Contribution from the Faculty of Pharmaceutical Sciences,
Nagoya City University, Mizuho-ku, Nagoya 467, Japan

Synthesis and Spectral Characterization of Tetracyanoferrate(II) and Tetracyanoferrate(III) Chelates with 1,3-Diamines

Masafumi Goto,* Hiroko Nakayabu, Hitoshi Ito, Hisao Tsubamoto, Kyoko Nakabayashi,
Yoshitaka Kuroda, and Tomoya Sakai

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Low-spin tetracyano(diamine)ferrate(II) chelates and the corresponding Fe(III) chelates were prepared with four 1,3-diamines: 1,3-diaminopropane (tn), 1,3-diaminobutane (bn), *meso*-2,4-diaminopentane (*meso*-ptn), and (2*R*,4*R*)-diaminopentane (*R*-ptn). The Fe(III) chelates were prepared by oxidation of the Fe(II) chelates under acidic conditions. A CD spectrum of [Fe(CN)$_4$-(*R*-ptn)]$^{2-}$ showed two CD components of opposite signs at 22 200 and 26 000 cm^{-1} in the region of the first absorption band, which are ascribed to a λ-skew-boat conformation. A CD spectrum of [Fe(CN)$_4$(*R*-ptn)]$^-$ is different from those of 1,2-diamine chelates in the CN → metal charge-transfer region but an MCD spectrum is analogous to those of 1,2-diamine chelates. ^{1}H and ^{13}C NMR of the Fe(II) chelates showed the preference of the chair conformation for the tn, bn, and *meso*-ptn chelates. Well-resolved signals were observed for the Fe(III) chelates in the regions between 40 and −10 ppm for the ^{1}H NMR and 210 and −50 ppm for the ^{13}C NMR spectra. The isotropic shifts are different from those found for Ni(II) chelates. The analysis of the isotropic shifts leads to an estimation of 50:50 contribution of λ-skew-boat and chair conformations for the *R*-ptn chelates.

Substitution of tris(diamine)iron(II) with strong coordination ligands, four cyano anions, leads to the formation of a low-spin Fe(II) chelate, tetracyano(diamine)ferrate(II).[1-3] Structural studies of the chelates have been carried out with several 1,2-diamines by using electronic, CD,[2,3] and ^{1}H and ^{13}C NMR spectroscopy.[4] These chelates exhibit an interesting chemical reactivity of an oxidative ligand dehydrogenation.[1] The oxidation under acidic and basic conditions leads to the corresponding metal-oxidized tetracyano(1,2-diamine)ferrate(III) and the ligand-oxidized tetracyano(1,2-diimine)ferrate(II), respectively.[1,3] A redox reaction of tetracyano(1,2-diamine)ferrate(III) takes place in basic solution and results in simultaneous formations of metal-reduced tetracyano(1,2-diamine)ferrate(II) and ligand-oxidized Fe(II) chelates, predominantly tetracyano(1,2-diimine)ferrate(II).[5,6] Different chemical behavior is expected for the oxidation of the 1,3-diamine chelates, because the dehydrogenation of a 1,3-diamine coordinated to a metal ion will yield a nonconjugative 1,3-diimine.

Low-spin tetracyanoferrate(II) chelates have been known with aromatic diimines, such as bipyridine (bpy) and 1,10-phenanthroline (phen),[7] and α-amino acids,[8] as well as 1,2-diamines. Studies on the 1,3-diamine chelates are desirable to extend the chemistry of this class of compounds.

The conformation of the six-membered chelate rings formed by 1,3-diamines has been the subject of many investigations. The geometry of the six-membered chelate rings is different from that of cyclohexane in the long metal–nitrogen bond length and the reduced nitrogen–metal–nitrogen bond angle. Four conformers, **1–4**, are conceivable for 1,3-diaminopropane (tn) chelates.

1   **2**

3   **4**
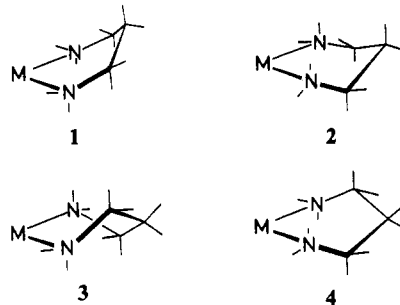
The boat form, **1**, suffers considerable steric repulsion between hydrogens of the masthead carbon atom and the apical ligand and has not been reported for the formation. The chair form, **2**, is the most sterically unhindered on a molecular force field calculation.[9] The skew-boat conformers, **3** and **4**, are chiral and are reported to be at slightly higher energy (6.7 kJ mol^{-1}) than the chair form.[9] Though the counterparts for cyclohexanes rarely exist, the occurrence of the skew-boat conformation has been demonstrated by the crystal structural analysis of [Cr(tn)$_3$][Ni-(CN)$_5$]·2H$_2$O, where one of the three tn chelate rings takes a skew-boat and the other two take a chair conformation.[10]

Substitution of hydrogen atoms with methyl groups introduces steric interactions between the methyl groups and other atoms within the complex ion molecule. The methyl group equatorial to the chelate ring is sterically less hindered than the axial group. The chelate ring of *meso*-2,4-diaminopentane (*meso*-ptn) takes exclusively a chair form in which both methyl groups are equatorial. But for a chelate ring of *rac*-2,4-diaminopentane (*rac*-ptn), the preference of a chair form is incompatible with the preference of the equatorial orientation of a methyl group, because one of the two methyl groups should take an axial orientation in a chair form. Therefore a skew-boat is possible in which both the methyl groups take the equatorial orientation. The preference between

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a chair and a skew-boat seems to be affected by several factors, such as metal ion and solvent.[11] Optically resolved (2R,4R)-diaminopentane (R-ptn) discriminates between two skew-boats: both the methyl groups adopt axial and equatorial orientations for δ-skew-boat, **3**, and λ-skew-boat, **4**, respectively. In fact skew boat conformations have been found in the crystal structures of (−)$_{546}$-[Co(R-ptn)$_3$]Cl$_3$·2H$_2$O[12] and (+)$_{546}$-[Co(R-ptn)$_3$]Cl$_3$·H$_2$O,[13] but a chair form has been reported in the crystal structural study of [Pt(S-ptn)$_2$]Cl$_2$·H$_2$O.[14]

Several methods have been used in the investigation of this subject: CD spectra,[15] coupling constants between ^{195}Pt and the observed nucleus in ^{1}H and ^{13}C NMR,[16] X-ray crystallography,[11-14] and molecular force field calculation.[9] Hawkins et al. have reported detailed conformational analyses of 1,3-diamines coordinated to Co(III) and Pt(II) by an NMR method.[17] Well-separated ^{1}H and ^{13}C NMR spectra of tetracyano(diamine)ferrate(III) chelates are expected to provide a useful probe for the conformation analysis of 1,3-diamines coordinated to the Fe(III) center as the paramagnetic NMR of Ni(II) chelates.[18]

To these ends, Fe(II) and Fe(III) chelates that contain four cyano anions and one of four 1,3-diamines such as tn, bn, *meso*-ptn, and R-ptn were prepared. Their spectroscopic properties related to their conformations are described.

Experimental Section

Materials. 1,3-Diaminopropane (Tokyo Kasei) and Fe(ClO$_4$)$_2$·6H$_2$O (Alfa) were used without further purification. (2R,4R)-Diaminopentane and *meso*-2,4-diaminopentane were prepared according to the method of Bosnich.[19] 1,3-Diaminobutane was kindly supplied by Drs. Ajioka and Yano of the University of Tokyo.

