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The Oxidation Products of Tetracyanoferrate(II) Chelates with Optically Active 1,2-Diamines : Tetracyano(1,2-diamine)ferrate(III)s and Tetracyano(1,2-diimine)ferrate(II)s

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Optically active diamagnetic title complexes were oxidized with hydrogen peroxide under acidic and basic aqueous conditions. The corresponding low-spin tetracyano(diamine)ferrate(III) complexes with (*R*)-1,2-propanediamine, (1*R*,2*R*)-1,2-cyclopentanediamine, and (1*R*,2*R*)-1,2-cyclohexanediamine as diamines formed under acidic conditions and were characterized with several spectral measurements including the CD spectra. Each CD spectrum showed a moderate positive Cotton effect at *ca.* 24700 cm^{-1} and was assigned to a d-d transition. However a ligand oxidation took place, yielding tetracyano(1,2-diimine)ferrate(II) complexes under neutral and basic conditions; their electronic and ^{1}H- and ^{13}C-NMR spectra are also reported.

Diamagnetic and low-spin Fe^{II} and Fe^{III} complexes with a simple ligand system have been scarcely investigated. Tetracyanoferrate(II) chelates of 1,2-diamines are diamagnetic as a result of the strong ligand field produced by cyano groups and have been well characterized.[1,2] The diamagnetic complexes are oxidized with various oxidizing agents to yield metal-oxidized tetracyano(1,2-diamine)ferrate(III) and ligand-oxidized tetracyano(1,2-diimine)ferrate(II) depending on the reaction conditions.[1] Optically active Fe^{III} chelates can be expected to be prepared from the corresponding Fe^{II} chelates with optically active diamines, such as (*R*)-1,2-propanediamine(*R*-pn), (1*R*,2*R*)-1,2-cyclopentanediamine(*R*-cptn), and (1*R*,2*R*)-1,2-cyclohexanediamine(*R*-chxn), under acidic conditions. The chemistry of cyanoammineferrate(III)s has not been fully investigated except for pentacyanoferrate(III)s.[3] Their electronic spectra are still ambiguous because of their many allowed electronic transitions. Hexacyanoferrate(III) and several pentacyano complexes with OH_2, NH_3, $As(C_6H_5)_3$, NCS^-, and $P(C_6H_5)_3$ have been investigated with magnetic circular dichroism spectra as well as electronic spectra.[4] The CD spectra of tetracyano(*R*-diamine)ferrate(III)s will provide unique information on the nature of the electronic transitions.

The other product is ligand-oxidized tetracyano(1,2-diimine)ferrate(II); it has been characterized by visible and ^{1}H-NMR spectroscopies.[1] The diimines examined up to the present bear substituents at the nitrogen atoms(*e. g.*, 1,10-phenanthroline and *N*,*N'*-dimethyl-2,3-butanediimine), but this dehydrogenation yields diimines which have no substituents at the nitrogens. The dehydrogenation of amines coordinated to transition-metal ions has been reported with Cu^{II},[5] Ni^{II},[6] Ru^{II},[7] Co^{II},[8] and Fe^{II},[9] and it is generally accepted that a higher oxidation state of transition-metal ions is responsible for the reaction.[10] Tetracyano(1,2-ethanediamine)ferrate(III) undergoes a spontaneous metal reduction, yielding a mixture of ligand-oxidized and ligand-intact Fe^{II} chelates, in basic solutions.

This paper will deal with the preparation and some spectral properties of these complexes.

Experimental

Materials. 1,4-Dimethyl-1,4-diazabicyclo[2,2,2]octanediium diiodide(dimethyldabconium iodide) was prepared according to the method of Oae *et al.*[11] $Na_2[Fe(CN)_4(R\text{-pn})]\cdot 0.5NaClO_4\cdot 0.5H_2O$,[2] $Na_2[Fe(CN)_4(R\text{-cptn})]\cdot 0.5NaClO_4\cdot 0.5H_2O$,[12] and $Na_2[Fe(CN)_4(R\text{-chxn})]\cdot 0.5NaClO_4\cdot 0.5H_2O$[2] were prepared according to the methods reported previously. $Na[Fe(CN)_4(en)]\cdot 3H_2O$ and dimethyldabconium tetracyano(1,2-ethanediimine)ferrate(II) were prepared according to the method of Goedken.[1] *cis*-1,2-Cyclohexanediamine was separated from a commercially available mixture of 1,2-cyclohexanediamines(Tokyo Kasei) according to the method of Kidani and Saito.[13]

