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# The Conformational Interconversion of 1,3-Diamine Chelate: Tetracyano(1,3-propanediamine)ferrate(III)

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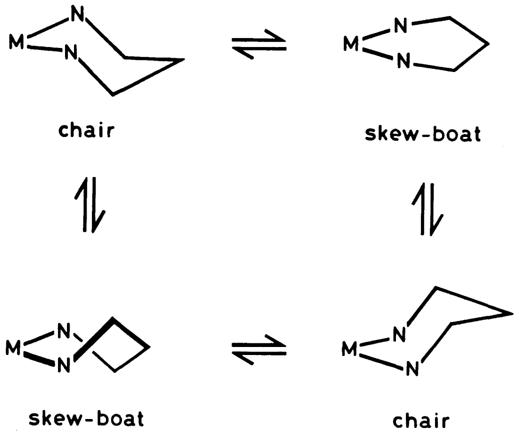
The activation parameters for the chair-to-chair interconversion of the six-membered chelate ring of [Fe$^{III}$(CN)$_4$(1,3-propanediamine)]$^-$ have been determined from a line-shape analysis of the $^1$H NMR spectra of the paramagnetic complex by taking advantage of the large differences in the chemical shift: $\Delta H^{\neq}=32.2\pm4.6$ kJ mol$^{-1}$, $\Delta S^{\neq}=31.2\pm28.6$ J mol$^{-1}$ K$^{-1}$, and $\Delta G^{\neq}_{298}=22.9\pm3.9$ kJ mol$^{-1}$. The $\Delta H^{\neq}$ and $\Delta S^{\neq}$ values are larger by 7.5 kJ mol$^{-1}$ and 31 J mol$^{-1}$ K$^{-1}$ than those of the corresponding 1,2-ethanediamine chelate, [Fe$^{III}$(CN)$_4$(1,2-ethanediamine)]$^-$, respectively. The kinetic data supported the transition state with a half-boat conformation.

Five- and six-membered chelate rings are formed by the coordination of multidentate ligands to transition metal ions.[1,2] Five-membered chelates are known to take either $\delta$ or $\lambda$ *gauche* conformations, while for six-membered ones, chair, skew-boat, and boat forms are possible.[1—4] These chelate rings rapidly change their conformations among such conformers at the ambient temperature.[2—8]

The stereochemistry of the chelate ring of 1,3-propanediamine has been the subject of many studies.[1—4] The most populated conformers are both chair forms, but the interconversion between them has been considered to occur through skew-boat forms as intermediates.[1—4]



The determination of the rate constant for the conformational interconversion would be desirable for understanding the stereochemistry of metal complexes. We have developed a method of determining the rate constants for paramagnetic compounds by means of NMR spectroscopy; an application to the five-membered chelate ring has been reported in a previous paper.[6]

There have been few reports on the dynamics of the conformational change of six-membered chelate rings except for [Mo$^0$(CO)$_4$(tmtn)] (tmtn=*N,N,N′,N′*-tetramethyl-1,3-propanediamine), the activation free energy of which has been estimated as $\Delta G^{\neq}_{178}<34$ kJ mol$^{-1}$ for the chair-to-chair interconversion, based on the broadening of $^{13}$CH$_3$ NMR line-shape at 178 K.[9] Tetracyano(1,3-diamine)ferrate(III) complexes show well-resolved and strongly orientation-dependent $^1$H and $^{13}$C NMR spectra.[4] These characteristics are suitable for line-shape analysis. We have now applied the method to the chair-to-chair interconversion of the six-membered chelate ring of tetracyano(1,3-propanediamine)ferrate(III).

## Experimental

**Materials.** Tetracyano(1,3-diamine)ferrate(III) complexes, H[Fe$^{III}$(CN)$_4$(tn)]·2H$_2$O·(CH$_3$)$_2$CHOH and H[Fe$^{III}$(CN)$_4$(*meso*-ptn)]·2H$_2$O·3/4(C$_2$H$_5$OH) (tn=1,3-propanediamine and *meso*-ptn=(2*R*,4*S*)-2,4-pentanediamine), were prepared as has been reported previously.[4]

**NMR Measurements.** The measurements were carried out as has been reported previously[6] with a JEOL FX-100 spectrometer at 183—323 K. The positive chemical shifts indicate downfield shifts from sodium 3-(trimethylsilyl)-propionate-2,2,3,3-$d_4$ (TSP).