Preparation of Iron(II) and Iron(III) Complexes. Na$_2$[Fe(CN)$_4$-(tn)]·4H$_2$O. Into a three-necked 300-mL round-bottomed flask equipped with a mechanical stirrer and a serum cap was placed Fe(ClO$_4$)$_2$·6H$_2$O (40.8 g, 0.112 mol), and nitrogen was passed through, followed by addition of methanol (100 mL). A methanol solution (50 mL) of 1,3-diaminopropane (25.0 g, 0.337 mol) was added to the Fe(ClO$_4$)$_2$ solution with vigorous stirring under nitrogen at 0 °C, followed by addition of sodium cyanide (22.0 g, 0.450 mol) dissolved in 50 mL of water. After 30 min, the resultant yellow-brown mixture was filtered with suction using a Buchner funnel of 20-cm o.d. Ethanol (1 L) was added to the yellow filtrate. The mixture was allowed to stand at −15 °C overnight. Separated yellow crystals were collected on a filter and washed with cold ethanol and ether subsequently. Yield: 29.0 g (73.5%). The crude product was recrystallized by dissolving it in water, followed by addition of ethanol, and letting the mixture stand overnight at −15 °C. Separated yellow needles were collected and dried in vacuo. Anal. Calcd for Na$_2$[Fe(CN)$_4$(C$_3$H$_{10}$N$_2$)]·4H$_2$O: C, 23.88; H, 5.15; N, 23.87. Found: C, 23.89; H, 5.33; N, 23.90.

Na$_2$[Fe(CN)$_4$(bn)]·2NaClO$_4$·2H$_2$O. A methanol solution (10 mL) of 1,3-diaminobutane (7.0 g, 79 mmol) was added to a methanol solution (50 mL) of Fe(ClO$_4$)$_2$ (9.56 g, 26.5 mmol) under nitrogen at 0 °C. An aqueous solution (15 mL) of NaCN (5.2 g, 106 mmol) was added dropwise to the resultant dark olive green mixture under vigorous stirring at 0 °C. The mixture was stirred for 30 min at this temperature after the completion of the addition of NaCN. The mixture was concentrated with a rotatory evaporator below 40 °C. Ethanol (150 mL) was added to the resultant yellow residue, and the mixture was kept at 0 °C overnight. Separated yellow crystals were collected on a filter, washed with ether, and dried in vacuo. Yield: 9.05 g (59.8%). These crystals were

taken into 25 mL of water, and the mixture was centrifuged. Ethanol (50 mL) was added to the dark orange supernatant. Colorless substances were separated and filtered. The filtrate was concentrated and redissolved in 8 mL of water, and a methanol solution of NaClO$_4$ (18 g in 75 mL) was added. The separated yellow crystals were thoroughly washed with ethanol and ether successively. Yield: 4.50 g (29.7%).

The yellow crystals were recrystallized by dissolving them in 3 mL of water, followed by addition of a methanol solution of NaClO$_4$ (12 g in 40 mL). Anal. Calcd for Na$_2$[Fe(CN)$_4$(C$_4$H$_{12}$N$_2$)]·2NaClO$_4$·2H$_2$O: C, 16.71; H, 2.80; N, 14.62. Found: C, 16.75; H, 2.68; N, 14.78.

Na$_2$[Fe(CN)$_4$(*meso*-ptn)]·2NaClO$_4$. A methanol solution (10 mL) of *meso*-2,4-diaminopentane (4 g, 39 mmol) was added to a methanol solution (30 mL) of Fe(ClO$_4$)$_2$·6H$_2$O (4.68 g, 12 mmol) under nitrogen at 0 °C, followed by addition of aqueous sodium cyanide (2.6 g, 53 mmol) in 6 mL of water. The resultant yellow brown solution was concentrated to near dryness under reduced pressure on a rotatory evaporator below 40 °C. To the residue formed was added ethanol (100 mL), and the mixture was cooled to 0 °C for 1 h. Separated yellow crystals were collected on a filter and washed with ethanol and ether subsequently. They were dissolved in 5 mL of water, and the mixture was centrifuged to remove undissolved materials. A methanol solution of sodium perchlorate (20 g) in 100 mL of methanol was added to the supernatant, and the mixture was allowed to stand in a refrigerator overnight. Separated yellow crystals were collected on a filter and washed with ethanol and ether, subsequently. Yield: 4.10 g (61.8%). Anal. Calcd for Na$_2$[Fe(CN)$_4$(C$_5$H$_{14}$N$_2$)]·2NaClO$_4$: C, 19.55; H, 2.55; N, 15.20. Found: C, 19.58, 19.51; H, 2.79, 2.63; N, 14.88, 15.15.

Na$_2$[Fe(CN)$_4$(R-ptn)]·2H$_2$O. Crude products were prepared according to the method described above by replacing the diamine with (2R,4R)-diaminopentane. The crude products were dissolved in 5.6 mL of water, and the mixture was filtered. To the filtrate was added ethanol (16 mL). The mixture was allowed to stand in a refrigerator overnight. Separated yellow crystals were collected on a filter and washed with ethanol and ether subsequently. Anal. Calcd for Na$_2$[Fe(CN)$_4$(C$_5$H$_{14}$N$_2$)]·2H$_2$O: C, 31.41; H, 5.27; N, 24.42. Found: C, 30.93; H, 4.50; N, 24.51.

Sodium perchlorate adducts were crystallized by dissolving the dihydrate complex in a minimum amount of a mixture of methanol and water (2:1), followed by addition of a saturated methanolic solution of NaClO$_4$. Separated yellow crystals were collected on a filter and washed with acetone thoroughly. These crystals gave the same electronic spectrum as that of the dihydrate. Anal. Calcd for Na$_2$[Fe(CN)$_4$(C$_5$H$_{14}$N$_2$)]·1.5NaClO$_4$: C, 21.98; H, 2.87; N, 17.09. Found: C, 22.16; H, 3.11; N, 17.52.

Na[Fe(CN)$_4$(tn)]·1.5H$_2$O and H[Fe(CN)$_4$(tn)]·2H$_2$O·(CH$_3$)$_2$CHOH. Concentrated aqueous hydrogen peroxide (30%, 2 mL) was added dropwise to Na$_2$[Fe(CN)$_4$(tn)]·4H$_2$O (3.16 g, 9 mmol) suspended in a mixture of 60% perchloric acid and ethanol (1:20) (30 mL) under vigorous stirring at 0 °C. The ivory-colored and pale yellow precipitates formed were collected with suction and washed with cold ethanol. These were dissolved in 2 M HClO$_4$ (10 mL) and filtered. To the filtrate was added a mixture of equal volume of 2-propanol and ether until the solution became turbid. The mixture was allowed to stand at −15 °C overnight. Separated pale yellow crystals were collected on a filter and washed with cold ethanol and ether subsequently. Yield: 1.67 g (65.3%). Anal. Calcd for Na[Fe(CN)$_4$(C$_3$H$_{10}$N$_2$)]·1.5H$_2$O: C, 29.60; H, 4.61; N, 29.59. Found: C, 29.62; H, 4.94; N, 29.53.

Successive crystallization from a mixture of 2 M HClO$_4$ and 2-propanol afforded orange crystals. Anal. Calcd for H[Fe(CN)$_4$(C$_3$H$_{10}$N$_2$)]·2H$_2$O·C$_3$H$_8$O: C, 36.27; H, 7.00; N, 25.38. Found: C, 35.90; H, 7.40; N, 25.53.

H[Fe(CN)$_4$(bn)]·1.5H$_2$O·(CH$_3$)$_2$CHOH. Into an ice-cold mixture of methanol (8 mL) and 60% HClO$_4$ (0.5 mL) was dissolved Na$_2$[Fe(CN)$_4$(bn)]·2NaClO$_4$·2H$_2$O (0.691 g, 1.28 mmol). The mixture was stirred, and 6% aqueous hydrogen peroxide (1.25 mL) was added dropwise at 0 °C. The mixture turned from yellow to dark violet via green. To the mixture was added 2-propanol (15.5 mL), and separated violet substances were filtered off and ether (2.7 mL) was added until the filtrate became turbid. The mixture was allowed to stand at −15 °C for 2 h. Separated violet substances were filtered off again. Ether (3.5 mL) was added, and the mixture was kept at −15 °C overnight. An oily brown substance separated, and the supernatant was removed by decantation. An additional 12.5-mL portion of ether was added to the residue, and the mixture was allowed to stand at −15 °C for 3 days. The residue crystallized as orange crystals. The crystals were collected on a filter and washed with ether. These crystals were recrystallized from a mixture of methanol (5 mL), 60% HClO$_4$ (0.5 mL), 2-propanol (5 mL), and ether (20 mL). Yield: 0.63 g (17%). Anal. Calcd for H[Fe(CN)$_4$(C$_4$H$_{12}$N$_2$)]·1.5H$_2$O·C$_3$H$_8$O: C, 39.29; H, 7.21; N, 25.00. Found: C, 38.89; H, 7.20; N, 25.00.

