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^{1}H- AND ^{13}C-NMR OF LOW-SPIN TETRACYANOIRON(III) CHELATES FORMED WITH 1,2-DIAMINES OF FIXED CONFORMATIONS

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Well resolved ^{1}H- and ^{13}C-NMR signals of the title compounds were assigned with the aid of change in chemical shift by varying the composition of the mixture of Fe^{II} and Fe^{III} complexes of an identical set of ligands. Distinct differences in chemical shift between axial and equatorial protons of the chelate rings and ^{13}C-isotropic shifts alternating in sign with each separation from Fe^{III} center by C-C bond were observed.

NMR studies of low-spin Fe^{III} chelates have been reported with conjugated diimines such as bipyridyl and 1,10-phenanthroline as ligands[1,2] but not with saturated diamines. A low-spin Fe^{III} center is expected to cause paramagnetic shifts through dipole-dipole interaction which can differentiate a fine displacement around the central metal. Tetracyano(1,2-diamine)ferrate(III) chelates with ethylenediamine (en), R-1,2-propanediamine(R-pn), (1R,2R)-cyclopentanediamine(R-cptn), and (1R,2R)-cyclohexanediamine(R-chxn) were isolated as sodium salts by oxidation of the corresponding Fe^{II} chelates[3-5] with hydrogen peroxide under acidic conditions. The conformations of the chelate rings formed with R-pn, R-cptn, R-chxn are fixed in λ as judged from their CD spectra.[4,5] Their magnetic moments at room temperature are between 2.2 and 2.6 B.M. as expected for low-spin Fe^{III} compounds.

^{1}H-NMR spectra of diamagnetic Fe^{II} and paramagnetic Fe^{III} chelates were measured with JEOL MH-100 and FX-100 spectrometers, repectively, using D_2O solutions containing 10^{-2} mol dm^{-3} DCl and sodium 2,2-dimethyl-2-silapentanesulfonate(DSS) as an internal reference at room temperature. The spectral change of $[Fe^{II}(CN)_4(R\text{-pn})]^{2-}$ upon addition of small amounts of $[Fe^{III}(CN)_4(R\text{-pn})]^{-}$ is shown in Fig. 1. NMR signals of $[Fe(CN)_4(R\text{-pn})]^{2-}$ have been assigned in reference to those of the corresponding isoelectronic complex, $[Co(CN)_4(\underline{R}\text{-pn})]^-$.[4,6] The extent of chemical shift of each signal was dependent on the amounts of the Fe^{III} chelate added. Plots of chemical shifts against mole fraction of the Fe^{III} chelate ($f_{Fe}III$) gave a straight line for each signal and the extrapolation of $f_{Fe}III$ to 1.0 gave the chemical shift which is in agreement with that for the isolated Fe^{III} chelate, as shown in Fig. 2. The linear dependency of observed chemical shifts on the mole fraction arises from rapid electron exchange between the Fe^{II} and Fe^{III} centers. Electron exchange reactions of the couples, $[Fe(CN)_6]^{4-/3-}$ [7] and $[Fe(CN)_5(pyridine)]^{3-/2-}$,[8] have been reported to have second-order rate constants of 5×10^3 and 7×10^5 $dm^3mol^{-1}s^{-1}$, respectively. The rate for $[Fe(CN)_4(\underline{R}\text{-pn})]^{2-/-}$ is in the region of fast-limit on NMR time scale. The rate constant is expected to increase with decrease in charges of the reactant couple.

Analogous behavior was observed for each mixture of $[Fe(CN)_4(\underline{R}\text{-cptn})]^{2-/-}$ and $[Fe(CN)_4(\underline{R}\text{-chxn})]^{2-/-}$. The complicated ^1H-NMR signals of the diamagnetic chelates between -1.0 and -2.7 ppm separated from each other and spread between -1.0 and -17 ppm upon addition of their Fe^{III} counterparts. These signals were assigned on selective proton decoupled ^{13}C-NMR measurements and on the assumption that an equatorial proton resonates at lower-field than an axial one bonded to the same carbon atom for the diamagnetic Fe^{II} chelates. The chemical shifts of Fe^{II} and Fe^{III} chelates are listed in Table together with numberings of nuclei.

^1H-NMR spectra of $[Fe(CN)_4(en)]^{2-/-}$ exhibited single signals due to their fast conformational interconversion. The chemical shift of the signal for the Fe^{III} chelate is almost the mean of those of the equatorial and axial protons found for $[Fe(CN)_4(\underline{R}\text{-pn})]^-$.

