz}-\chi_{yy}-\chi_{xx})G_{A}+3(\chi_{xx}-\chi_{yy})G_{B}], \tag{9}$$

$$G_{A} = (3\cos^{2}\theta - 1)/r^{3},\ G_{B} = \sin^{2}\theta\cos 2\phi/r^{3}, \tag{10}$$

$$\chi_{qq}=\mu_{0}\beta^{2}[k_{B}T\sum_{i=1}^{3}\exp(-E_{i}/k_{B}T)]^{-1}[\sum_{i=1}^{3}\exp(-E_{i}/k_{B}T)\cdot <\mu_{q}>_{ii}{}^{2}-2k_{B}T\sum_{i=1}^{2}\sum_{j=i+1}^{3}Q_{ij}<\mu_{q}>_{ij}{}^{2}], \tag{11}$$

$$Q_{ij}=[\exp(-E_{i}/k_{B}T)-\exp(-E_{j}/k_{B}T)][E_{i}-E_{j}]^{-1}, \tag{12}$$

$$\delta^{con}=10^{6}a_{N}\beta[6k_{B}T\gamma\hbar\sum_{i=1}^{3}\exp(-E_{i}/k_{B}T)]^{-1}\sum_{q=x,y,z}[\sum_{i=1}^{3}\exp(-E_{i}/k_{B}T)<\mu_{q}>_{ii}<s_{q}>_{ii}-2k_{B}T\sum_{i=1}^{2}\sum_{j=i+1}^{3}Q_{ij}<\mu_{q}>_{ij}<s_{q}>_{ij}], \tag{13}$$

where δ_{M}^{dip} and δ^{con} are in the unit of ppm, and their positive values indicate downfield shifts. G_{A} and G_{B} are geometric factors, and the distance r and angles θ and ϕ are defined as shown in Fig. 1. χ_{qq} ($q=x$, y, and z) is the principal axis component of the susceptibility tensor. μ_{0}, β, k_{B}, T, a_{N}, γ, and $\hbar$ are magnetic permeability of vacuum, the Bohr magneton, the Boltzmann constant, absolute temperature, Fermi contact coupling constant, magnetogyric ratio, and the Planck constant. $<\mu_{q}>_{ij}$ and $<s_{q}>_{ij}$ ($q=x$, y, z and i, $j=1$, 2, 3) are defined as follows:

$$\begin{aligned}
<\mu_{x}>_{ij} &\equiv -A_{i}A_{j} + B_{i}B_{j} + C_{i}C_{j} + k(B_{i}C_{j} + B_{j}C_{i}),\\
<\mu_{y}>_{ij} &\equiv \quad A_{i}A_{j} - B_{i}B_{j} + C_{i}C_{j} + k(C_{i}A_{j} + C_{j}A_{i}),\\
<\mu_{z}>_{ij} &\equiv \quad A_{i}A_{j} + B_{i}B_{j} - C_{i}C_{j} + k(A_{i}B_{j} + A_{j}B_{i}),\\
<s_{x}>_{ij} &\equiv -A_{i}A_{j} + B_{i}B_{j} + C_{i}C_{j},\\
<s_{y}>_{ij} &\equiv \quad A_{i}A_{j} - B_{i}B_{j} + C_{i}C_{j},
\end{aligned}$$

and

$$<s_{z}>_{ij} \equiv \quad A_{i}A_{j} + B_{i}B_{j} - C_{i}C_{j}.$$

Since the three Kramers doublets belong to a single 1/2 spin state, Fermi coupling constants for them, a_{N}, are represented by a single value in Eq. 13, according to the theory of Kurland and McGarvey.[8,9]

Results and Discussion

Temperature Dependence of ^{1}H NMR Spectra. It is well-known that the 1,2-diamine coordinated to a metal ion takes λ and δ gauche conformations.[24] The λ and δ forms of the en chelate are enantiomeric and identical in energy and, hence, a conformational

Table 1. Temperature Dependence of the Chemical Shifts, Isotropic, Dipolar, and Fermi Contact Shifts of $[Fe^{III}(CN)_{4}(1,2\text{-ethanediamine})]^{-}$