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H[Fe(CN)₄(*meso*-ptn)]·2H₂O·³/₄(C₂H₅OH). Concentrated aqueous hydrogen peroxide (0.5 mL, 5 mmol) was added dropwise to Na₂[Fe-(CN)₄(*meso*-ptn)]·2NaClO₄ (2.0 g, 3.6 mmol) suspended in a mixture of 60% HClO₄ (1 mL) and ethanol (20 mL) with vigorous stirring at 0 °C. The mixture was diluted with cold water (20 mL) to dissolve the remaining materials. To the mixture were added ethanol (20 mL), 60% HClO₄ (2 mL), and ether (120 mL), and the mixture was allowed to stand in a refrigerator overnight. Separated orange needles were collected. Yield: 0.90 g (75%).

These were dissolved in a mixture of 2 M HClO₄ (10 mL) and ethanol (30 mL), and a small amount of ether was added until the mixture became turbid. Separated crystals were collected and washed with ether. Anal. Calcd for H[Fe(CN)₄(C₅H₁₄N₂)]·2H₂O·³/₄C₂H₅OH: C, 37.79; H, 7.10; N, 25.19. Found: C, 37.72; H, 6.89; N, 25.04.

H[Fe(CN)₄(*R*-ptn)]·1.5H₂O·³/₄(CF₃CH₂OH). Concentrated aqueous hydrogen peroxide (0.36 mL, 3 mmol) was added dropwise to Na₂[Fe-(CN)₄(*R*-ptn)]·2H₂O (1.22 g, 3.74 mmol) suspended in a mixture of perchloric acid (60%, 0.6 mL) and ethanol (15 mL) with stirring at 0 °C. To the resultant mixture was added water (3 mL), and the mixture was filtered to remove undissolved materials. A mixture of trifluoroethanol and ether was added to the filtrate until the solution became turbid. Separated dark violet substances were removed by filtration. This procedure was repeated until the filtrate became yellow orange. To the filtrate was added trifluoroethanol, and the mixture was allowed to stand at −15 °C. Pale yellow needles separated and were collected and washed with ether. Yield: 0.52 g (56%).

Recrystallization was carried out by adding trifluoroethanol (1.0 mL) to a solution of the crude product in 2 M HClO₄ (3.5 mL). Anal. Calcd for H[Fe(CN)₄(C₅H₁₄N₂)]·1.5H₂O·³/₄CF₃CH₂OH: C, 34.54; H, 5.59; N, 23.01. Found: C, 34.57, 34.56; H, 5.35, 5.22; N, 23.24, 22.96.

Physical Measurements. Electronic spectra of the aqueous solutions of the Fe(II) chelates and hydrochloric acid (1.0 × 10⁻³ M) solutions of the Fe(III) chelates were recorded with a Shimadzu UV-210A spectrophotometer. CD and MCD spectra were recorded with a Jasco J-40 recording polarimeter with an electromagnet attachment for the latter with the same solvents used as for electronic spectra. Infrared spectra were recorded with a Jasco IRA-2 spectrophotometer by using Nujol mulls. ¹H and ¹³C NMR spectra of the Fe(II) chelates used weighed sample (40–50 mg) dissolved in D₂O (0.35 mL), which was previously degassed by several freeze–pump–thaw cycles and which contained sodium 3-(trimethylsilyl)propionate-2,2,3,3-*d*₄ as an internal standard (−0.02 ppm for ¹H NMR and −1.91 ppm for ¹³C NMR), in a sealed tube of 5-mm diameter. The ¹H and ¹³C NMR spectra were recorded with a JEOL MH-100 and a JEOL FX-100 spectrometers, respectively. For ¹H and ¹³C spectra of the Fe(III) chelates, the samples were dissolved in D₂O, which contained sodium 2,2-dimethyl-2-silapentane-5-sulfonate (0.0 ppm) and dioxane (67.4 ppm) as internal standards for ¹H and ¹³C NMR measurements, respectively. The spectra were recorded with a JEOL FX-100 spectrometer.

Results and Discussion

Preparation of Fe(II) and Fe(III) Chelates. A Comparison with Analogues of 1,2-Diamines. Tetracyanoferrate(II) chelates with four 1,3-diamines were prepared according to a slightly modified method used for the 1,2-diamine chelates. The procedures for the ligand substitution, which are assumed to be

R = H or CH₃
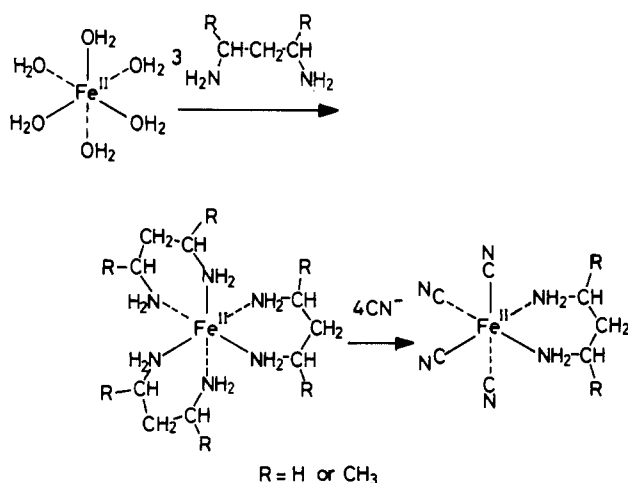
were carried out at a lower temperature than that used for the preparation of 1,2-diamine chelates. If less than 3 equiv of di-

Table I. Maxima of Electronic Spectra of [Fe(CN)₄(1,3-diamine)]²⁻ and [Fe(CN)₄(1,3-diamine)]⁻ and Selected 1,2-Diamine Counterparts

	diamine	$\nu/10^3$ cm⁻¹ ($\epsilon/$(L mol⁻¹ cm⁻¹))
Fe^IIa	tn	25.5 (465), 31.7 (443 sh), 42.2 (10 300), 45.0 (10 000)
	bn	25.3 (501), 31.3 (495 sh), 42.5 (10 900), 44.0 (10 600)
	meso-ptn	25.4 (460), 31.7 (590 sh), 42.6 (10 100)
	R-ptn	25.4 (460), 31.7 (440 sh), 42.6 (10 600), 45.0 (10 600)
	en^c	25.6 (378), 31.7 (429 sh), 45.5 (11 800)
	R-chxn^d	25.5 (407), 32.0 (457 sh), 44.8 (9770)
Fe^IIIb	tn	26.7 (672 sh), 27.4 (681), 32.4 (845), 34.3 (798), 43.5 (8730), 48.8 (16 300)
	bn	26.7 (662 sh), 27.4 (675), 32.0 (809), 34.2 (779), 43.5 (8910), 48.8 (16 200)
	meso-ptn	26.7 (692 sh), 27.4 (705), 32.3 (851), 34.3 (825), 43.5 (9600), 48.8 (15 600)
	R-ptn	26.7 (668 sh), 27.7 (676), 32.0 (804), 34.5 (756), 43.5 (8700), 48.8 (14 700)
	en^c	27.3 (792), 32.6 (930)
	R-chxn^d	26.6 (759), 32.5 (1020), 34.5 (870), 43.5 (9000 sh)

*ᵃ*Aqueous solution. *ᵇ*1.0 × 10⁻³ M hydrochloric acid solution. *ᶜ*Reference 5. *ᵈ*Reference 3.

amines was used, the yield was poor and the product was contaminated with considerable amounts of byproducts. Thus the formation of tris(diamine)iron(II) is necessary prior to the addition of cyanide. The crude product obtained by addition of ethanol to a concentrated reaction mixture contained a large amount of dark brown compounds, which were slightly soluble in water. These were removed by centrifugation. Three chelates, [Fe-(CN)₄(bn)]²⁻, [Fe(CN)₄(*meso*-ptn)]²⁻ and [Fe(CN)₄(*R*-ptn)]²⁻, were isolated as sodium perchlorate adducts, but the addition of sodium perchlorate was not effective for crystallization of [Fe-(CN)₄(tn)]²⁻. The products were stored under vacuum at −15 °C, because these chelates in the solid state tend to decompose at room temperature with formation of green substances.

