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The Conformation of N-Ethyl Group in Tetracyano(N-ethylethylenediamine) Complexes of Iron(II), Iron(III), and Cobalt(III)

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The 400 MHz ^{1}H NMR spectrum of tetracyano(N-ethylethylenediamine)cobaltate(III) has shown a pair of methylene resonaces of the ethyl group at 2.87 and 3.23 ppm, while the corresponding ferrate(II) complex has shown them at 2.65 and 3.09 ppm. The coupling constant, $^3J_{HCNH}$, for the upfield and downfield resonaces of the Co(III) complex are 9.8 and ca. 2.0 Hz, respectively. The paramagnetic tetracyano(N-ethylethylenediamine)-ferrate(III) showed two methylene signals of the ethyl group at -14.02 and -21.79 ppm at room temperature. Based on these results it was concluded that the methyl group of the N-ethyl group is predominantly in anti position relative to the central metal ion.

The use of transition metal complexes as catalysts presumes the central metal ion to be a catalytic center. Since many catalysts are bifunctional, it is desirable to design a molecular catalyst in which an acid and a base site or an oxidation and a reduction site fixed in such a way that the both sites cannot interact directly but can interact simultaneously with a substrate. One of the first steps in this line will be the alkyl substitution at a donor atom to introduce a functional group. Therefore we have investigated the conformations of N-alkyl groups of the coordinated N-alkylethylenediamines.

The stereochemistry of the coordinated N-alkylethylenediamines has not been studied in detail except N-methyl groups.$^{1)}$ The structure of a 1,2-diamine chelate is described by combination of the configuration at the asymmetric nitrogen center and the conformation of the five-membered chelate ring. In Fig. 1A, the possible structures with R configuration at the nitrogen center are drawn schematically: δ and λ gauche conformers with a pseudoequatorial and a pseudoaxial alkyl group, respectively. The former arrangement is more stable than the latter in octahedral complexes due to the repulsion between the alkyl group and an apical ligand (Y).$^{2)}$ The latter case has been reported for the complexes without Y, e.g., [Pt(bpy)-(Meen)]$^{2+}$, where bpy and Meen denote bipyridyl and N-methylethylenediamine.$^{1)}$

If the alkyl group is denoted as -CH$_2$-R, the orientation of R must be taken into account in order to specify the structure except R = H. The Newman projection looking down the CH$_2$-N bond reveals that there are three different staggered conformations defined by the dihedral angle of M-N-C-R for each gauche form as shown in Fig. 1B. In this communication the conformations of the ethyl group in tetracyano(N-ethylethylenediamine)metalates of Fe^{II}, Fe^{III}, and Co^{III} are reported.

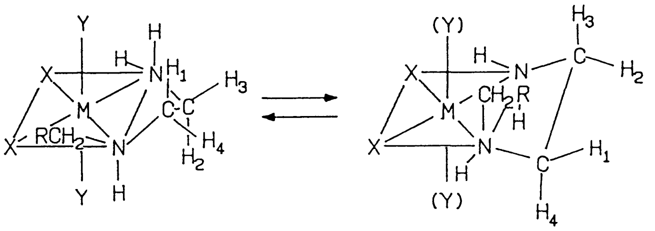

Fig. 1A. Perspective view of $[MX_2Y_2(RCH_2\text{-}NH\text{-}CH_2CH_2\text{-}NH_2)]^{n+}$.

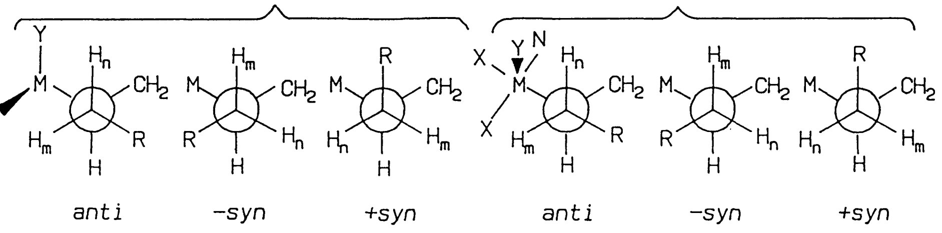

Fig. 1B. Newman projections through RCH_2-NH bond.

The Co^{III} complex was prepared by stirring the mixture of N-ethylethylenediamine (Eten) and $K[Co(CN)_5Cl]$ in water at 60 °C for 3 h. The methanol extract from the products was concentrated and then separated on Dowex 1X8 with 0.2 M hydrochloric acid eluent. The pale yellow eluate was collected, neutralyzed with 1 M sodium hydroxide, and evaporated to dryness. The Co^{III} complex was obtained as sodium salt by adding ether to the ethanol solution of the residue. The Fe^{II} complex was prepared according to the general method for tetracyano(diamine)ferrate(II).3) The Fe^{III} complex was prepared in situ by oxidizing the Fe^{II} complex with sodium persulfate under acidic conditions. The isolated complexes have visible spectral characteristics of tetracyano(diamine)metalates as shown in Table 1. The ^1H and ^{13}C NMR spectra were recorded with a JEOL GSX-400 at room temperature, using sodium 3-trimethylsilylpropionate-2,2,3,3,-d_4 (TSP; 0.00 ppm) and 1,4-dioxane (67.44 ppm) as refereces.