Preparation of Complexes. $Na[Fe(CN)_4(R\text{-}pn)]\cdot H_2O$. The corresponding diamagnetic Fe^{II} chelate, $Na_2[Fe(CN)_4(R\text{-pn})]\cdot 0.5NaClO_4\cdot 0.5H_2O$ (3.5 g, 0.01 mol), was dissolved in a mixture of acetic acid (1 cm^3), ethanol (20 cm^3), and water (6 cm^3) at 0 °C. Into the mixture, 30% aqueous hydrogen peroxide (1.5 cm^3) was then stirred in small portions. The resultant mixture was filtered after 5 min at 0 °C to remove the undissolved green materials. Ethanol (20 cm^3) and ether were added to the filtrate until the solution became turbid. The mixture was then allowed to stand in a refrigerator overnight. The pale yellow crystals thus separated were collected on a filter, washed with absolute ethanol and subsequently with ether, and dried *in vacuo*. Yield, 2.3 g (84%). Found: C, 30.16; H, 4.47; N, 30.43%. Calcd for $Na[Fe(CN)_4(C_3H_{10}N_2)]\cdot H_2O$: C, 30.55; H, 5.10; N, 30.56%.

$Na[Fe(CN)_4(R\text{-}cptn)]\cdot 2H_2O$. In a mixture of acetic acid (1 cm^3) and ethanol (10 cm^3), $Na_2[Fe(CN)_4(R\text{-cptn})]\cdot 0.5NaClO_4\cdot 0.5H_2O$ (1.5 g, 4 mmol) was suspended: after the mixture had been cooled to 0 °C, 2 M (1 M = 1 mol dm^{-3}) perchloric acid (2 cm^3) and water (1 cm^3) were added to dissolve the complex. A portion of aqueous hydrogen peroxide (30%, 0.3 cm^3) was then stirred into the mixture. To the resultant mixture, ether (3 cm^3) was added, and the mixture was filtered at 0 °C. A mixture of ethanol (10 cm^3) and ether (10 cm^3) was added to the filtrate, and the mixture was allowed to stand at −15 °C overnight. The separated crystals were collected on a filter, washed with ether, and dried *in vacuo*. Yield, 1.5 g (quantitative).

This substance was dissolved in a mixture of 2 M $HClO_4$ (0.65 cm^3) and ethanol (5.35 cm^3) at 0 °C, after which the mixture was filtered. Ether (5 cm^3) was added, and the mixture was allowed to stand overnight at −15 °C. The crystals thus separated were collected on a filter, washed with ether, and dried *in vacuo*. Yield, 160 mg (12%).

Found: C, 34.41; H, 5.31; N, 26.41%. Calcd for $Na[Fe(CN)_4(C_5H_{12}N_2)]\cdot 2H_2O$: C, 33.87; H, 5.05; N, 26.34%.

$Na[Fe(CN)_4$(R-chxn)$]\cdot 3H_2O$. Into a solution of $Na_2[Fe(CN)_4$(*R*-chxn)$]\cdot 0.5NaClO_4\cdot 0.5H_2O$ (3.0 g, 7.7 mmol) in a mixture of acetic acid (3 cm^3), ethanol (30 cm^3), and water (3 cm^3) in an ice–water bath, 15% aqueous hydrogen peroxide (6 cm^3) was stirred, drop by drop, at 0 °C. A mixture of methanol (10 cm^3), acetic acid (4 cm^3), and ether (30 cm^3) was added to the yellow mixture until the mixture became turbid. The mixture then allowed to stand at -15 °C overnight. The yellow crystals thus separated were collected on a filter, washed with ice–cold ethanol and subsequently with ether, and stored *in vacuo*. Yield, 2.0 g (74%).