**Calculation of the Line-Width and the Interconversion Rate Constant.** The line-width and the interconversion rate were calculated by using two least-squares programs, SALS[10] and MULTI,[11] on the NEAC ACOS 850 apparatus of the computing center of this university.

## Results

**Variable-Temperature $^1$H NMR Spectra.** The 100-MHz $^1$H NMR spectra of [Fe$^{III}$(CN)$_4$(tn)]$^-$ (tn=1,3-propanediamine) at 8 different temperatures are reproduced in Fig. 1. The temperature range was limited to 183—323 K by the boiling and freezing points of the solvent (CD$_3$OD containing 0.25% DCl).[6] Two resonances with an area ratio of 2:1 were observed between 183 and 323 K. The upfield signal showed a small temperature dependence, while the downfield signal showed a significant downfield shift, with the decrease in the temperature. These spectra show that the predominant species are the chair forms, which rapidly interconvert on the NMR time scale.

The 100-MHz $^1$H NMR spectra of [Fe$^{III}$(CN)$_4$(*meso*-ptn)]$^-$ (*meso*-ptn=(2*R*,4*S*)-2,4-pentanediamine) at 8 different temperatures are reproduced in Fig. 2. Apart from the signals of the solvent impurities (H$_2$O and

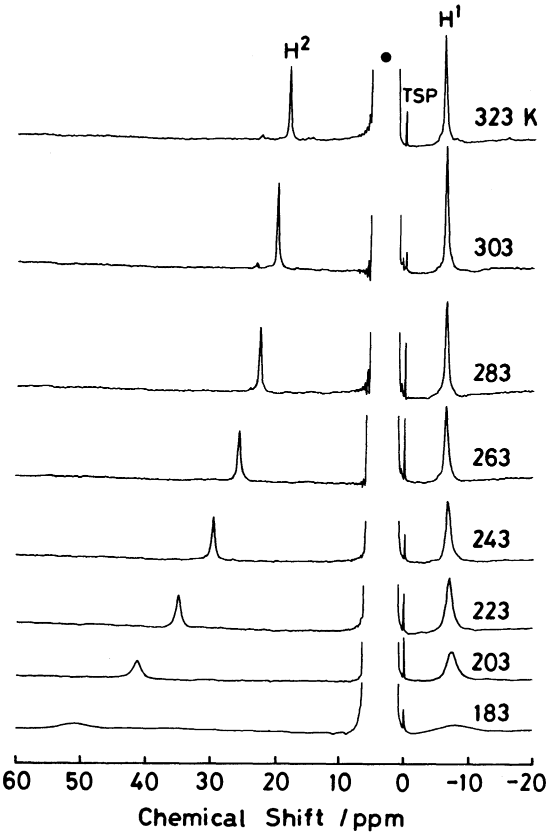
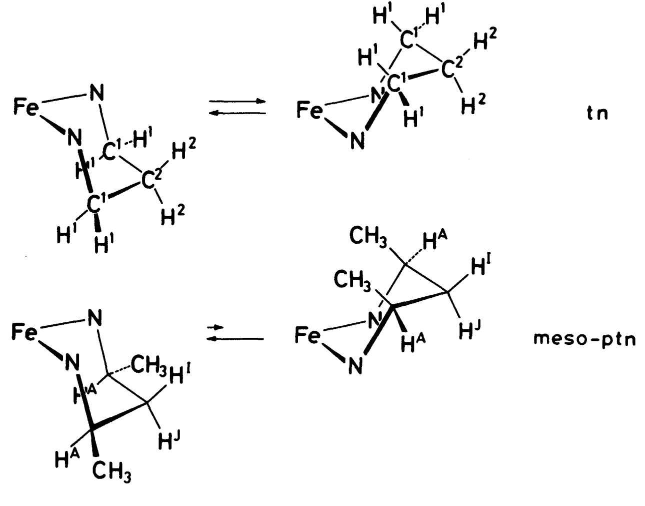


Fig. 1. Temperature-dependent $^1$H NMR spectra of $[Fe^{III}(CN)_4(tn)]^-$ in $CD_3OD$ containing 0.25% DCl. A dot (●) indicates signals of the solvent impurities ($H_2O$ and $CH_3OH$) and $(CH_3)_2CHOH$ included in the sample.