The Fe(III) chelates were prepared by oxidation of the corresponding Fe(II) chelates with hydrogen peroxide under acidic conditions:

R = H or CH₃
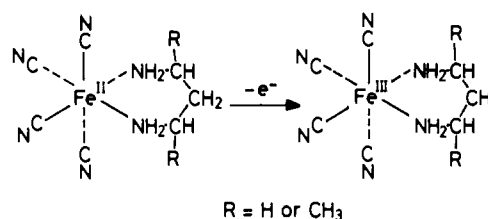
The initially isolated substances showed pale yellow color and the elemental analyses indicated the formation of sodium salts of the anion chelates, but these complex salts were not well-defined. Recrystallizations from 2 M HClO₄ by addition of a mixture of suitable alcohol and ether were repeated and afforded well-defined crystals that showed the presence of the alcohol in the elemental analyses and the NMR spectra. Significant changes in infrared spectra were brought by this recrystallization (vide infra) and suggested the formation of oxonium salts. One of the chelates, [Fe(CN)₄(*R*-ptn)]⁻ was recrystallized from a mixture containing trifluoroethanol instead of ethanol because the latter alcohol also gave well defined crystals but made one of the ¹H NMR signals ambiguous due to superposition of the methyl signal.

Characterization of Fe(II) Chelates. The isolated compounds are yellow in color and diagmagnetic as described below. Infrared spectra showed intense C≡N stretchings at 2050 cm⁻¹. Two sharp N–H stretchings were found between 3260 and 3350 cm⁻¹ as well as strong N–H₂ bending at 1600 cm⁻¹.

Electronic spectra in water are tabulated in Table I. The first and the second absorption bands appear at 25 500 and 31 700 cm⁻¹, respectively. The isostructural and isoelectronic compound [Co(CN)₄(tn)]⁻ has been reported to have the absorption maxima
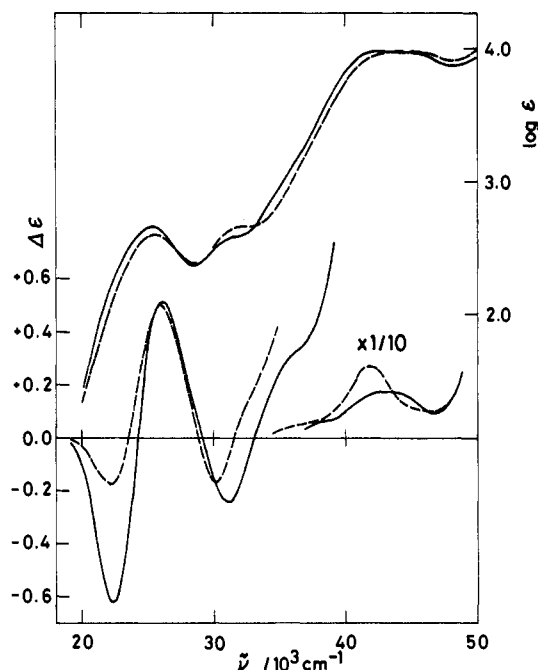
Figure 1. Electronic and CD spectra of [Fe(CN)$_4$(R-ptn)]$^{2-}$ (—) and [Fe(CN)$_4$(R-chxn)]$^{2-}$ (- - -) in aqueous solution.

Figure 3. Electronic and CD spectra of [Fe(CN)$_4$(R-ptn)]$^-$ (—) and [Fe(CN)$_4$(R-chxn)]$^-$ (- - -) in 10^{-3} M HCl.

at 27900 and 35000 cm^{-1}.[20] The electronic and circular dichroism (CD) spectra of Na$_2$[Fe(CN)$_4$(R-ptn)]·2H$_2$O are shown in Figure 1 along with those of Na$_2$[Fe(CN)$_4$(R-chxn)]·0.5NaClO$_4$·0.5H$_2$O.[2] Two CD components with opposite signs are found in the region of the first absorption band as have been found for [Fe(CN)$_4$-(R-pn)]$^{2-}$ and [Fe(CN)$_4$(R-chxn)]$^{2-}$.[2] (R-pn = (R)-1,2-diaminopropane; R-chxn = (1R,2R)-diaminocyclohexane). These CD components have been assigned to the components relating to ^{1}A$_{1g}$ → ^{1}A$_{2g}$ and ^{1}A$_{1g}$ → ^{1}E$_g$ transitions under D_{4h} symmetry.[2] The locations of the maxima of two CD components are almost the same between the 1,2- and 1,3-diamine chelates. While the magnitude of the positive components (^{1}A$_{1g}$ → ^{1}E$_g$) of the R-ptn chelate is almost the same as that of [Fe(CN)$_4$(R-chxn)]$^{2-}$, the magnitude of the negative component (^{1}A$_{1g}$ → ^{1}A$_{2g}$) of the R-ptn chelate exceeds that of the R-chxn chelate. Fujita et al. have reported that CD spectra of *trans*-[Co(CN)$_2$(R-ptn)$_2$]$^+$ and *trans*-[CoCl$_2$(R-ptn)$_2$]$^+$ have positive ^{1}A$_{1g}$ → ^{1}E$_g$ components and negative ^{1}A$_{1g}$ → ^{1}A$_{2g}$ components. The magnitudes of the latter components are larger than those of the corresponding 1,2-diamine complexes, which form five-membered chelate rings with λ-conformation, while the magnitudes of ^{1}A$_{1g}$ → ^{1}E$_g$ are little influenced by the size of chelate rings. Thus the CD spectrum of the Fe(II) chelate is accounted for by the predominance of the λ-skew-boat conformer of coordinated R-ptn. The resemblance of the two components in relative intensities between the Fe(II) and the Co(III) chelates indicates the preference of λ-skew-boat conformer for the low-spin Fe(II) chelate and supports the invariance of CD components of isostructural and isoelectronic transition-metal complexes.[2]

The UV absorption spectra of [Fe(CN)$_4$(R-ptn)]$^{2-}$ and [Fe-(CN)$_4$(R-chxn)]$^{2-}$ are similar to each other, but the CD spectrum of the former shows weaker components at 40 500 cm^{-1}.

Characterization of Fe(III) Chelates. The Fe(III) chelates were isolated as oxonium or sodium salts. Marked differences are observed in infrared spectra as shown in Figure 2 (supplementary material). A sharp absorption at 2160 cm^{-1} and broad absorptions at 1900–1650 cm^{-1} were observed for the former. However, sharp absorptions at 2100 and 2130 cm^{-1} were observed for the latter. Oxonium salts of this type have been reported for H[Fe(CN)$_4$-

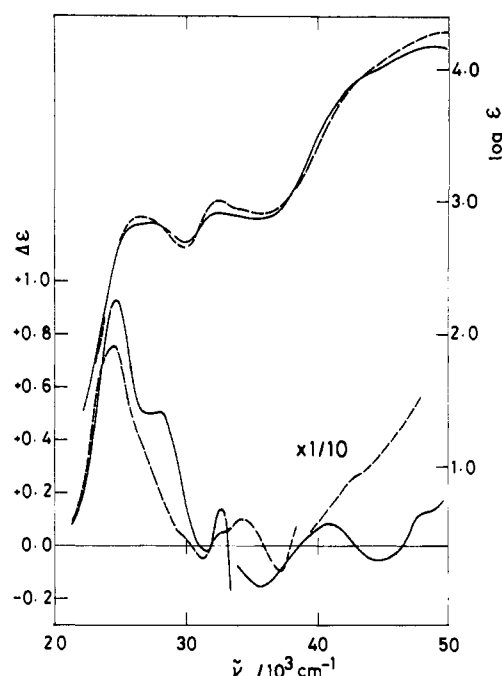(phen)]·2H$_2$O and H[Fe(CN)$_4$(bpy)]·2H$_2$O.[7,22] The broad absorption centered at 1750 cm^{-1} supports the postulation that a hydrogen is attached to the coordinated C≡N group, thus reducing the bond order of the C≡N group.