These were recrystallized by adding ether to a solution of the crude product in a mixture of acetic acid, water, and ethanol (1: 2: 15) until the solution became turbid. This procedure was carried out at 0 °C. The pale yellow needles thus separated were collected on a filter, washed with ethanol and subsequently with ether, and dried *in vacuo*. Found: C, 34.45; H, 5.62; N, 23.60%. Calcd for $Na[Fe(CN)_4(C_6H_{14}N_2)]\cdot 3H_2O$: C, 34.04; H, 5.62; N, 23.60%.

*Sodium Tetracyano(*cis*-1.2-cyclohexanediamine)ferrate(II) Dihydrate.* A methanol solution (40 cm^3) of *cis*-1,2-cyclohexanediamine(*cis*-chxn) (22.8 g, 0.2 mol) was vigorously stirred into a methanol solution (200 cm^3) of iron(II) perchlorate hexahydrate (35.2 g, 0.098 mol) under nitrogen at 0 °C, followed by the addition of aqueous sodium cyanide (19.1 g, 0.39 mol) in 80 cm^3 of water. The resultant yellow brown solution was concentrated to near dryness under reduced pressure below 40 °C. To the oily residue, ethanol (200 cm^3) was added, and a yellow precipitate was collected on a filter, washed with ethanol and subsequently with ether, and dried *in vacuo*. Found: C, 34.20; H, 4.36; N, 23.84%. Calcd for $Na_2[Fe(CN)_4(C_6H_{14}N_2)]\cdot 2H_2O$: C, 33.72; H, 5.09; N, 23.59%.

$Na[Fe(CN)_4$(cis-chxn)$]\cdot 0.5NaClO_4\cdot H_2O$. In a mixture of concentrated $HClO_4$ (3 cm^3), methanol (20 cm^3), and water (4 cm^3), $Na_2[Fe(CN)_4$(*cis*-chxn)$]\cdot 2H_2O$ (3.9 g, 0.011 mol) was dissolved, and the mixture was cooled to 0 °C. Concentrated aqueous hydrogen peroxide (30%, 1.4 cm^3) was then stirred, drop by drop, into the mixture. A mixture of 1-propanol (40 cm^3) and diisopropyl ether (20 cm^3) was added to the mixture. The crystals thus separated were collected on a filter. Yield, 3.9 g (70%).

The crude product was dissolved in a mixture of 2 M $HClO_4$ (3 cm^3) and ethanol (20 cm^3), and the undissolved materials were filtered off. A mixture of ethanol (35 cm^3) and diisopropyl ether (25 cm^3) was added, and the mixture was allowed to stand at -15 °C overnight. The crystals thus separated were collected on a filter, washed with ether, and dried *in vacuo*. Found: C, 31.77; H, 4.83; N, 21.55%. Calcd for $Na[Fe(CN)_4(C_6H_{14}N_2)]\cdot 0.5NaClO_4\cdot H_2O$: C, 31.91; H, 4.29; N, 22.33%.

Dimethyldabconium Tetracyano(1,2-propanediimine)ferrate(II) Trihydrate, $[C_8H_{18}N_2][Fe(CN)_4$(o-pn)$]\cdot 3H_2O$. The designations of the diimines formed by dehydrogenation are abbreviated by adding the prefix *o*- to the corresponding diamines, as is shown in Table 1 (*vide infra*). Into an aqueous solution of $Na_2[Fe(CN)_4$(*R*-pn)$]\cdot 0.5NaClO_4\cdot 5H_2O$ (2.25 g, 6.5 mmol) in 10 cm^3 of water, 2 M hydrogen peroxide (18 cm^3) was stirred, drop by drop, at 40 °C. The resultant deep red solution was concentrated with a rotatory evaporator. A red residue was dissolved in 10 cm^3 of water, and dimethyldabconium iodide (2.6 g) was added to the solution. Ethanol (200 cm^3) was added until the solution became turbid, after which the mixture was allowed to stand in a refrigerator overnight. The red crystals thus separated were collected on a filter and washed with ethanol and subsequently with ether. Found: C, 42.03; H, 6.44; N, 26.69%. Calcd for $[C_8H_{18}N_2][Fe(CN)_4(C_3H_6N_2)]\cdot 3H_2O$: C, 42.26; H, 7.09; N, 26.29%.