$CH_3OH$) and ethanol included in the sample, four paramagnetically shifted resonances were observed. These resonances moved downfield with the decrease in the temperature. The x mark in Fig. 2 denotes a noise which appeared at the central frequency of the irradiation pulses. These spectral changes show that the conformational interconversion can be regarded as occurring between the two chair forms which are shown below, along with the numbering for the $^1$H and $^{13}$C nuclei:



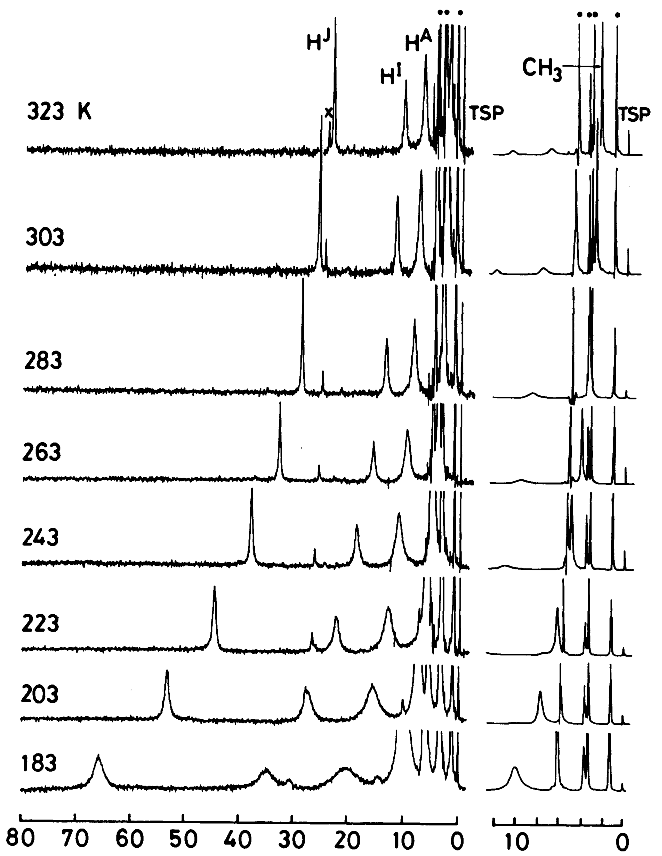


Fig. 2. Temperature-dependent $^1$H NMR spectra of $[Fe^{III}(CN)_4(\textit{meso}\text{-ptn})]^-$ in $CD_3OD$ containing 0.25% DCl. A dot (●) indicates signals of the solvent impurities ($H_2O$ and $CH_3OH$) and ethanol included in the sample. The x-shaped mark denotes a noise which appeared at the central frequency of the irradiation pulses.

The signal assignments for these complexes have been described in a previous paper.[4] The large difference in chamical shift between the $H^I$ and $H^J$ of the *meso*-ptn chelate shows that the conformation is fixed to the chair form with two equatorial methyl groups.[4] The alteration of the tn chelate between the two chair forms is supported by the observation that the chemical shift of $H^2$ was almost the same as the mean of the $H^I$ and $H^J$ shifts of the *meso*-ptn chelate.

The plots of the chemical shift vs. $T^{-1}$ showed that the dependence of each $^1$H shift of the tn and *meso*-ptn complexes on the temperature was not represented by a straight line but by a concave line. This non-Curie law behavior is caused by the participation of both the Fermi contact and pseudocontact mechanisms for this class of complexes. Although the separation of the $H^1$ or $H^2$ signal into two peaks, corresponding to the axial and equatorial protons in a frozen conformation, could not be attained even at 183 K, the broadening of these signals, e.g., the half-line-width at the half-height of 236 Hz at 183 K relative to 20 Hz at 303 K for the H$^2$ signal, were large enough to obtain the rate constant of the interconversion by means of line-shape analysis. The decrease in the temperature made all signals of the *meso*-ptn chelate broad according to the reduction in the spin-relaxation times. However, the further signal broadening for the tn chelate is caused by an additional factor, i.e., the exchange of resonance sites between the two chair forms.