Electronic spectral data are listed in Table I and the electronic and CD spectra of [Fe(CN)$_4$(R-ptn)]$^-$ in 10^{-3} M HCl are shown in Figure 3 along with those of [Fe(CN)$_4$(R-chxn)]$^-$. Electronic spectra of the 1,3-diamine chelates are similar to those of the 1,2-diamine chelates[3] and contain three major absorptions at 27 000, 33 000, and 43 500 cm^{-1}. Their absorption coefficients exceed 500 and suggest that they arise from charge-transfer excitations, but the CD spectrum reveals that each absorption contains more than two components. The lowest energy absorption at ca. 27 000 cm^{-1} is related to two positive CD components at 24 600 and 28 000 cm^{-1}.

The second absorption between 30 000 and 38 000 cm^{-1} exhibits one CD component, in sign opposite to that of [Fe(CN)$_4$(R-chxn)]$^-$. This region is prevailed by CN → Fe charge-transfer bands. A charge-transfer band of *trans*-[CoCl$_2$(R-ptn)$_2$]$^+$ has a negative component at ca. 32 000 cm^{-1},[15] but *trans*-[CoCl$_2$(R-chxn)$_2$]$^+$ and *trans*-[CoCl$_2$(R-pn)$_2$]$^+$ have a positive CD component in this region, which has been assigned to the Cl → Co charge-transfer band.[23] Inversion in sign between six-membered chelate rings and five-membered chelate rings for the Fe(III) and Co(III) complexes suggests that the sign of the CD component of this charge-transfer band is affected by N–M–N bond angle.

The UV region absorptions correspond to three CD components. The CD component at 46 000 cm^{-1} has a sign opposite to that of [Fe(CN)$_4$(R-chxn)]$^-$ and [Fe(CN)$_4$(R-pn)]$^-$.

Magnetic circular dichroism (MCD) spectra of [Fe(CN)$_4$(en)]$^-$ and [Fe(CN)$_4$(tn)]$^-$ are shown in Figure 4. The main feature of these spectra is their resemblance to that of [Fe(CN)$_6$]$^{3-}$.[24] The electron-transfer bands due to t$_{1u}$ → t$_{2g}$ and t$_{2u}$ → t$_{2g}$ transitions involve positive and negative Faraday C terms.[25] The maximum of the positive components is located at 26 400 cm^{-1}, which is

(20) Ohkawa, K.; Fujita, J.; Shimura, Y. *Bull. Chem. Soc. Jpn.* **1965**, *38*, 66.
(21) Kashiwabara, K.; Kojima, M.; Fujita, J. *Bull. Chem. Soc. Jpn.* **1979**, *52*, 772.
(22) Infrared spectra of these showed a broad absorption centered at 1750 cm^{-1} in addition to sharp absorptions around 2050 cm^{-1}.
(23) (a) Wentworth, R. A. D.; Piper, T. S. *Inorg. Chem.* **1965**, *4*, 202. (b) Treptow, R. S. *Inorg. Chem.* **1966**, *5*, 1593.
(24) Gale, R.; McCaffery, A. J. *J. Chem. Soc. Dalton Trans.* **1973**, 1344 and references cited therein.
(25) Cotton, F. A.; Wilkinson, G. *Advanced Inorganic Chemistry*; 4th ed.; Wiley: New York, 1980; p 674.
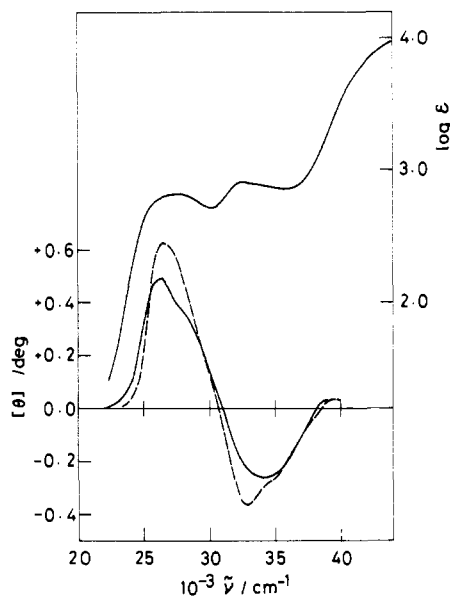
Figure 4. Electronic and magnetic circular dichroism spectra of [Fe-(CN)₄(tn)]⁻ (—) and [Fe(CN)₄(en)]⁻ (---) in 10^{-3} M HCl.
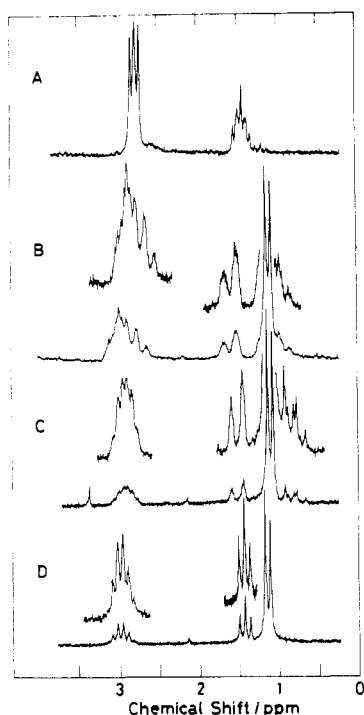
Figure 5. ¹H NMR spectra of Fe^{II} chelates: A, [Fe(CN)₄(tn)]²⁻; B, [Fe(CN)₄(bn)]²⁻; C, [Fe(CN)₄(*meso*-ptn)]²⁻; D, [Fe(CN)₄(*R*-ptn)]²⁻.

higher in energy by 1800 cm⁻¹ than the lowest energy absorption in the CD spectra of [Fe(CN)₄(*R*-ptn)]⁻.

NMR Spectra of Fe(II) and Fe(III) Chelates and Conformations of Coordinated 1,3-Diamines. Fe(II) Chelates. The NMR measurements were carried out by using degassed D₂O as a solvent, because an aqueous solution of the Fe(II) chelate decomposes slightly on contact with air, yielding small amounts of precipitates.

¹H NMR spectra of the Fe(II) chelates are reproduced in Figure 5. The numerical data of ¹H and ¹³C NMR measurements are tabulated in Table II. The coupling constants reported in this paper were derived from first-order analysis of the spectra. The numbering of each nucleus is indicated in the text and is used throughout this paper.

The ¹H NMR spectrum of [Fe(CN)₄(tn)]²⁻ shows two multiplets at 1.41 and 2.78 ppm as shown in Figure 5A. A rapid interconversion among chair and skew-boat forms will yield an

Table II. Chemical and Isotropic Shifts of [Fe(CN)₄(1,3-diamine)]²⁻ and [Fe(CN)₄(1,3-diamine)]⁻

diamine	nucleus[a]	chem shift/ppm[b]		isotropic shift/ppm[c]
		Fe^{II}	Fe^{III}	
tn	H^A, H^C	2.78	−5.25	8.03
	H^I, H^J	1.41	23.79	−22.38
	C^1	42.3	222.4	−180.1
	C^2	28.6	29.4	−0.8
	CN	182.7		
		183.7		
bn	H^A	2.92	6.30	−3.38
	H^B	2.91	−11.35	14.26
	H^C	2.65	5.73	−3.08
	H^I	1.03	14.64	−13.62
	H^J	1.62	32.70	−31.08
	H^M	1.24	3.97	−2.73
	C^1	42.4	202.9	−160.5
	C$^{1'}$	49.4	239.8	−190.4
	C^2	35.7	39.5	−3.8
	C^3	26.7	−39.4	66.1
	CN	183.0		
		184.0		
meso-ptn	H^A	2.78	6.66	−3.88
	H^I	0.86	14.51	−13.65
	H^J	1.60	32.70	−31.10
	H^M	1.19	3.78	−2.59
	C^1	49.8	214.9	−165.1
	C^2	43.2	50.8	−7.6
	C^3	26.7	−35.9	62.6
	CN	182.3		
		183.4		
R-ptn	H^C, H^D	2.98	0.89	2.09
	H^I, H^J	1.42	18.45	−17.03
	H^M	1.13	2.63	−1.50
	C^1	44.9	216.3	−171.4
	C^2	40.3	46.9	−6.6
	C^3	25.5	−21.0	46.5
	CN	182.4		
		183.9		

[a] For abbreviation, see text. [b] δ_{DSS} = 0.0 for ¹H NMR and $\delta_{dioxane}$ = 67.4 for ¹³C NMR. [c] Isotropic shift = $-(\delta_{Fe^{III}} - \delta_{Fe^{II}})$.