Dimethyldabconium Tetracyano(1,2-cyclopentanediimine)ferrate(II) Hemi(sodium perchlorate), $[C_8H_{18}N_2][Fe(CN)_4$(o-cptn)$]$-$0.5NaClO_4$. Into an aqueous solution of $Na_2[Fe(CN)_4$(*R*-cptn)$]\cdot 0.5NaClO_4\cdot 0.5H_2O$ (1.0 g, 2.7 mmol) in 10 cm^3 of water, 1 M hydrogen peroxide (17 cm^3) was stirred, drop by drop, at 40 °C, the pH of the mixture being kept at 10.5 by adding 1 M aqueous NaOH. The resultant intense red solution was concentrated with a rotatory evaporator. The red residue was dissolved in 4 cm^3 of water, and the mixture was filtered to remove brown precipitates. To the filtrate, dimethyldabconium iodide (1.0 g) was added, and then ethanol (6 cm^3) was added. The blue precipitates thus separated were removed by filtration, and another 30-cm^3 portion of ethanol was added to the filtrate. The mixture was allowed to stand in a refrigerator overnight. The purple crystals thus separated were collected on a filter and washed with ethanol and subsequently with ether. Found: C, 43.88; H, 6.00; N, 24.17%. Calcd for $[C_8H_{18}N_2][Fe(CN)_4(C_5H_8N_2)]\cdot 0.5NaClO_4$: C, 44.43; H, 5.70; N, 24.39%.

Dimethyldabconium Tetracyano(1,2-cyclohexanediimine)ferrate(II) Tetrahydrate, $[C_8H_{18}N_2][Fe(CN)_4$(o-chxn)$]\cdot 4H_2O$. To an aqueous solution of $Na_2[Fe(CN)_4$(*R*-chxn)$]\cdot 0.5NaClO_4\cdot 0.5H_2O$ (2.0 g, 5.06 mmol) in 10 cm^3 of water, 2 M hydrogen peroxide (20 cm^3) was added, drop by drop, at 48 °C. The resultant intensely red solution was concentrated with a rotatory evaporator. The red residue was dissolved in 8 cm^3 of water, after which dimethyldabconium iodide (2 g) and then ethanol (18 cm^3) were added. The red crystals thus separated were collected on a filter and washed with ethanol and subsequently with ether.

The crude product was dissolved in 3 cm^3 of water, and a 30-cm^3 portion of absolute ethanol was added. The red crystals thus separated were collected and dried *in vacuo*. Found: C, 44.63; H, 7.25; N, 23.30%. Calcd for $[C_8H_{18}N_2][Fe(CN)_4(C_6H_{10}N_2)]\cdot 4H_2O$: C, 44.63; H, 7.49; N, 22.13%.

Physical Measurements. The electronic spectra of 10^{-3} M hydrochloric acid solutions of tetracyano(diamine)ferrate(III)s and aqueous solutions of Fe^{II} complexes were recorded with a Shimadzu UV-210A spectrophotometer. The CD spectra were measured with a JASCO J-40 recording polarimeter. The ^{1}H-NMR were recorded with a JEOL JNM-MH-100 spectrometer using D_2O solutions and sodium 2,2-dimethyl-2-silapentane-5-sulfonate (DSS) as the internal standard. The ^{13}C-NMR were recorded with a JEOL FX-100 spectrometer using a D_2O solution and dioxane as the internal standard (67.4 ppm). The infrared spectra were measured with a JASCO IRA-2 spectrophotometer using Nujol mulls. The magnetic susceptibilities were measured with a Shimadzu magnetic balance.

Results and Discussion

Tetracyano(*cis*-1,2-cyclohexanediamine)ferrate(II) showed a typical electronic spectrum of tetracyano(1,2-diamine)ferrate(II) chelates:[2] $\tilde{\nu}_{max}(\varepsilon_{max})=25400(439)$, 31800(*ca.* 450), 43100(8600), and 46200 cm^{-1}(9430).