Nucleus	Temp/K	Chemical shift/ppm[a]	δ^{iso}/ppm[a,b] Obsd.	δ^{iso}/ppm[a,b] Calcd.	δ_{M}^{dip}/ppm[a] Calcd.	δ^{con}/ppm[a] Calcd.
$C\underline{H}_{2}$	303	−1.15	−3.65	−4.16	16.21	−20.37
	293	−0.84	−3.34	−3.72	17.36	−21.08
	283	−0.49	−2.99	−3.23	18.61	−21.84
	273	−0.01	−2.51	−2.65	20.00	−22.65
	263	0.44	−2.06	−1.99	21.53	−23.52
	253	1.17	−1.33	−1.22	23.23	−24.45
	243	1.87	−0.63	−0.33	25.12	−25.45
	233	3.04	0.54	0.69	27.22	−26.53
	223	3.69	1.19	1.89	29.58	−27.69
	213	5.27	2.77	3.27	32.22	−28.95
	203	6.87	4.37	4.87	35.19	−30.32
	193	9.29	6.79	6.74	38.55	−31.81
	185	12.04	9.54	8.46	41.56	−33.10
$N\underline{H}_{2}$	300	145	145[c]	145	6.8	138.2
$\underline{C}H_{2}$	300	251.6[d]	206.4	206.4	38.8	167.4[e]

a) Positive values indicate downfield shifts. b) Isotropic shift is defined as the difference in chemical shift between the Fe^{III} and Fe^{II} complexes. The chemical shifts for $C^{1}\underline{H}_{2}$ and $^{13}\underline{C}H_{2}$ of $[Fe^{II}(CN)_{4}(1,2\text{-ethanediamine})]^{2-}$ at 300 K were 2.50 and 45.2 ppm, respectively (Ref. 6). c) The chemical shift for $N\underline{H}_{2}$ of the Fe^{II} 1,2-ethanediamine complex is expected to be a few ppm, although it was not be measured owing to a rapid H-D exchange. The chemical shift observed for the Fe^{III} complex was hence regarded as isotropic shift. d) Ref. 6. e) The value is the sum of δ^{con} and δ_{L}^{dip}.

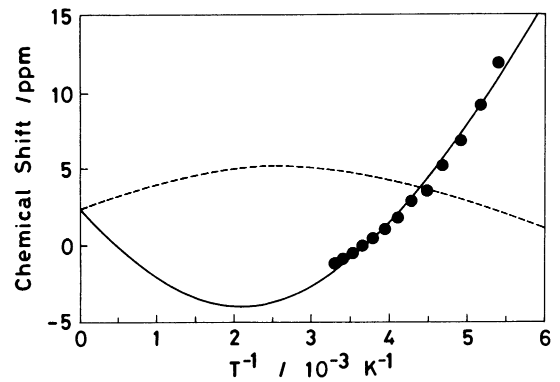


Fig. 2. Temperature dependence of ^{1}H NMR shift of the methylene protons of [$Fe^{III}(CN)_4$(1,2-ethanediamine)]$^-$. The observed chemical shift (solid circle) is a time-averaged shift of the axial and equatorial protons due to a rapid conformational interconversion of the chelate between λ and δ gauche forms. Positive values indicate downfield shifts. The solid line shows the best-fitted curve of temperature dependence, and the broken line represents the results obtained from improper assignments of g values. The value at $T^{-1}=0$ represents the chemical shift observed for the diamagnetic Fe^{II} complex, [$Fe^{II}(CN)_4$(1,2-ethanediamine)]$^{2-}$.