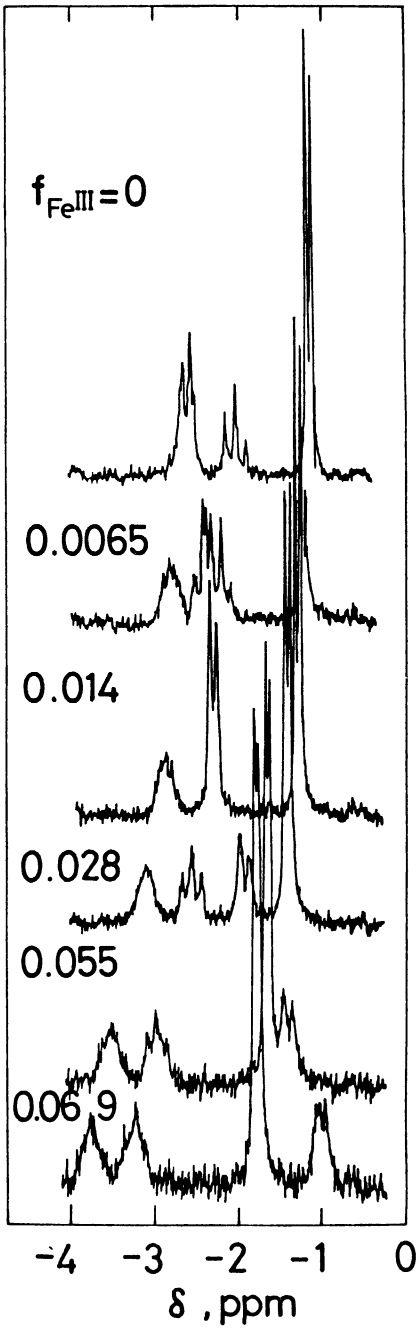

Fig. 1. ^1H-NMR spectral change of $[Fe(CN)_4(\underline{R}\text{-pn})]^{2-}$ on addition of $[Fe(CN)_4(\underline{R}\text{-pn})]^-$ in D_2O containing 10^{-2} $moldm^{-3}$ DCl. $f_{Fe}III$: mole fraction of the Fe^{III} chelate to total Fe chelates.

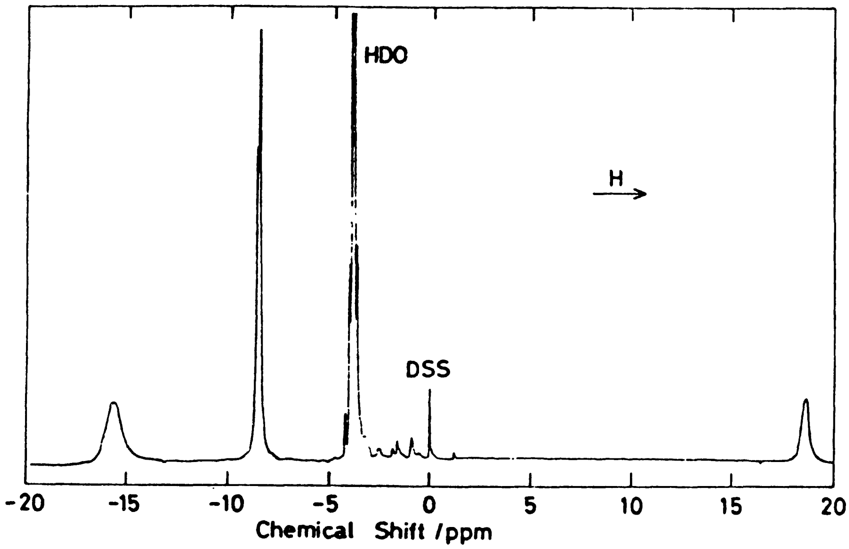

Fig. 2. ^{1}H-NMR of Na[Fe-(CN)$_4$(R-pn)]H_2O in D_2O containing 10^{-2} mole dm^{-3} DCl.

As for the three Fe^{III} chelates of fixed conformation, axial protons resonate at low field and the magnitude of isotropic shift for the R-chxn chelate decreases as the separation from the Fe^{III} center increases but a considerable isotropic shift was found for H^3 of the R-cptn chelate. The equatorial protons in the five-membered chelate ring exhibit up-field shifts by ca. 20 ppm, but the equatorial protons of C^2 carbons of the R-cptn and R-chxn chelates showed significant down-field shifts. These isotropic shifts could not be accounted for by the dipole-dipole interaction only on the model which assume molecular C_2 axis coincides to the principal axis.