AA′BB′XY spectrum for a coordinated tn with fully deuterated nitrogen atoms. The AA′BB′XY spectrum would be too complicate to obtain each coupling constants from the spectrum shown in Figure 5A, but the "triplet" type of the methylene parts adjacent to the nitrogens shows the coupling constant of 10.8 Hz. This value is almost the same as those found for [Pd(tn)₂]²⁺ and [Pt(tn)₂]²⁺ (11 Hz) but is smaller than that of tn·2HCl (15 Hz).[16b] The rapid interconversion between two chair forms (**5** and **6**) is expected to occur from the spectrum of [Fe(CN)₄(tn)]⁻ as described in a later section.

5   **6**
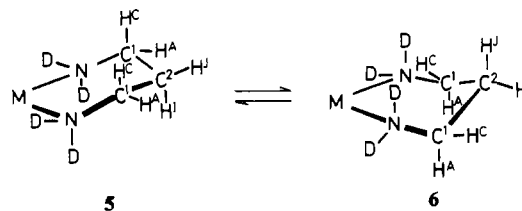
The ¹H NMR spectrum of Na₂[Fe(CN)₄(*meso*-ptn)]²⁻ (Figure 5C) is in agreement with the structure of the chair form in which both methyl groups adopt equatorial positions, **7**. The assignments


7   **8**
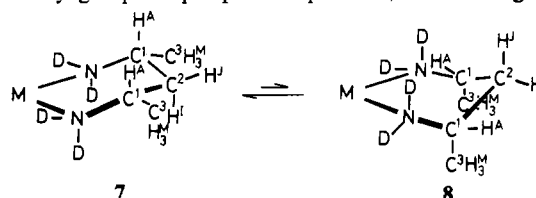
of signals are listed in Table II. Two protons of the central methylene bridge resonate separately and appear as a composite

derived from an AB quartet (J_{gem} = 14.6 Hz). The signals at higher and lower fields are assigned to the axial(H^I) and equatorial (H^J) methylene protons, which couple with the axial methine protons (H^A) with vicinal coupling constants of 11.3 and ca. 3 Hz, respectively. The vicinal coupling constant of 11.3 Hz shows a predominant contribution of conformer **7**.

The ¹H NMR spectrum of [Fe(CN)₄(bn)]²⁻ (Figure 5B) looks complicated due to the superposition of several resonances. The resonances between 0.5 and 2.0 ppm are attributed to the methyl protons and axial and equatorial protons attached to the central methylene bridge, H^I and H^J. The composite signals between 2.5 and 3.5 ppm were reduced to an AB quartet (2.65 and 2.91 ppm, J_{vic} = 12.1 Hz) and a singlet at 2.89 ppm on irradiation at the region over methyl protons and the resonances at 1.03 ppm. The AB quartet is assigned to the axial and equatorial protons attached to the methylene carbon next to the nitrogen atom, H^C and H^B. The singlet at 2.89 ppm was assigned to the methine proton, H^A. The resonances between 0.5 and 2.0 ppm were also reduced to an AB quartet (1.03 and 1.62 ppm, J = 12.0 Hz) and a singlet (1.10 ppm) on strong irradiation in the region between H^A and H^C. These are assigned to H^I, H^J, and methyl protons. The coupling constants $^3J_{H^C,H^I}$ and $^3J_{H^A,H^I}$ were determined to be 12.0 Hz.

The observation of separate signals for the resonances of (a) H^A and H^C and (b) H^I and H^J are consistent with a predominant chair conformation, and the coupling constant of 12 Hz for $J_{H^I-H^A}$ shows predominance of the chair form with an equatorial methyl group, **9**, over the skew-boat form, **10**. The dihedral angle of

9   **10**
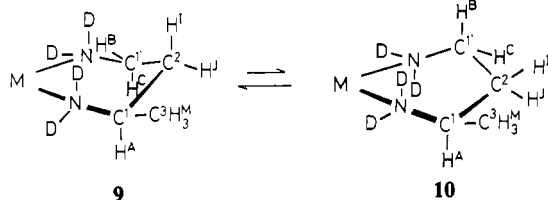
$H^I-C^2-C^1-H^A$ is expected to be nearly 180° and 120° for the chair and the skew-boat form, respectively.

The ¹H NMR spectrum of [Fe(CN)₄(R-ptn)]²⁻ showed three signals at 1.13, 1.42, and 2.98 ppm, and these are assigned to the methyl, methylene, and methine protons, respectively. The conformation of a coordinated R-ptn is complicated because the preference of a chair form for a six-membered chelate ring and the equatorial preference of substituted methyl groups compete with each other. Four conformers are conceivable for a coordinated R-ptn. The two skew-boat conformers are not energetically equivalent. The δ-skew-boat conformer, **13**, is destabilized by the

11   **12**

13   **14**
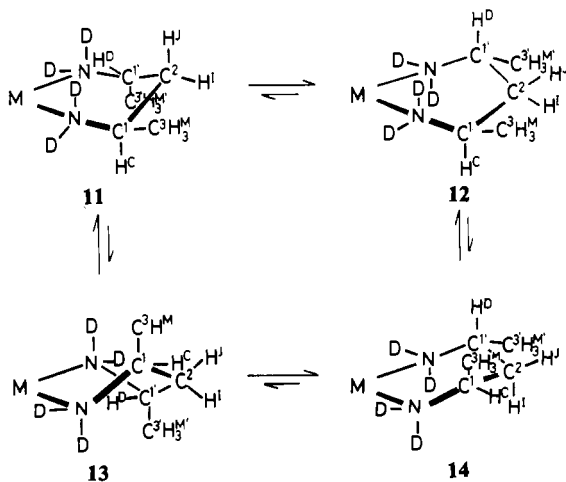
skew-boat conformation and the two axial methyl substituents. But the λ-skew-boat conformer, **12**, is favored by the presence of the two equatorial methyl groups. The chair forms, **11** and **14**, are energetically equivalent but are hampered by the axial methyl group, which causes 1,3-diaxial interaction within the chelate ring and steric repulsion with the apical ligands.
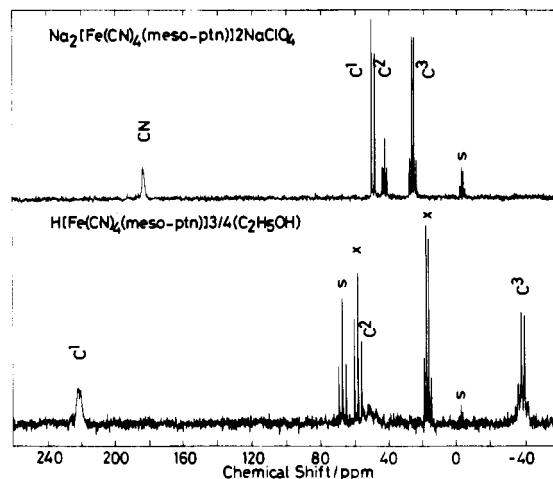
Figure 6. Off-resonance ¹³C NMR spectra of [Fe(CN)₄(*meso*-ptn)]²⁻ (top) and [Fe(CN)₄(*meso*-ptn)]⁻ (bottom).

The accessibility of rac- or R-ptn to the three conformers is evident from the X-ray crystal structural analyses. The distribution of both conformers have been estimated on the coupling constants of J_{vic}. According to Hawkins the value of this coupling constant varies with the structure of chelates.[17] Large values have been reported for tris octahedral complexes: 8.69 Hz for Δ-[Co(R-ptn)₃]³⁺ [17] and 8.40 Hz for Λ-[Co(R-ptn)₃]³⁺.[17] Values around 7 Hz are reported for mono rac-ptn and R-ptn octahedral complexes: 7.62 Hz for [Co(rac-ptn)(NH₃)₄]³⁺,[26] 7.03 Hz for [Co(CN)₄(rac-ptn)]³⁺,[17] 7.0 Hz for [PtCl₂(NH₃)₂(R-ptn)]²⁺,[16a] and 7.5 Hz for [Pt(OH₂)₂(NH₃)₂(R-ptn)]⁴⁺.[16a] Small values below 6 Hz are reported for square-planar complexes and an octahedral complex with large bond distance between metal and the nitrogen atom of the chelate: 5.5 Hz for [Pt(NH₃)₂(R-ptn)]²⁺,[16a] 5.3 Hz for [Pt(OH₂)₂(R-ptn)]²⁺,[16a] 5.9 Hz for [Pt(bpy)(R-ptn)]²⁺,[17] and 6.3 Hz for [Mo(CO)₄(R-ptn)].[27]

The methylene protons appeared as a triplet having the coupling constant of 6.9 Hz. If the vicinal coupling constants, J_{trans} and J_{gauche}, are assumed to be 11.3 and 3.0 Hz as found for [Fe(CN)₄(*meso*-ptn)]²⁻, the averaged vincinal coupling constants for a chair and λ-skew-boat are estimated to be 5.1 and 7.5 Hz, respectively. The observed coupling constants give a ratio of **12** to (**11** + **14**) of 80:20. Although this estimation is close to that for [Pt(bpy)(rac-ptn)]²⁺,[16f] the assumption is not firm enough for an exact value.