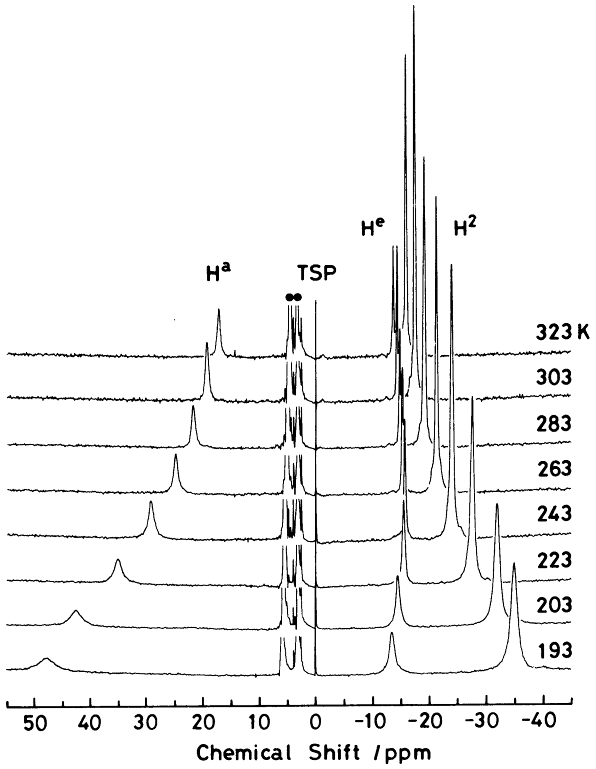


Fig. 3. ^{1}H NMR spectra of [$Fe^{III}(CN)_4$(N,N'-dimethyl-1,2-ethanediamine)]$^-$ in CD_3OD containing 0.25% DCl at 323—193 K. A dot (●) indicates a solvent signal.

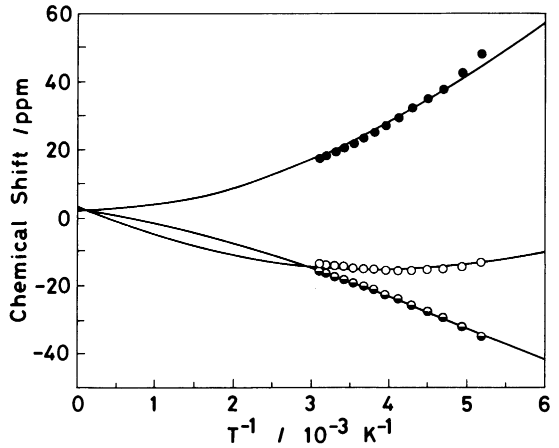


Fig. 4. Temperature dependence of ^{1}H NMR shifts of [$Fe^{III}(CN)_4$(N,N'-dimethyl-1,2-ethanediamine)]$^-$. The solid lines are the curves best-fitted to the observed temperature dependence: H^a (●), H^e (○), and H^2 (◒). The values at $T^{-1}=0$ represent the chemical shifts observed for the diamagnetic Fe^{II} complex, [$Fe^{II}(CN)_4$(N,N'-dimethyl-1,2-ethanediamine)]$^{2-}$.

interconversion between them rapidly occurs on the NMR time scale near room temperature.[6,7] The C$\underline{H}_2$ signal of the Fe^{III} complex broadened with a decrease in temperature, but did not split into two peaks corresponding to the axial and equatorial methylene protons, even at 185 K.[7] The downfield shift of the time-averaged signal accelerated with a decrease in temperature. The observed chemical shifts at 185—303 K are summarized in Table 1 and plotted in Fig. 2.

We reported in a previous paper[6] that a geometric isomerism exists for the Fe^{III} s-Me_2en complex, i.e., racemic and meso forms with respect to the N-methyl groups, and that the isolated complex was a racemic isomer. The five-membered chelate ring of s-Me_2en can be treated as fixed in either a δ or λ gauche conformation; in fact, the axial and equatorial protons (H^a and H^e) appeared as separated peaks at 20.45 and −14.59 ppm, even at room temperature, respectively. The NMR spectra of the racemic isomer measured at 193—323 K are reproduced in Fig. 3. The observed chemical shifts are summarized in Table 2 and plotted in Fig. 4. The decrease in temperature broadened all signals and moved H^a and H^2 signals toward downfield and upfield, respectively. The temperature dependence of H^e is unique: the direction of the variation of the chemical shift reversed at around 243 K. Figures 2 and 4 clearly show the non-Curie behavior of the Fe^{III} complexes.

Chemical Shifts of Amino Protons and Carbon Atoms. Resonances of N$\underline{H}$ of both the Fe^{III} en and s-Me_2en complexes were observed at 145 ppm at 300 K as a broad peak with a width of 290 and 380 Hz, respectively. The N$\underline{H}$ signals of the corresponding Fe^{II} complexes could not be observed due to a rapid H-D exchange between the amino protons and the solvent. The ^{13}C shifts of the Fe^{III} and Fe^{II} complexes reported previously[6] are collected together in Tables 1 and 2.