The rate of the conformational interconversion can be calculated if we can estimate the chemical shifts and line-widths intrinsic to a fixed chair conformer of the tn chelate. In this work, the calculation of the rate for the tn chelate was carried out on the assumption that the H$^I$ and H$^J$ values of the *meso*-ptn chelate are magnetically equivalent to the axial (H$^{ax}$) and equatorial (H$^{eq}$) H$^2$ values of the tn chelate fixed in a chair conformation.

The "one-way" rate constants for the interconversion, *k*, were calculated from the line-shapes of the H$^2$ peaks at 183—213 K using the Gutowsky-McCall-Slichter equation[12] according to the method reported previously.[6] The intrisic chemical shifts ($\nu_{ax}$ and $\nu_{eq}$) and transverse relaxation times ($T_{2ax}$ and $T_{2eq}$) expected for the tn chelate fixed in a chair conformation at each temperature were estimated from Eqs. 2 and 5 of Ref. 6, which represent the difference in chemical shift between H$^I$ and H$^J$ ($\Delta$) and the half-line-widths at their half-height ($W$). The *k* values at 183, 193, 203, and 213 K were obtained as follows: $1.0\times10^5$, $4.0\times10^5$, $8.2\times10^5$, and $2.5\times10^6$ s$^{-1}$. If we assume errors as much as 10% for both $\Delta$ and $W$, the ranges of *k* were estimated to be $(0.68—1.5)\times10^5$, $(2.0—6.5)\times10^5$, $(0.32—1.6)\times10^6$, and $(1.2—5.7)\times10^6$ s$^{-1}$ at 183, 193, 203, and 213 K respectively. The *k* values above 213 K could not be determined with sufficient accuracy, since the extent of line-broadening was not large enough.

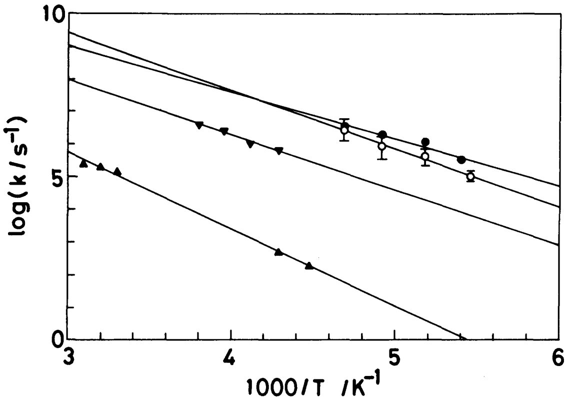


Fig. 3. Arrhenius plots for the conformational interconversion of the chelate ring of [Fe$^{III}$(CN)$_4$(diamine)]$^-$ in CD$_3$OD-DCl: diamine=tn (○), en (●), *meso*-bn (▼), and *cis*-chxn (▲). The I-shaped marks indicate the maximum and minimum of the inversion rate constants.

The activation parameters were calculated from the Eyring equation:[13]

$$k = \kappa(k_B T/h)[\exp(-\Delta H^{\neq}/RT)][\exp(\Delta S^{\neq}/R)]$$

where $k_B$ is the Boltzmann constant and $\kappa$ is the transmission coefficient, which was set as unity. The $\Delta H^{\neq}$ and $\Delta S^{\neq}$ values were obtained by a least-squares linear regression analysis of $-R\ln(kh/k_B T)$ on $T^{-1}$: they are summarized in Table 1, along with those obtained for the 1,2-diamine chelates.[6] The Arrhenius plots are shown in Fig. 3.

The errors in the activation parameters are primarily derived from the estimated values of the intrinsic $\nu_{ax}$, $\nu_{eq}$, $T_{2ax}$, and $T_{2eq}$. The experimental errors in the temperature (±1 K) and the chemical shift were much smaller than the estimated errors.