As for ^{13}C-NMR, obtained with a JEOL FX-100 spectrometer using dioxane as an internal reference(-67.4 ppm), analogous change in chemical shifts was found for the mixture of the diamagnetic and paramagnetic chelates as the composition was varied and the chemical shifts are summarized in Table. Off-resonance spectra of Fe^{III} chelates showed clear ^{13}C-^{1}H couplings. The signs of the isotropic shifts alternated along each separation from the Fe^{III} center by C-C bond. The difference in the isotropic shifts for C^3 between the R-cptn and R-chxn chelates can be accounted for on the assumption that low-field isotropic shifts superimpose for the R-cptn chelate but opposite field shifts from the both nitrogens superimpose for the R-chxn chelate. The magnitudes of isotropic shifts are attenuated considerably as the separation from the paramagnetic center increases, as expected on the basis of spin-polarization mechanism, but not parallel with those found for Ni^{II} chelates.[9-11)]

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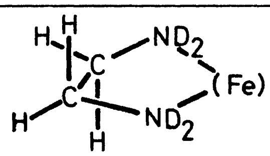
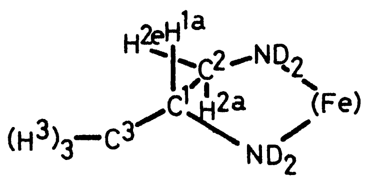
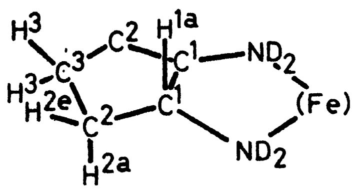
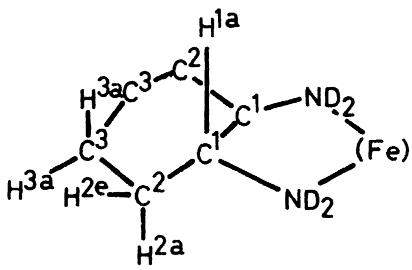
Table. ^{1}H- and ^{13}C-NMR Chemical Shifts of $[Fe^{II,III}(CN)_4(diamine)]^{2-,-}$

Diamine	Nucleus	Chemical Shift/ppm Fe^{II}	Chemical Shift/ppm Fe^{III}	Isotropic Shift/ppm
	H	-2.49	+0.87	+3.36
	C	-45.2	-242.0	-196.8
	H^{1a}	-2.72	-17.04	-14.32
	H^{2a}	-2.06	-17.04	-14.96
	H^{2e}	-2.62	+19.89	+22.51
	H^{3}	-1.12	-9.15	-8.03
	C^{1}	-53.7	-241.1	-187.4
	C^{2}	-51.9	-247.2	-195.3
	C^{3}	-19.6	+47.2	+66.8
	H^{1a}	-2.84	-14.02	-11.18
	H^{2a}	-1.23	-9.49	-8.26
	H^{2e}	-1.80	-7.97	-6.17
	H^{3}	-1.80	-12.95	-11.15
	C^{1}	-65.5	-297.5	-232.2
	C^{2}	-27.7	+21.7	+49.4
	C^{3}	-24.4	-71.9	-47.5
	H^{1a}	-2.05	-16.06	-14.01
	H^{2a}	-1.14	-10.96	-9.82
	H^{2e}	-1.92	-10.96	-9.04
	H^{3a}	-1.14	-6.65	-5.51
	H^{3e}	-1.66	-1.46	+0.20
	C^{1}	-60.6	-248.0	-187.4
	C^{2}	-35.6	+17.3	+52.9
	C^{3}	-25.3	-29.2	-3.9

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1) G. N. LaMar and G. R. VanHecke, J. Am. Chem. Soc., 91, 3442 (1969). 2) R. E. DeSimone and R. S. Drago, Inorg. Chem., 11, 668 (1972), and references cited therein. 3) V. L. Goedken, Chem. Commun., 1972, 207. 4) M. Goto, M. Takeshita, and T. Sakai, Inorg. Chem., 17, 314 (1978). 5) M. Goto, M. Takeshita, and T. Sakai, Bull. Chem. Soc. Jpn., 52, 2589 (1979). 6) S. Yano, H. Ito, Y. Koike, J. Fujita, and K. Saito, Bull. Chem. Soc. Jpn., 42, 3184 (1969). 7) S. G. Wolenuk and J. H. Espenson, Inorg. Chem., 11, 2034 (1972). 8) N. V. Hrepic and J. M. Malin, Inorg. Chem., 18, 409 (1979). 9) F. F. -Lo and C. N. Reilley, Anal. Chem., 41, 1835 (1969). 10) C. E. Strouse and N. A. Matwiyoff, Chem. Commun., 1970, 439. 11) I. Morishima, K. Okada, T. Yonezawa, and K. Goto, J. Am. Chem. Soc., 93, 3922 (1971).

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