Table 2. Temperature Dependence of the Chemical Shifts, Isotropic, Dipolar, and Fermi Contact Shifts of $[\mathrm{Fe^{III}(CN)_4}(N,N'\text{-dimethyl-1,2-ethanediamine})]^-$

Nucleus	Temp/K	Chemical shift/ppm[a)]	δ^{iso}/ppm[a,b)]		$\delta^{\mathrm{dip}}_{\mathrm{M}}$/ppm[a)]	δ^{con}/ppm[a)]
			Obsd.	Calcd.	Calcd.	Calcd.
$\mathrm{H^a}$	323	17.15	15.03	15.80	15.49	0.31
	313	18.02	15.90	16.84	16.52	0.32
	303	19.27	17.15	17.98	17.65	0.33
	293	20.45	18.33	19.24	18.90	0.34
	283	21.79	19.67	20.62	20.26	0.36
	273	23.33	21.21	22.14	21.77	0.37
	263	24.92	22.80	23.82	23.44	0.38
	253	27.10	24.98	25.69	25.29	0.40
	243	29.22	27.10	27.76	27.35	0.41
	233	32.13	30.01	30.07	29.64	0.43
	223	34.99	32.87	32.66	32.21	0.45
	213	37.72	35.60	35.55	35.08	0.47
	203	42.75	40.63	38.82	38.32	0.50
	193	48.05	45.93	42.50	41.98	0.52
$\mathrm{H^e}$	323	−13.64	−16.42	−17.69	12.96	−30.65
	313	−13.95	−16.73	−17.84	13.83	−31.67
	303	−14.30	−17.08	−17.97	14.77	−32.74
	293	−14.59	−17.37	−18.07	15.81	−33.88
	283	−14.86	−17.64	−18.15	16.96	−35.11
	273	−15.12	−17.90	−18.19	18.22	−36.41
	263	−15.33	−18.11	−18.19	19.61	−37.80
	253	−15.54	−18.32	−18.14	21.16	−39.30
	243	−15.65	−18.43	−18.02	22.88	−40.90
	233	−15.65	−18.43	−17.84	24.80	−42.64
	223	−15.54	−18.32	−17.56	26.95	−44.51
	213	−15.27	−18.05	−17.18	29.36	−46.54
	203	−14.51	−17.29	−16.67	32.06	−48.73
	193	−13.33	−16.11	−16.01	35.12	−51.13
$\mathrm{H^2}$	323	−15.86	−18.38	−18.31	−5.64	−12.67
	313	−16.52	−19.04	−19.10	−6.01	−13.09
	303	−17.39	−19.91	−19.95	−6.42	−13.53
	293	−18.24	−20.76	−20.88	−6.88	−14.00
	283	−19.15	−21.67	−21.88	−7.37	−14.51
	273	−20.21	−22.73	−22.97	−7.92	−15.05
	263	−21.27	−23.79	−24.15	−8.53	−15.62
	253	−22.67	−25.19	−25.44	−9.20	−16.24
	243	−24.02	−26.54	−26.85	−9.95	−16.90
	233	−25.82	−28.34	−28.41	−10.79	−17.62
	223	−27.57	−30.09	−30.11	−11.72	−18.39
	213	−29.19	−31.71	−32.00	−12.77	−19.23
	203	−32.04	−34.56	−34.09	−13.95	−20.14
	193	−34.90	−37.42	−36.41	−15.28	−21.13
N$\underline{\mathrm{H}}$	300	145	145[c)]	145	9.9	135.1
$\mathrm{C^1}$	300	301.1[d)]	246.9	246.9	38.8	208.1[e)]
$\mathrm{C^2}$	300	156.1[d)]	114.3	114.3	−3.0	117.3[e)]

a) Positive values indicate downfield shifts. b) Isotropic shift is defined as the difference in chemical shift between the $\mathrm{Fe^{III}}$ and $\mathrm{Fe^{II}}$ complexes. The chemical shifts for $\mathrm{H^a}$, $\mathrm{H^e}$, $\mathrm{H^2}$, $\mathrm{C^1}$, and $\mathrm{C^2}$ of $[\mathrm{Fe^{II}(CN)_4}(N,N'\text{-dimethyl-1,2-ethanediamine})]^{2-}$ at 300 K were 2.12, 2.78, 2.52, 54.2, and 41.8 ppm, respectively (Ref. 6). c) The chemical shift for N$\underline{\mathrm{H}}$ of the $\mathrm{Fe^{II}}$ complex is expected to be a few ppm, although it was not be measured owing to a rapid H–D exchange. The chemical shift observed for the $\mathrm{Fe^{III}}$ complex was hence regarded as isotropic shift. d) Ref. 6. e) The value is the sum of δ^{con} and $\delta^{\mathrm{dip}}_{\mathrm{L}}$.