## Discussion

There are three types of conformations of six-membered chelate rings: chair, skew-boat, and boat.[2,3] The chair form is the most stable conformation, as has been confirmed by X-ray diffraction analysis,[1] NMR spectroscopy,[7,8] and force-field calculation.[14—16] The conformation of the six-membered chelate ring of [Fe$^{III}$(CN)$_4$(*meso*-ptn)]$^-$ is fixed in a chair form, with two equatorial methyl groups at 183—323 K, as has been described in the preceding section. The time-averaged H$^2$ shift of [Fe$^{III}$(CN)$_4$(tn)]$^-$ was nearly equal to the mean of the H$^I$ and H$^J$ shifts of the *meso*-ptn chelate between 183 and 323 K. Therefore, the six-membered chelate ring of the tn complex rapidly alternates between two chair forms, and the population of skew-boat conformers is small in contrast to the chelate ring formed by (2*R*,4*R*)-2,4-pentanediamine,[4] which showed a population of skew-boat and chair conformers of 80:20.[4]

In a previous paper,[6] we have reported that the five-membered chelate rings of tetracyano(1,2-diamine)-

Table 1. Activation Parameters for Conformational Interconversion of [Fe$^{III}$(CN)$_4$(diamine)]$^-$ in CD$_3$OD-DCl

| Diamine | $\Delta H^{\neq}$/kJ mol$^{-1}$ | $\Delta S^{\neq}$/J mol$^{-1}$ K$^{-1}$ | $\Delta G^{\neq}_{298}$/kJ mol$^{-1}$ |
|---|---|---|---|
| tn | 32.2±4.6 | 31.2±28.6 | 22.9±3.9 |
| en[a] | 24.7±4.5 | 0.0±27.0 | 24.7±3.6 |
| *meso*-bn[a] | 30.1±3.9 | −2.9±19.1 | 31.0±1.8 |
| *cis*-chxn[a] | 42.7±2.0 | −7.7± 8.4 | 45.0±0.5 |

a) Ref. 6.

ferrate(III) (1,2-diamine=1,2-ethanediamine (en), (2*R*,3*S*)-2,3-butanediamine (*meso*-bn), and *cis*-(1*R*,2*S*)-1,2-cyclohexanediamine (*cis*-chxn)) alternate between $\delta$ and $\lambda$ conformers through an envelope structure as the transition state. Their activation parameters are collected in Table 1. Figure 3 and Table 1 show that the rate of the interconversion of the tn chelate is slower than that of the en chelate below 240 K, but at 298 K the former becomes faster than those of the en as well as *meso*-bn and *cis*-chxn chelates. This difference between the 1,2- and 1,3-diamine chelates is attributable to: (1) the $\Delta H^{\neq}$ of the tn chelate, which is larger by 7.5 kJ mol$^{-1}$ than that of the en chelate,[6] and (2) the positive $\Delta S^{\neq}$ value of the tn chelate, in contrast to a zero or small negative $\Delta S^{\neq}$ value for the 1,2-diamine chelates.[6] The transition state for the tn chelate is, hence, more endothermic than that for the en chelate.

Gollogly and Hawkins have reported the results of energy-minimization calculations for octahedral transition metal–1,3-diamine complexes with a metal–nitrogen bond length of 200 pm.[14] The minimum energy pathway between two chair forms involves a transition state with a conformation where one C$^1$ is out of the coordination plane, while the other C$^1$ and C$^2$ lie on the plane. This pathway has the skew-boat conformation as an intermediate, and the $\Delta H^{\neq}$ value for this pathway is ca. 32 kJ mol$^{-1}$. A $\Delta H^{\neq}$ value larger than 42 kJ mol$^{-1}$ has been obtained for two other pathways which pass successively through a symmetrical boat conformation and a transition state with the N–C$^1$–C$^2$–C$^1$–N or C$^1$–N–M–N–C$^1$ fragment coplanar.[9]

The $\Delta H^{\neq}$ value for the tn chelate was obtained as 32.2 kJ mol$^{-1}$; this value is in close agreement with the value estimated by Gollogly and Hawkins.[14] The tn chelate is, therefore, expected to change its conformation through the pathway predicted by Gollogly and Hawkins.[14]