Tetracyano(1,2-diamine)ferrate(III) Chelates. Diamagnetic tetracyano(1,2-diamine)ferrate(II) chelates with C-substituted 1,2-diamines, *R*-pn, *R*-cptn, *R*-chxn, and *cis*-chxn, yield two types of oxidation products with hydrogen peroxide, depending on the acidity of the reaction medium, as tetracyano(1,2-ethanediamine)-

ferrate(II).[1]

In an acidic solution, oxidation took place at the central metal ion, yielding the corresponding Fe^{III} chelates at 0 °C. The chelates with *R*-pn, *R*-cptn, and *R*-chxn were prepared with acetic acid as an acid, but that with *cis*-chxn was prepared with perchloric acid as an acid because a successive oxidation to the diimine chelate occurred with acetic acid. These were isolated as sodium salts in pale yellow crystals. These complexes tend to undergo disproportionation at room temperature with atmospheric moisture and so were kept in a refrigerator under a vacuum. The magnetic susceptibilities of the crystals were measured with a magnetic balance by means of the Faraday method at room temperature. The values of the mole magnetic moments were 2.3, 2.4, and 2.4 BM for the *R*-pn, *R*-cptn, and *R*-chxn respectively. These values are in accordance with the low-spin Fe^{III} complexes. These complexes are stable in an acidic solution. The IR spectra contained sharp C≡N stretchings at 2120 cm^{-1}, higher by 80 cm^{-1} than those of the corresponding Fe^{II} chelates.[2] The higher wave numbers of the C≡N stretching absorptions are compatible with the smaller contribution of the back donation from Fe^{III} to coordinated C≡N than from Fe^{II}. The IR absorptions are almost the same as those of the corresponding Co^{III} chelates, as is shown in Fig. 1. These complexes exhibit well-separated ^1H- and ^{13}C-NMR: preliminary results have previously reported.[14] The results are consistent with the bidentate coordination of these diamines.

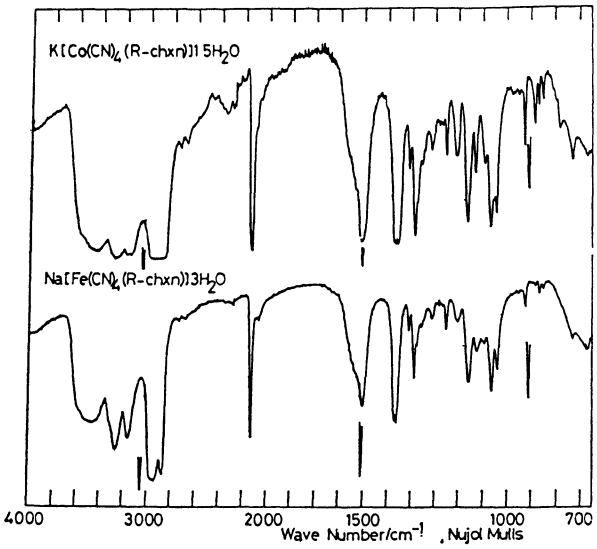


Fig. 1. Infrared spectrum of $K[Co(CN)_4(R\text{-chxn})]\cdot 1.5H_2O$[2] and $Na[Fe(CN)_4(R\text{-chxn})]\cdot 3H_2O$.

The electronic and CD spectra of these complexes in 10^{-3} M HCl are shown in Fig. 2. The CD spectra of these chelates are similar to each other and reflect the conformation of five-membered chelate rings, because the diamines may be expected to coordinate in the λ conformation. These optically active diamines, *R*-pn, *R*-cptn, and *R*-chxn, have been reported to coordinate to Fe^{II}, forming chelate rings of the λ conformation.[2,12]