ESR Spectrum of $[\mathrm{Fe^{III}(CN)_4(en)}]^-$. The general expression of δ^{iso} given by Kurland and McGarvey[8,9] suggests that the eigenvalues and eigenfunctions of the excited as well as the ground Kramers doublets associated with the $^2\mathrm{T_{2g}}$ term should be determined in order to analyze δ^{iso} which does not obey the Curie law. Since the required quantities are obtained from the analysis of g values, we measured the ESR spectrum of $[\mathrm{Fe^{III}(CN)_4(en)}]^-$ shown in Fig. 5 at liquid-helium temperatures, using a polycrystalline sample diluted

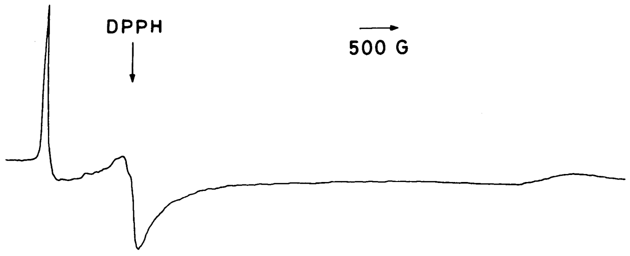


Fig. 5. ESR spectrum of $[Fe^{III}(CN)_4(1,2\text{-ethanediamine})]^-$ measured at liquid-helium temperatures. The Fe^{III} complex was magnetically diluted to ca. 1/100 with $K[Co^{III}(CN)_4(1,2\text{-ethanediamine})]$.

magnetically to ca. 1/100 with the isostructural Co^{III} complex, $[Co^{III}(CN)_4(en)]^-$. The g values obtained after a correction of the magnetic field with DPPH were 3.15, 1.99, and 0.82.

The following expression of the product $g_{xx}g_{yy}g_{zz}$ is obtained from Eq. 5 with $k=1$:

$$g_{xx}g_{yy}g_{zz} = -8[(A_1 + B_1)^2 - C_1^2][(B_1 + C_1)^2 - A_1^2]\cdot[(C_1 + A_1)^2 - B_1^2].$$

For a complex with a crystal field largely distorted from O_h symmetry, the product is positive. A negative product is obtained for a complex close to O_h symmetry. Since the tetracyano en complex has two kinds of ligands (CN^- and en), which are different in crystal-field strength,[25—27] the complex is expected to have a largely distorted crystal field. The product was, hence, assumed to be positive in an analysis of the g values. To justify this assumption, we measured the Mössbauer spectra of $[Fe^{III}(CN)_4(en)]^-$ at 95—260 K. The temperature dependence of the quadrupole splitting supported $g_{xx}g_{yy}g_{zz}>0$.[28]

The following six sets satisfy Eq. 7 and give a norm close to unity, 0.961: $(g_{xx}, g_{yy}, g_{zz})=(3.15, 1.99, 0.82)$, $(1.99, 3.15, 0.82)$, $(3.15, -0.82, -1.99)$, $(-0.82, 3.15, -1.99)$, $(1.99, -0.82, -3.15)$, and $(-0.82, 1.99, -3.15)$. With the first set, the coefficients for the ground Kramers doublet were calculated from Eq. 6: $A_1=0.2030$, $B_1=0.4043$, and $C_1=0.8918$. These values were corrected to 0.2108, 0.4141, and 0.8855 by Eq. 5 with $k=0.905$, respectively. Using the corrected values, we obtained $U/\zeta=-1.849$ and $R/\zeta=-1.758$ from Eqs. 3 and 4. Substitution of the U/ζ and R/ζ values into the perturbation matrix followed by diagonalization gave the following eigenvalues and coefficients for the lowest three Kramers doublets:

Set 1

$A_1 = 0.2108, B_1 = 0.4141, C_1 = 0.8855, E_1/\zeta = -1.5862,$
$A_2 = 0.1382, B_2 = 0.8841, C_2 = -0.4464, E_2/\zeta = -0.0882,$

and

$A_3 = -0.9677, B_3 = 0.2165, C_3 = 0.1292, E_3/\zeta = 1.6744.$

The remaining five g-value sets give the same values of E_i/ζ; the coefficients for each set were obtained by rotating the values of Set 1. For example, Set 2 was obtained from the second set of g values:

Set 2

$A_1 = 0.4141, B_1 = 0.2108, C_1 = 0.8855, E_1/\zeta = -1.5862,$
$A_2 = 0.8841, B_2 = 0.1382, C_2 = -0.4464, E_2/\zeta = -0.0882,$

and

$A_3 = 0.2165, B_3 = -0.9677, C_3 = 0.1292, E_3/\zeta = 1.6744.$

Estimation of Geometric Factors. The geometric factors for the present diamine chelates were calculated from Eq. 10, based on the assumption that the present Fe^{III} complexes have the same configuration of diamine chelate as the Co^{III} complex, *trans*-$[Co^{III}Cl_2(en)_2]Cl\cdot(H_5O_2)^+Cl^-$, the crystal structure of which was analyzed with neutron diffraction by Rozire and Williams.[29] The coordinates of the axial amino protons and the equatorial methyl groups of the Fe^{III} *s*-Me$_2$en complex were estimated, based on an assumption that these nuclei locate at the vertices of tetrahedron with bond lengths of C–H=1.09, N–H=1.02, and C–N=1.48 Å.

The following values of G_A and G_B were obtained: for the en chelate; H, −1.554, 1.883; N$\underline{H}$, −4.355, −1.832; C, −4.275, $3.884\times10^{28}\,m^{-3}$, where the former four values are the means of G_A and G_B values for the axial and equatorial protons, and for the *s*-Me$_2$en chelate; H^a, −1.270, 2.346; H^e, −1.838, 1.419; H^2, −0.9783, −1.864; N$\underline{H}$, −3.813, −0.9187; C^1, −4.275, 3.884; C^2, −2.735, $-2.441\times10^{28}\,m^{-3}$. The methyl protons of the *s*-Me$_2$en chelate was assumed to rotate freely.

Analysis of Isotropic Shifts. The observed values of δ^{iso} listed in Tables 1 and 2 were obtained by using the ^1H and ^{13}C chemical shifts for the diamagnetic Fe^{II} complexes, $[Fe^{II}(CN)_4(en)]^{2-}$ and $[Fe^{II}(CN)_4(s\text{-}Me_2en)]^{2-}$, reported previously.[6] Since the chemical shifts for N$\underline{H}$ of the Fe^{III} complexes were very large, i.e. 145 ppm, and N$\underline{H}$ shifts of the corresponding Fe^{II} complexes are expected to be at most a few ppm, δ^{iso} of the N$\underline{H}$'s was taken as 145 ppm.

The least-squares fitting of Eqs. 8—13 to the δ^{iso} values for C$\underline{H}_2$ of the en complex yielded $\zeta=160\,cm^{-1}$ and $a_N=-0.69$ MHz when Set 1 was used as eigenvalues and eigenvectors. The δ^{iso}, δ_M^{dip}, and δ^{con} estimated by this fitting are shown in the fifth-seventh columns of Table 1. The calculated shifts are compared with the observed shifts in Fig. 2. Set 1 gave the better fit (solid curve), but other sets, e.g. Set 2 gave unsatisfactory results (broken curve). The g values were therefore assigned as follows: $g_{xx}=3.15$, $g_{yy}=1.99$, and $g_{zz}=0.82$.

δ_M^{dip} values for other ^1H and ^{13}C nuclei of the en complex were calculated from Eqs. 9—12 by using Set

1 and ζ=160 cm^{-1}. The difference between the δ_M^{dip} and the observed δ^{iso} values corresponds to δ^{con} for ^{1}H nuclei and $\delta^{\mathrm{con}}+\delta_L^{\mathrm{dip}}$ for ^{13}C nuclei. These values are collected together in Table 1.

The Fe$^{\mathrm{III}}$ *s*-Me$_2$en complex offers an opportunity to investigate the δ^{iso} for H^a and H^e independently, since the complex has a fixed conformation in which both *N*-methyl groups take pseudoequatorial positions (eq-form).[30] The procedure mentioned above was applied to this complex, using Set 1 and ζ=160 cm^{-1}. The calculated results are summarized in Table 2, and the comparison of the observed and calculated shifts is shown in Fig. 4.