The more elaborate treatment of the coupling constants using a Karplus type approximation have been reported by Hawkins et al.[17] A similar population (70:30) is obtained by the treatment described by them.

The *meso*-ptn and R-ptn chelates described above have shown that each proton resonates at a higher magnetic field by 0.22 to 0.01 ppm than that of the corresponding tetracyano(diamine)-cobaltate(III).[17]

Chemical shifts of the ¹³C NMR spectra of the four Fe(II) chelates are tabulated in Table II. The off-resonance spectrum of [Fe(CN)₄(*meso*-ptn)]²⁻ is shown in Figure 6.

Fe(III) Chelates. The spectral changes on varying the composition of a mixture of [Fe(CN)₄(*meso*-ptn)]²⁻ and [Fe(CN)₄(*meso*-ptn)]⁻ are shown in Figure 7. Plots of the observed chemical shifts against the mole fraction of Fe(III) chelate showed a linear relationship. All the signals moved downfield on addition of the Fe(III) chelate: the resonances corresponding to H^J moved downfield most significantly and appeared at 2.36 ppm for the mixture with Fe(III) fraction of 0.032; the other methylene proton signal appeared as a broad band at 2.52 ppm for the mixture with a Fe(III) fraction of 0.125. By extrapolation of the mole fraction to 1.0, the chemical shift of the Fe(III) chelate for each proton

(26) Hambley, T. W.; Hawkins, C. J.; Palmer, J. A.; Snow, M. R. *Aust. J. Chem.* **1981**, *34*, 45.

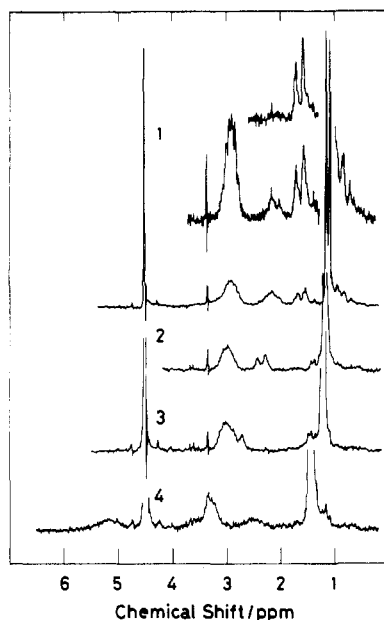(27) Cotton, F. A.; Wing, R. A. *Inorg. Chem.* **1965**, *4*, 314.

Figure 7. NMR spectral change of mixtures of [Fe(CN)₄(*meso*-ptn)]²⁻ and [Fe(CN)₄(*meso*-ptn)]⁻. The mole fractions of the Feᴵᴵᴵ chelate for each spectrum are as follows: 1, 0.0; 2, 0.032; 3, 0.050; 4, 0.125.

is estimated and is in agreement with that for [Fe(CN)₄(*meso*-ptn)]⁻. This phenomenon is in accordance with a rapid electron exchange between low-spin Fe(II) and Fe(III) centers.[4,28]

Paramagnetic NMR has been used to elucidate the conformations of the five- and six-membered chelate rings of coordinated diamines to Ni(II) by Reilley et al.[18,29] Tetracyano(diamine)-ferrate(III) chelates exhibit well-separated ¹H and ¹³C NMR spectra.[4] The paramagnetic shift of the Fe(III) chelates arises from a composite of the dipole–dipole interaction and the Fermi contact interaction and is expected to be different from that of Ni(II) chelates for which the isotropic shift is ascribed to the Fermi contact shift. The nature of the paramagnetic shift may be clarified by evaluation of these interactions, but an application to the analysis of conformation of the six-membered chelate ring is described in this report.

¹H NMR spectra of the four Fe(III) chelates are reproduced in Figure 8, and the numerical data and isotropic shifts defined as $-(\delta_{Fe(III)} - \delta_{Fe(II)})$ are listed in Table II. The ¹H resonances were observed in the region between +35 and −15 ppm. The width of each signal is small. Each signal is assigned on the basis of a change in chemical shift on varying the composition of the mixture of Fe(II) and Fe(III) chelates of an identical set of ligands, as well as on the relative intensity of each signal.

The magnitude of the isotropic shift of the proton attached to the carbon atom next to nitrogen, C¹, is smaller than that of 1,2-diamine Fe(III) chelates.[4] Methyl proton resonances show downfield shift like those of 1,2-diamine chelates, but their magnitudes are also smaller. On the contrary, protons attached to the central methylene carbon, C², showed large downfield shifts.

¹³C NMR spectra of these Fe(III) chelates showed well-separated signals in the region between +240 and −50 ppm and the splitting due to ¹J_{C-H} was observed on off-resonance spectra as exemplified in Figure 6B. The isotropic shift of C¹ is about −180 ppm, almost the same value as those found for [Fe(CN)₄(1,2-diamine)]⁻. The methyl carbons showed large upfield shifts, but C² carbons showed far less downfield isotropic shifts.

[Fe(CN)₄(*meso*-ptn)]⁻. As stated in the previous section, the six-membered chelate ring composed of *meso*-ptn takes exclusively the form of conformer 7. Four signals appeared at 32.70, 14.51, 6.66, and 3.78 ppm for the ¹H NMR spectrum and are assigned
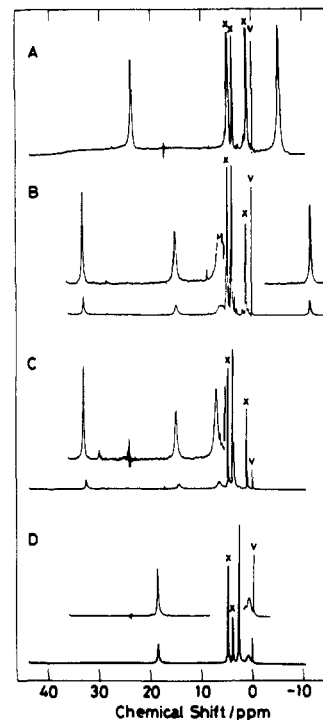

Figure 8. ¹H NMR spectra of Feᴵᴵᴵ chelates: A, H[Fe(CN)₄(tn)]·2H₂O·(CH₃)₂CHOH; B, H[Fe(CN)₄(bn)]·1.5H₂O·(CH₃)₂CHOH; C, H[Fe(CN)₄(*meso*-ptn)]·2H₂O·³/₄C₂H₅OH; D, H[Fe(CN)₄(*R*-ptn)]·1.5H₂O·³/₄CF₃CH₂OH. V and X indicate signals due to DSS and HDO or to alcohols included in molecular formula.

to the equatorial methylene proton, Hᴶ, the axial methylene proton, Hᴵ, the methine proton, Hᴬ, and the methyl protons, Hᴹ, respectively. The two methylene protons resonate separately with a separation of 18.19 ppm and the most downfield signal due to Hᴶ is narrower than the next signal due to Hᴵ. The fixed conformation of 7 is in agreement with this large separation.

Tetraaquo(*meso*-2,4-diaminopentane)nickel(II) has been reported to give isotropic shifts of −36.8, +17.3, +8.3, and −25.1 ppm for Hᴬ, Hᴵ, Hᴶ, and Hᴹ, respectively.[18] The signs of isotropic shifts of Fe(III) and Ni(II) complexes are not opposite as required from the differences in number of d electrons, and the relative order of the isotropic shifts within the individual molecules is different.