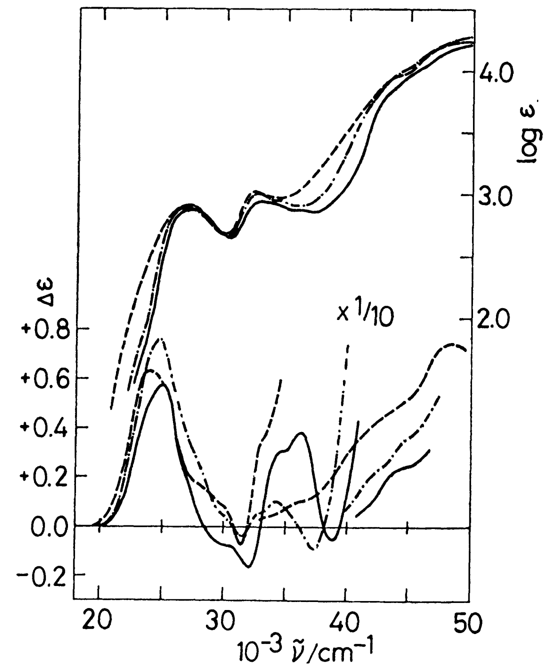


Fig. 2. Electronic and CD spectra of $[Fe(CN)_4(\text{diamine})]^-$ in 10^{-3} M hydrochloric acid. diamine: *R*-pn, ——; *R*-cptn, ——; *R*-chxn, -·-·-.

A large number of measurements and interpretations of the electronic spectra of $[Fe(CN)_6]^{3-}$ and several pentacyanoferrate(III) complexes have been reported.[4] The electronic configurations of these complexes are low-spin d^5, *i. e.*, $(t_{2g})^5$. The electronic transitions of these complexes are expected to arise from (i) ligand-to-metal charge transfer (LMCT), (ii) metal-to-ligand charge transfer (MLCT), and (iii) d-d transition. McCaffery and Gale assigned electronic absorptions with the aid of the magnetic circular dichroism spectra.[4] The absorptions with d-d transitions are partially hidden by LMCT bands, but are located at 29800, $E_g''(^2T_{2g})\rightarrow U_g'(^2T_{1g})$, 30200$\rightarrow E_g''(^2A_{2g})$, and 33200 $cm^{-1}\rightarrow U_g'(^2E_g)$. The remaining bands below 40000 cm^{-1} originate from LMCT, 25500$(^2T_{2g}\rightarrow {}^2T_{1u}(\pi))$, 32700$(\rightarrow {}^2T_{2u}(\pi))$, and 40000 cm^{-1} $(\rightarrow {}^2T_{2u}(\sigma))$. They also measured several pentacyanoferrate(III) complexes, but did not assign the d-d transitions. Furthermore, complexes with ligands which have lone pairs of relatively high energies, such as triphenylphosphine and azido, show intense absorptions in the visible region. These absorptions are assigned to the LMCT bands arising from the ligand σ bond to the t_{2g} orbital. From this band, the energy difference between the ligand lone pair and the metal t_{2g} orbital are estimated: *e. g.*, 26600 cm^{-1} for NH_3.

The electronic transitions of $Na[Fe(CN)_4(R\text{-diamine})]^-$ are composed of d-d, LMCT, and MLCT transitions. The electronic spectra show moderate bands at 27000 and 30000—35000 cm^{-1} of ε of *ca.* 800. In this region, d-d and LMCT bands are to be expected if the LMCT band of $NH_3\rightarrow t_{2g}$ retains its energy. The maxima of the electronic spectra in the visible region, 27000 cm^{-1}, seem to arise from CT bands, for the molar-absorption coefficient of 800 is large for a d-d transition. The maxima of the CD spectra are located at *ca.* 24700 cm^{-1} and correspond to a shoulder of each absorption spectrum. The corresponding d-d transitions of $Na_2[Fe(CN)_4(R\text{-diamine})]^{2-}$ have a minor negative component at 23300 and a positive component at 26000 cm^{-1} for the *R*-pn and the *R*-chxn complexes and a positive component at 25200 cm^{-1} for the *R*-cptn complex. The magnitudes of the major CD components decreased in the order of; *R*-cptn>*R*-chxn>*R*-pn as the ligands. The analogous CD components have been observed for isoelectronic Co^{III} chelates at 25000 and 28700 cm^{-1} for *R*-pn and *R*-chxn as *R*-diamines.[2] The wave numbers and magnitudes of the positive CD components for $[Fe(CN)_4(R\text{-diamine})]^-$ suggest that this component corresponds to the d-d transitions. Two transitions are expected for the first absorption band ($^2T_{2g}\rightarrow{}^2T_{1g}$ parentage) of the $(t_{2g})^5$ configuration, but the energy difference between these bands should be smaller than for the $(t_{2g})^6$ configuration because the interelectron repulsion in the highest t_{2g} orbitals is absent for the d^5 configuration. The minor components appearing in diamagnetic Fe^{II} and Co^{III} chelates will be hidden for the d^5 configuration.