The magnitude of the ζ value is considered to be appropriate to the low-spin Fe$^{\mathrm{III}}$ complexes for the following reasons. (1) μ_{eff}=2.32 BM[31] at 303 K estimated from ζ=160 cm^{-1} is in good agreement with those observed for a series of tetracyano(1,2-diamine)ferrate(III) complexes: (*R*)-1,2-propanediamine, 2.3; (1*R*,2*R*)-1,2-cyclopentanediamine, 2.4; (1*R*,2*R*)-1,2-cyclohexanediamine, 2.4 BM.[22] (2) Merrithew et al.[32] employed the spin-orbit coupling constant of ζ=150 cm^{-1} in their Mössbauer study of H[Fe$^{\mathrm{III}}$(CN)$_4$(bpy)] and [Fe$^{\mathrm{III}}$(CN)$_2$(bpy)$_2$]ClO$_4$. (3) We have obtained ζ=150—230 cm^{-1} from the temperature dependence of Mössbauer quadrupole splitting of [Fe$^{\mathrm{III}}$(CN)$_4$(en)]$^-$ at 95—260 K.[28]

Since the application of ζ=160 cm^{-1} to the *s*-Me$_2$en complex gave good agreement between the observed and calculated shifts, as shown in Fig. 4, the variation of ζ is small in this class of Fe$^{\mathrm{III}}$ complexes. The combination of Set 1 and ζ=160 cm^{-1} leads to (1) the largest population of the electron hole in d$_{x^2-y^2}$ and (2) the first and the second excited states which are higher in energy by 2.9 and 6.2 kJ mol^{-1} than the ground state, respectively.

Dipolar Shift and Fermi Contact Shift. The δ_M^{dip} for the present Fe$^{\mathrm{III}}$ complexes calculated from Set 1 and Eq. 9 (Tables 1 and 2) is zero on the elliptical cone which intersects the *xz* and *yz* planes at 47.3 and 68.9°, respectively. The nuclei inside and outside the cone have negative and positive δ_M^{dip}, respectively. Since the methyl protons of the *s*-Me$_2$en chelate locate inside the cone and the other atoms are outside, δ_M^{dip} is negative for the former and positive for other atoms. The δ_M^{dip} for the methyl carbon is almost zero because this atom exists near the cone.

Subtracting δ_M^{dip} from δ^{iso} gave δ^{con} for each ^{1}H nucleus (Tables 1 and 2). The δ^{con} for H^a is near zero, i.e. $\delta^{\mathrm{iso}}\simeq\delta_M^{\mathrm{dip}}$. But H^e has large negative δ^{con}, i.e. upfield shift of 30—50 ppm at 193—323 K. H^a and H^e have different δ^{con} values, although they are bound to the same carbon atom.

The δ_M^{dip} for H^e is positive and considerably small in magnitude compared with the negative δ^{con} for H^e. The magnitude of the δ^{iso} for H^e is, hence, reduced and its variation with temperature is small. The characteristics of δ^{iso} for the tetracyanoferrate(III) complexes, e.g. the different sign of δ^{iso} for H^a and H^e and the peculiar temperature dependence of δ^{iso} for H^e, are the results of the different contribution of δ_M^{dip} and δ^{con} for these protons.

The δ_M^{dip} and δ^{con} for H^2 are both upfield shifts, and the δ^{con} of −12.7—−21.1 ppm at 193—323 K is close to the mean of δ^{con}'s for H^a and H^e, i.e. −15.2—−25.3 ppm. This fact suggests that the unpaired spin is transferred to the freely rotating H^2 in a way similar to H^a and H^e.

The large δ^{iso} observed for $\mathrm{N\underline{H}}$ was ascribed to large δ^{con}, ca. 135 ppm, which is larger than at least 4 times that for $\mathrm{C\underline{H}}$.

For ^{13}C nuclei, δ^{iso} was separated into δ_M^{dip} and $\delta^{\mathrm{con}}+\delta_L^{\mathrm{dip}}$ (Tables 1 and 2). The carbon atoms constituting the five-membered chelate rings have $\delta^{\mathrm{con}}+\delta_L^{\mathrm{dip}}$ of 170—210 ppm, and its contribution to the δ^{iso} is over 80%. Since δ_L^{dip} for ^{13}C nucleus is not zero,[8,23] an estimation of δ^{con} for the ^{13}C nucleus requires an elimination of the δ_L^{dip} contribution. A calculation of δ_L^{dip}, however, requires many approximations, as shown in the treatment of ^{13}C NMR shift for [Fe$^{\mathrm{III}}$(CN)$_6$]$^{3-}$ by Kurland and McGarvey;[8,23] hence, the separation of δ^{con} and δ_L^{dip} may be a problem to settle in future.