The isotropic shift of −3.88 ppm is derived for Hᴬ. This is considerably small compared to those of the proton attached to the carbon atoms of the five-membered chelate ring in [Fe(CN)₄(1,2-diamine)]⁻, where the axial protons have shown isotropic shifts of ca. 14 ppm.[4]

[Fe(CN)₄(tn)]⁻. Two signals observed at 23.79 and −5.25 ppm are assigned to the methylene protons of the C² carbon (Hᴵ + Hᴶ) and those of the C¹ carbon (Hᴬ + Hᶜ), respectively. The rapid interconversion between conformers 5 and 6 results in the observation of time-averaged signals of the axial and the equatorial protons. The isotropic shift of −22.38 ppm for Hᴵ + Hᴶ coincides with the mean of those for Hᴵ and Hᴶ of [Fe(CN)₄(*meso*-ptn)]⁻. The isotropic shift of +8.03 ppm for Hᴬ + Hᶜ is reasonably assumed to be the mean of the isotropic shifts for the axial and equatorial protons of the chair conformer. If we assume that the value of −3.88 ppm found for Hᴬ in [Fe(CN)₄(*meso*-ptn)]⁻ is applicable to the tn chelate as the isotropic shift of the axial proton, an isotropic shift of +19.94 ppm is deduced for the equatorial protons.

[Fe(CN)₄(bn)]⁻. As stated in the previous section, the bn chelate is expected to interconvert between conformers of 9 and 10 with predominance of the former. Six signals were observed for the ¹H NMR spectrum. Sarneski and Reilley have evaluated the distribution of conformers 9 and 10 and a chair conformer with an axial methyl to be 0.88, 0.08, and 0.04, respectively, for [Ni(OH₂)₄(bn)]²⁺.[18] If we assume the interconversion between

(28) Chan, M.-S.; Wahr, A. C. *J. Phys. Chem.* **1968**, *82*, 2442.
(29) (a) Ho, F. F.-L.; Reilley, C. N. *Anal. Chem.* **1970**, *42*, 600. (b) Ho, F. F.-L.; Reilley, C. N. *Anal. Chem.* **1969**, *41*, 1835. (c) Evilia, R. F.; Young, D. C.; Reilley, C. N. *Inorg. Chem.* **1971**, *10*, 433.

9 and 10 and the isotropic shifts of +19.94 and −3.88 ppm are applicable to this chelate, the fractions X_9 and X_{10} will be derived on the basis of observed isotropic shifts for H^B and H^C from the sets of equations of (1) and (3) and of (2) and (3). These lead

$$X_9(+19.94) + X_{10}(-3.88) = +14.26 \qquad (1)$$

$$X_9(-3.88) + X_{10}(19.94) = -3.08 \qquad (2)$$

$$X_9 + X_{10} = 1.0 \qquad (3)$$

to values of 0.76 and 0.96 for X_9. On the other hand, the magnitudes of the isotropic shifts of H^I and H^J and the separation between them are almost the same as those of the *meso*-ptn chelate. The estimation of the distribution based on the isotropic shift of H^B seems to overestimate the contribution of 10. The methine proton, H^A, shows almost the same isotropic shift as that of the *meso*-ptn chelate, and it is concluded that the bn chelate takes exclusively the conformation of 9.

This view is supported further by the ^{13}C NMR spectrum. The isotropic shift of +66.1 ppm for the methyl carbon is almost the same as that of +62.6 ppm for [Fe(CN)₄(*meso*-ptn)]⁻.

[Fe(CN)₄(*R*-ptn)]⁻. Three signals appeared in both the ^1H and ^{13}C NMR spectra. These numbers of signals can be accounted for either by a rapid interconversion of the chelate rings among 11–13 or a predominant λ-skew-boat conformation, 12, which belongs to C_2 symmetry. But the rapid interconversion is reasonably assumed to take place for the Fe(II) chelate. The isotropic shift of 2.09 ppm for H^C + H^D is the middle point between that of −3.88 ppm for H^A of [Fe(CN)₄(*meso*-ptn)]⁻ and that of 8.03 ppm for the mean of H^A + H^B of [Fe(CN)₄(tn)]⁻. This suggests that the contribution from the axial proton exceeds that from the equatorial proton. Both protons are located in axial position in the conformer of 12, but one of the two protons takes an axial

position in the conformers of 11 and 14. On the basis of estimated isotropic shifts for the axial and equatorial protons on C^1, eq 4

$$X_{12}(-3.88) + (1 - X_{12})(19.94 - 3.88)/2 = 2.09 \qquad (4)$$

is derived, where the fraction of 12 is X_{12} and that of 11 and 14 are $(1 - X_{12})/2$. This equation leads to a value of 0.50 for X_{12}. The ratio of 50:50 for λ-skew-boat and chair forms is almost the same as that reported for Ni(OH₂)₄(*rac*-ptn)²⁺, i.e. 54:46.[18]

The isotropic shift for the methylene protons (H^I + H^J) is also smaller (−17.03 ppm) compared with the mean of those (−22.38 ppm) for the corresponding protons of [Fe(CN)₄(*meso*-ptn)]⁻.

The isotropic shift of +46.5 ppm for the methyl carbons of [Fe(CN)₄(*R*-ptn)]⁻ is considerably smaller than those for the bn and *meso*-ptn chelates, 66.1 and 62.6 ppm. For the latter two, methyl groups are oriented equatorially with the chelate ring with chair conformations. The smaller isotropic shift will be due to the axial orientation of one of the methyl groups in both of the chair conformers.

Contribution from the Department of Applied Chemistry, Faculty of Engineering,
Osaka University, Yamada-oka 2-1, Suita, Osaka 565, Japan

Multielectron Reductions of Alkyl Azides with [Mo₂Fe₆S₈(SPh)₉]³⁻ and [Mo₂Fe₆S₈(μ-SEt)₃(SCH₂CH₂OH)₆]³⁻ in Homogeneous Systems and with a (*n*-Bu₄N)₃[Mo₂Fe₆S₈(SPh)₉] Modified Glassy-Carbon Electrode in H₂O

Susumu Kuwabata, Koji Tanaka, and Toshio Tanaka*

The electrochemical behaviors of a (*n*-Bu₄N)₃[Mo₂Fe₆S₈(SPh)₉] modified glassy-carbon electrode ([Mo-Fe]/GC) have been studied in water. The [Mo-Fe]/GC works stably in water and undergoes the two-electron-redox reaction arising from a [Mo₂Fe₆S₈-(SPh)₉]³⁻/⁵⁻ couple. The electrochemical reductions of HOCH₂CH₂N₃ (or CH₃N₃) not only by the [Mo-Fe]/GC in water at −1.25 V vs. SCE but also by [Mo₂Fe₆S₈(SPh)₉]³⁻ and [Mo₂Fe₆S₈(μ-SEt)₃(SCH₂CH₂OH)₆]³⁻ dissolved in MeOH/THF (1:1 v/v) and in H₂O, respectively, with an Hg electrode at the same potential were carried out in order to compare the catalytic activity toward a multielectron reduction. In these systems, ammonia and hydrazine were formed for the first time as eight- and six-electron-reduction products of alkyl azide, respectively, together with the formation of HOCH₂CH₂NH₂ (or CH₃NH₂) and N₂ as two-electron-reduction products. The turnover number for the formation of NH₃ based on the amount of the cluster in the reduction with the [Mo-Fe]/GC attains 12 000 in 2 h, which is much larger than that (a maximum of 3.5) obtained in the latter. The reaction is initiated with the displacement of a terminal thiolate ligand of the reduced cluster by HOCH₂CH₂N₃, affording the 1:1 adduct, followed by successive two-electron reductions of HOCH₂CH₂N₃.

Introduction

It is well-known that dinitrogen molecules coordinated to Mo and W in low oxidation states are reduced by acid stepwise to afford N₂H₄ and NH₃ in compensation for an increase in the oxidation states of the central metal atoms, and various azenide and hydrazide complexes have been isolated as reaction intermediates.[1-11] In this connection, electrochemical reduction of

a hydrazide–molybdenum complex under dinitrogen has been proposed with the intention of regeneration of dinitrogen complexes, producing N₂H₄ or NH₃.[12] However such a catalytic

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