At least four CD components are observed in the region between 31000 and 38000 cm^{-1}. These CD components exhibit similar features for the *R*-pn and *R*-chxn complexes: *i. e.*, negative, positive, positive, and negative components in the order of their energies, and they resemble the MCD components of $[Fe(CN)_6]^{3-}$.[4] The probable origin of these CD components is the charge transfer from the coordinated C≡N to the t_{2g} orbital. Each CD component of the *R*-chxn chelate appears at an energy lower by 2000 cm^{-1} than the corresponding component of the *R*-pn chelate. Since the absolute energy level of coordineated C≡N is expected to be little affected by the structure of 1,2-diamine, this difference represents the difference in energy levels in the t_{2g} orbitals of these Fe^{III} chelates. The large fixed ligand, *R*-chxn, tends to lower d-orbitals. Large positive CD components dominate in the region between 33000 and 37000 cm^{-1} for the *R*-cptn chelate. Similar enhancements of positive CD components in the region of charge-transfer bands have been observed for dianionobis[(1*R*,2*R*)-1,2-cyclopentanediamine]cobalt(III) complexes;[12] they may be due to the strained structure of this ligand.

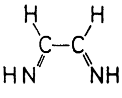
The remaining electronic bands and CD components, which appear at energies higher than 40000 cm^{-1}, have large absorption coefficients and large CD magnitudes. Two electronic bands and at least three CD components are recognized. MLCT bands are to be expected in this region. Positive CD components appear for $[Fe(CN)_4(R\text{-diamine})]^{2-}$ and $[Co(CN)_4(R\text{-diamine})]^-$ with *R*-pn and *R*-chxn. The invariance of the signs of the CD components on a change in the central metal ions suggests that these bands may be ascribed to the charge transfer from coordinated amine to e_g orbitals; the dependency of the magnitude of the CD components on the structure of 1,2-diamines supports this assignment.

Tetracyano(1,2-diimine)ferrate(II) Chelates. In a neutral or basic solution, the yellow solution of tetracyano(*R*-diamine)ferrate(II) turned an intense red on the addition of a slight excess of hydrogen peroxide at 40 to 50 °C. Tetracyano(1,2-diimine)ferrate(II)s were isolated as dimethyldabconium salts. This cation is almost the same size as the chelate anions, has a bivalent charge, and facilitates the crystallization of soluble-complex anions.[15] The structural identifications are confirmed by the electronic spectra and the ^1H- and ^{13}C-NMR spectra. Each ^1H- and ^{13}C-signal appeared in the normal region for the D_2O solution, indicating that these complexes are diamagnetic Fe^{II} complexes. The results are shown in Table 1, along with the abbreviations and structures of the 1,2-diimines.

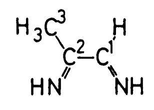
Table 1. ^1H- and ^{13}C-NMR of $[Fe(CN)_4(1,2\text{-diimine})]^{2-}$ in D_2O and abbreviations of 1,2-diimines

1,2-Diimine	^1H-Chemical shift[a)]/ppm	^{13}C-Chemical shift[b)]/ppm
o-en	8.50[c)]	166.8
o-pn	8.42,2.48	**1**,[d)] 169.1; **2**, 175.1; **3**, 22.3
o-cptn	**2**, 2.71; **3**, 2.35	**1**, 185.6; **2**, 31.5; **3**, 25.3
o-chxn	**2**, 2.90; **3**, 1.87	**1**, 176.8; **2**, 33.8; **3**, 22.6

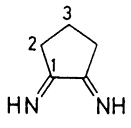
a) DSS=0.00 ppm. b) Dioxane=67.4 ppm. c) Ref. 1. d) The number denotes the assignment of the corresponding nucleus shown in the structure below.