Fermi Contact Coupling Constant and Spin Population. The a_N values obtained from the fitting calculation are listed in Table 3. The population of the unpaired spin in the 1s orbital of hydrogen, Q_{1s}, and that in the 2s orbital of carbon, Q_{2s}, were calculated from the a_N by the relations $Q_{1s}=a_N/1420$ and $Q_{2s}=a_N/3110$, where 1420 and 3110 MHz are the Fermi constants calculated for ^{1}H· and ^{13}C· radicals, respectively.[33] The estimated values of Q_{1s} and Q_{2s} are listed in Table 3.

The a_N value for H^e, −1.11 MHz, is similar in magnitude to those for ^{1}H nuclei of unsaturated ligands in low-spin Fe$^{\mathrm{III}}$ complexes: −1.08 MHz for ^{1}H nuclei at the position 6 and 6′ of 2,2′-bipyridyl in [Fe$^{\mathrm{III}}$(bpy)$_3$]$^{3+}$, and −1.03 MHz for ^{1}H nuclei at the

Table 3. Fermi Contact Coupling Constants (a_N) and Spin Populations Estimated for [Fe$^{\mathrm{III}}$(CN)$_4$(1,2-ethanediamine)]$^-$ and [Fe$^{\mathrm{III}}$(CN)$_4$(*N*,*N*′-dimethyl-1,2-ethanediamine)]$^-$

Diamine	Nucleus	a_N/MHz	Spin population
	$\mathrm{N\underline{H}}$	4.63	0.0033
en	H	−0.69	−0.0005
	C	1.42	0.0005
	$\mathrm{N\underline{H}}$	4.50	0.0032
	H^a	0.01	0.0000
s-Me$_2$en	H^e	−1.11	−0.0008
	H^2	−0.46	−0.0003
	C^1	1.74	0.0006
	C^2	0.98	0.0003

position 2 and 9 of 1,10-phenanthroline in $[Fe^{III}(phen)_3]^{3+}$.[34] The fact that the latter two values are the largest among the a_N values observed for ^1H nuclei within these complexes suggests that σ bonds are not lower in facility of spin propagation than π bonds. The a_N values for ^{13}C nuclei are 1.4—1.7 MHz, though it should be noted that these values were obtained by assuming $\delta_L^{dip}=0$.

Spin population (Table 3) is a better scale for a comparison of the heteronuclear NMR shifts than a_N, since the latter depends on the magnetogyric ratio. The positive spins on $N\underline{H}$ and $\underline{C}$ and the negative spins on $C\underline{H}$ suggest the propagation of spin by polarization effect which results in an alteration in the sign of the spin population with each σ bond.

The transfer of unpaired spin from the Fe^{III} ion to the diamine ligands is considered to occur mainly between the 3d orbitals and the sp^3 hybridized orbitals of the nitrogen atoms by a polarization mechanism.[35] Most of the unpaired spin resides in the $3d_{x^2-y^2}$ orbital, as Set 1 shows; thus, this feature of electronic configuration is expected to result in the predominant population of the unpaired spin near the planes of the chelate rings. The large difference between H^a and H^e can be explained by this anisotropic population.

This work was supported partly by the Joint Studies Program (1980—1981) of the Institute for Molecular Science. We wish to express thanks to Dr. Toshiaki Enoki of Tokyo Institute of Technology for assisting in the measurement of the ESR spectrum. We are grateful to Professor Mitsuo Sato of Teikyo University and Dr. Tetsuo Asaji of Nagoya University for valuable discussions.

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31) Molar magnetic susceptibility, χ_M, is related to effective magnetic moment, μ_{eff} (BM), by the equation, $\chi_M=\mu_0 N_A \beta^2 \mu_{eff}^2/(3k_B T)$, where N_A is Avogadro constant. χ_M is related to the average of χ_{xx}, χ_{yy}, and χ_{zz} in Eq. 11: $\chi_M=N_A(\chi_{xx}+\chi_{yy}+\chi_{zz})/3$. $\chi_M=2.79\times10^{-8}$ m^3 and $\mu_{eff}=2.32$ BM at 303 K were estimated from $\zeta=160$ cm^{-1}.

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