The Co^{III} complex showed the NH signal at 4.41 ppm in 0.01 M DCl-D_2O. The methylene regions of ^1H NMR spectra of the Co^{III} complex in 0.03 M NaOD-D_2O (ND condition) and in D_2O (NH condition) are reproduced in Figs. 2 and 3, respectively.

Table 1. Characterization of Tetacyano(N-ethylethylenediamine)metalates

Complex	Elemental analysis a) / %			Absorption spectrum b)	^{13}C NMR Shift / ppm	
	C	H	N	λ / nm (ε)	(D_2O)	
$Na_2[Fe(CN)_4(Eten)]\cdot$	24.35	5.13	20.07	390(468)	14.91	43.37
$0.5NaClO_4\cdot 0.5CH_3OH\cdot 3H_2O$	(24.00)	(4.74)	(19.76)	313(561)	49.31	50.58
$Na[Co(CN)_4(Eten)]$	34.71	4.86	30.79	356(207)	14.13	45.08
	(35.05)	(4.41)	(30.66)	289(115)	50.39	52.29

a) The values in parentheses indicate calculated values.

b) The spectra were measured in water.

A pair of apparent sextets at 2.87 and 3.23 ppm in Fig. 2 were reduced to an AB quartet on irradiation at the methyl region of the N-ethyl group (1.24 ppm). Thus these signals are assigned to H_m and H_n with $^2J_{HCH}$ of -13.6 Hz. Moreover, each peak splits into a doublet by coupling with H_1: $^4J_{HCNCH}$ of 1.2 and ca. 0.5 Hz were observed for the signals at 3.23 and 2.87 ppm, respectively. Under the NH condition, each peak of the H_m and H_n signals splits into a doublet by coupling with NH as shown in Fig. 3. The upfield and downfield signals have $^3J_{HCNH}$ of 9.8 and ca. 2 Hz, respectively. These differences indicate the predominant population of the anti conformation of the N-ethyl group shown in Fig. 1B. A LAOCN simulation[4] assuming 4 spin system for the ethylene moiety has led to the values of chemical shifts and coupling constants similar to those for $[Co(CN)_4(Meen)]^-$ as listed in Table 2.

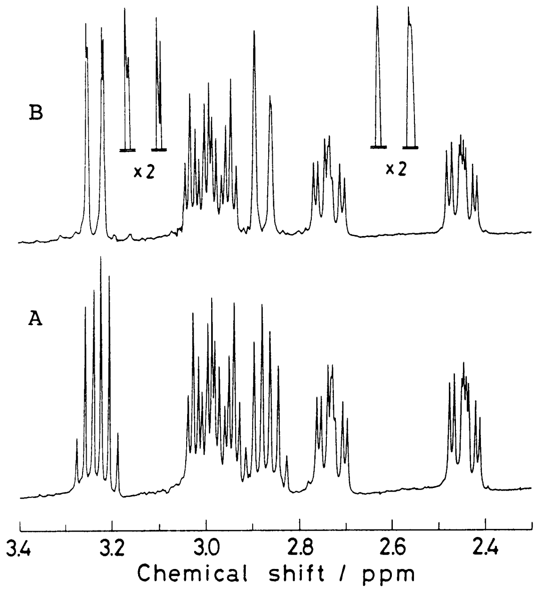

Fig. 2. Methylene region of 400 MHz ^1H NMR spectra of $[Co(CN)_4(Eten)]^-$ in 0.03 M NaOD-D_2O. A: Non-decoupled. B: Methyl proton decoupled.

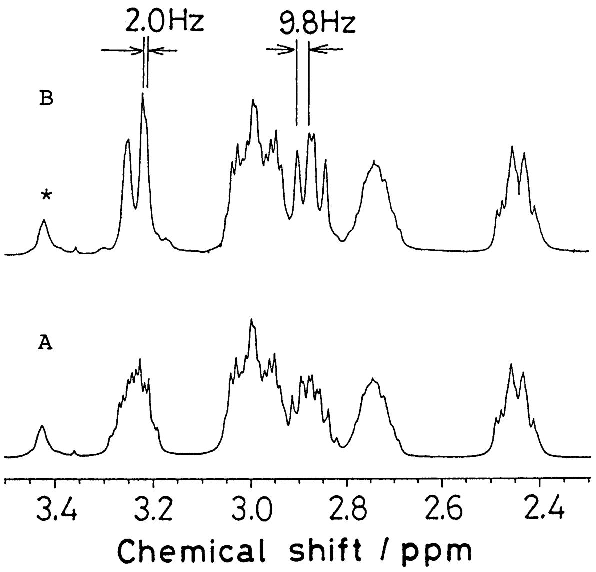

Fig. 3. Methylene region of 400 MHz ^1H NMR spectra of $[Co(CN)_4(Eten)]^-$ in 0.01 M DCl-D_2O. A: Non-decoupled. B: Methyl proton decoupled. The marked signal is due to impurity.