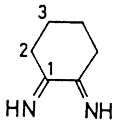
o-en



o-pn



o-cptn



o-chxn

An azomethine proton appeared at 8.42 ppm for the 1,2-propanediimine complex, as for 1,2-ethanediimine complex at 8.50 ppm[1] but no such protons were present for the 1,2-cyclopentanediimine and 1,2-cyclohexanediimine complexes. The methyl protons of the 1,2-propanediimine complex resonated at 2.48 ppm: the chemical shift moved downfield by 1.2 ppm from the methyl protons of the 1,2-propanediamine counterpart. Similar downfield shifts were observed for the methylene protons of the 1,2-cyclopentanediimine and 1,2-cyclohexanediimine complexes.

More reliable identifications can be obtained on the basis of the ^{13}C-NMR spectra. The parent material, $[Fe(CN)_4(o\text{-en})]^{2-}$, showed a single resonance at 166.8 ppm. All the 1,2-diimine chelates studied showed signals in the region between 166 and 186 ppm. These are assigned to azomethine carbons. The chemical shifts of the *o*-pn and *o*-chxn chelates showed that an alkyl substituent at the azomethine carbon cause a downfield shift of 9 ppm. The azomethine carbon of the *o*-cptn chelate resonates at a magnetic field lower by 8.8 ppm than that of the *o*-chxn chelate. The steric effect of the cyclopentane ring exerted on the chelate ring causes it to deform from a plane structure, and the conjugation of the diimine is reduced.

The electronic spectra of Fe^{II} complexes with 1,2-diimines have been studied extensively, and a characteristic intense band between 450 and 600 nm has been assigned to an electron-transfer band($t_{2g}\rightarrow$ligand).[16] The tetracyano(1,2-diimine)ferrate(II) has simple structures for the Fe^{II} 1,2-diimine chromophore. The electronic spectra of $[Fe(CN)_4(o\text{-pn})]^{2-}$, $[Fe(CN)_4(o\text{-chxn})]^{2-}$, and $[Fe(CN)_4(o\text{-cptn})]^{2-}$ in water are shown

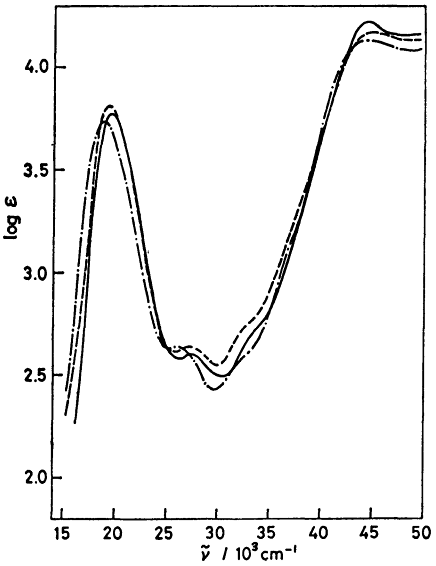


Fig. 3. Electronic spectra of $[Fe(CN)_4(diimine)]^{2-}$ in water.
Diimine: *o*-pn, ——; *o*-cptn, —•—; *o*-chxn, ——.

in Fig. 3. A sharp absorption appeared at 19400 and at 18700 cm^{-1} for the former two and the latter complexes respectively. Weak absorptions at 30300 and 33300 cm^{-1} are assigned to d-d transitions, based on the results of tris(1,2-diimine)iron(II).[17] The first absorption band ($^1A_{1g} \rightarrow {}^1T_{1g}$) moved to an energy higher by 4700 cm^{-1} than that for $[Fe(CN)_4(diamine)]^{2-}$. This is in agreement with the difference in the spectrochemical series between 1,2-diimine and 1,2-diamine.

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