According to the force-field calculation by Gollogly et al.,[14,17] the N–C–C angle of the five-membered chelate is larger by 3° in the envelope structure than in the *gauche* form. In the half-boat structure of the six-membered chelate, the angles of M–N–C$^1$ and N–C$^1$–C$^2$ have been reported to be 125.7 and 119.5° respectively, i.e., an increase of more than 7.5° compared with the chair form.[14] The increment in $\Delta H^{\neq}$ observed for the six-membered chelate is attributable to the increase in such angle and torsional strains.

The activation free energy for [Mo$^0$(CO)$_4$(tmtn)] has been estimated as $\Delta G^{\neq}_{178} < 34$ kJ mol$^{-1}$ from the line-width of the $^{13}$CH$_3$ signal at 178 K.[9] The $\Delta G^{\neq}_{178}$ for the tn chelate is evaluated as 26.6 kJ mol$^{-1}$ from the data in Table 1, so that the increment in $\Delta H^{\neq}$ due to the four methyl groups of the tmtn is estimated to be less than 7.4 kJ mol$^{-1}$, which is almost half of the 14.7 kJ mol$^{-1}$ [6] observed between [Fe$^{\text{III}}$(CN)$_4$(en)]$^-$ and [Cr$^0$(CO)$_4$(tmen)] (tmen=*N*,*N*,*N'*,*N'*-tetramethyl-1,2-ethanediamine). The difference between 1,2- and 1,3-diamine chelates can be explained by the repulsive interaction of the *N*-methyl groups if tmtn and tmen take half-boat and envelope conformations as transition states respectively. Since the distances between the *N*-methyl groups and the adjacent C$\underline{\text{H}}$'s for both tmtn and tmen are shorter in the transition state than in the ground state, the transition state can be expected to have a larger repulsion energy than the ground state. This difference causes the increase in $\Delta H^{\neq}$ for both diamine chelates. On the other hand, the repulsions between the *N*-methyl groups and other ligands and between the two pseudoaxial *N*-methyl groups are expected to be larger in the ground state than in the transition state in the case of tmtn, but the opposite situation is expected for tmen. Consequently, the $\Delta H^{\neq}$ for 1,2-diamine chelate increases further, but the increase of $\Delta H^{\neq}$ for 1,3-diamine chelate is reduced.

The $\Delta H^{\neq}$ value for the chair-to-chair interconversion of cyclohexane have been reported as 43.1—48.1 kJ mol$^{-1}$.[18–20] The $\Delta H^{\neq}$ value for the six-membered chelate ring of the tn complex is smaller by 11—16 kJ mol$^{-1}$ than that for cyclohexane, though the former has nonbonded interactions between the ring protons and the apical ligands which are absent in the latter.

Cyclohexane is believed to have a half-chair conformation in the transition state of the conformational interconversion.[21] Wiberg and Boyd,[22] in reporting the results of their force-field calculation for cyclohexane, say that the half-chair conformation is higher in energy by 2.5 kJ mol$^{-1}$ than the half-boat form. This difference has been attributed to the torsional and angle strains arising from the difference in the number of carbon atoms coplanar in the transition state.[22,23]

X-Ray diffraction analysis for [Co(tn)$_3$]Cl$_3$·H$_2$O has revealed a chair conformation of the tn chelate with the following angles: Co–N–C$^1$, 122.0°; N–C$^1$–C$^2$, 112.4°; C$^1$–C$^2$–C$^1$, 113.6°.[24] The transition state for the six-membered chelate, which is expected to have a structure with the N–Fe–N–C$^1$–C$^2$ fragment coplanar, corresponds to the half-boat form of cyclohexane. The six-membered chelate ring will be flattened more easily than cyclohexane with the C–C–C angle of 109.5°, since the angles in the former are closer to the angle of ca. 120° required for the transition state. This feature seems to reduce the $\Delta H^{\neq}$ value for the six-membered chelate by ca. 10 kJ mol$^{-1}$ relative to that for cyclohexane.

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