Table 2. ^1H NMR Shifts and Coupling Constants for Tetracyano(N-alkylethylenediamine)metalates

Complex	Chemical shift[a] / ppm							Coupling constant / Hz							
	δ_1	δ_2	δ_3	δ_4	δ_m	δ_n	δ_{Me}	J_{12}	J_{13}	J_{14}	J_{23}	J_{24}	J_{34}	J_{mn}	J_{Me}
$[Fe(CN)_4(Eten)]^{2-}$	2.09	2.43	2.75	2.75	3.09	2.65	1.15	9.1	3.6	-13.4	-13.1	4.0	3.9	-13.3	7.1
$[Co(CN)_4(Eten)]^-$	2.44	2.73	2.95	3.01	3.23	2.87	1.24	10.1	4.3	-12.2	-12.9	4.1	4.9	-13.6	7.2
$[Co(CN)_4(Meen)]^-$ [b]	2.46	2.69	2.93	2.96				10.5	4.7	-13.3	-13.1	4.5	4.0		

a) TSP was used as an internal standard (0.00 ppm). b) From Ref. 1.

The methylene regions of ^1H NMR spectra of the Fe^{II} complex in D_2O (ND condition) and in 0.01 M $DCl-D_2O$ (NH condition) are reproduced in Figs. 4 and 5, respectively. The entire signal patterns for the Fe^{II} complex are similar to those for the isoelectronic Co^{III} complex. Decoupling of the methyl signal reduced the H_m and H_n signals to an AB quartet with $^2\underline{J}_{HCH}$ of -13.3 Hz close to that for the Co^{III} complex. Therefore the ethyl group of the Fe^{II} complex takes the anti conformation predominantly.

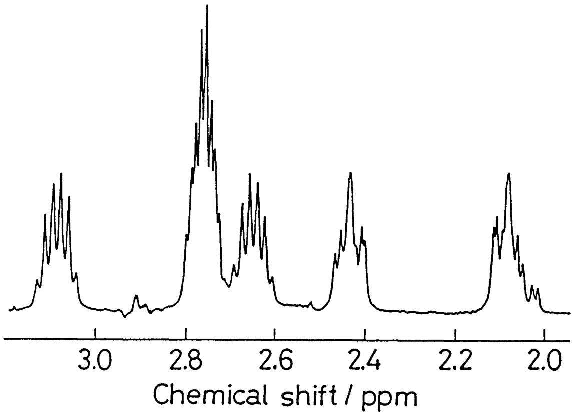

Fig. 4. Methylene region of 400 MHz ^1H NMR spectra of $[Fe(CN)_4(Eten)]^{2-}$ in D_2O. Non-decoupled.

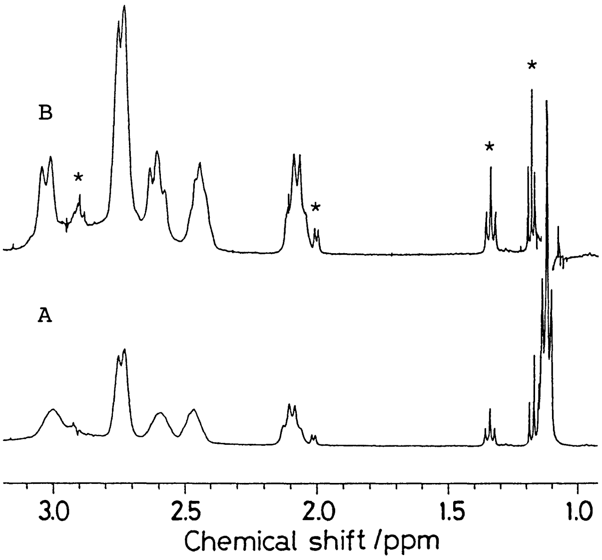

Fig. 5. Methylene region of 400 MHz ^1H NMR spectra of $[Fe(CN)_4(Eten)]^{2-}$ in 0.01 M $DCl-D_2O$. A: Non-decoupled. B: Methyl proton decoupled. The marked signals are due to solvent for recrystallization and dehydrogenation products formed during the measurement.

The Fe^{III} complex showed ^1H resonances of H_2, H_1, CH_3, H_4, H_3, H_m, and H_n at 14.69, 9.63, -1.61, -3.20, -6.86, -14.02, and -21.79 ppm with an area ratio of 1:1:3:1:1:1:1, respectively. The assignment is based on the linear relation between the mole fraction of the Fe^{III} complex and the time-averaged chemical shift for the mixture of the Fe^{III} and Fe^{II} complexes, which were caused by a rapid exchange between them.[5)] The large difference in chemical shift of 7.77 ppm between H_m and H_n confirms the particular conformation of the N-ethyl group in the Fe^{III} complex.

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