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COBALT-59 NUCLEAR MAGNETIC RESONANCE STUDY OF TRIS(PROPYLENEDIAMINE)-COBALT(III) COMPLEXES*

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The difference of cobalt-59 chemical shift is much larger in ob-lel isomerism than that in mer-fac isomerism. The line widths of lel-isomers are 0.10 gauss and ob-isomers 0.14 gauss. The chemical shift values of four $[Co(l\text{-}pn)_3]^{3+}$ are as follows: Δ(mer), 938 ppm; Δ(fac), 951 ppm; Λ(mer), 863 ppm; and Λ(fac), 859 ppm upfield from external $[Co(NH_3)_6]^{3+}$ standard.

The introduction of chiral ligands in an octahedrally symmetric complex increases the number of possible isomers. For tris(d,l-propylenediamine)cobalt(III) complexes, the number of possible isomers is expected to be 24 as the result of geometrical and optical isomerism. For tris(l-propylenediamine)cobalt(III) complexes, it is still possible to exist four isomers, i.e., two lel-type (Δ(mer) and Δ(fac)), and two ob-type (Λ(mer) and Λ(fac)). (see Fig. 1). The characterization of these isomers have been widely studied but remained still difficult and insufficient. The geometrical isomers of Δ-$[Co(l\text{-}pn)_3]^{3+}$ show the indistinguishable character in ultraviolet and visible absorption spectra, circular dichroism, and also proton magnetic resonance spectra at 60 MHz.[1-5] Only the 251 MHz proton magnetic resonance spectra with the aid of cobalt-59 decoupling showed a very slight noneqivalence of methyl protons with the shift of about 0.01 ppm.[6]

Cobalt-59 nuclear magnetic resonance spectroscopy is very sensitive to subtle changes of the environment of central cobalt nucleus.[7-11] For example, it is easy to detect and determine the various kinds of mixed hydroxoammine(ethylenediamine)cobalt(III) isomers separately.[10] The application of cobalt-59 nuclear magnetic resonance to the tris(propylenediamine)cobalt(III) complexes is briefly shown in the following.

Tris(l-propylenediamine)cobalt(III) complexes were synthesized by aerial oxidation of aqueous cobalt(II) chloride and l-propylenediamine under the presence of active charcoal. Δ and Λ isomers were separated by column chromatography[3]. after Dwyer et al. The authentic specimens of Λ(mer) and Λ(fac) isomers[12] were kindly supplied from Professor Kazuo Yamasaki, Nagoya University.

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Table I

Isomer	Chemical Shift$^{\#}$ (ppm)	Line Width (gauss)
Δ(mer)-[Co(l-pn)$_3$]Cl$_3$	938 ± 1	0.10
Δ(fac)-[Co(l-pn)$_3$]Cl$_3$	951 ± 1	0.10
Λ(mer)-[Co(l-pn)$_3$]Cl$_3$	863 ± 1	0.14
Λ(fac)-[Co(l-pn)$_3$]Cl$_3$	859 ± 1	0.14

#) [Co(en)$_3$]Cl$_3$ as external standard (from [Co(NH$_3$)$_6$]Cl$_3$ 1030 ppm). upfield = positive.

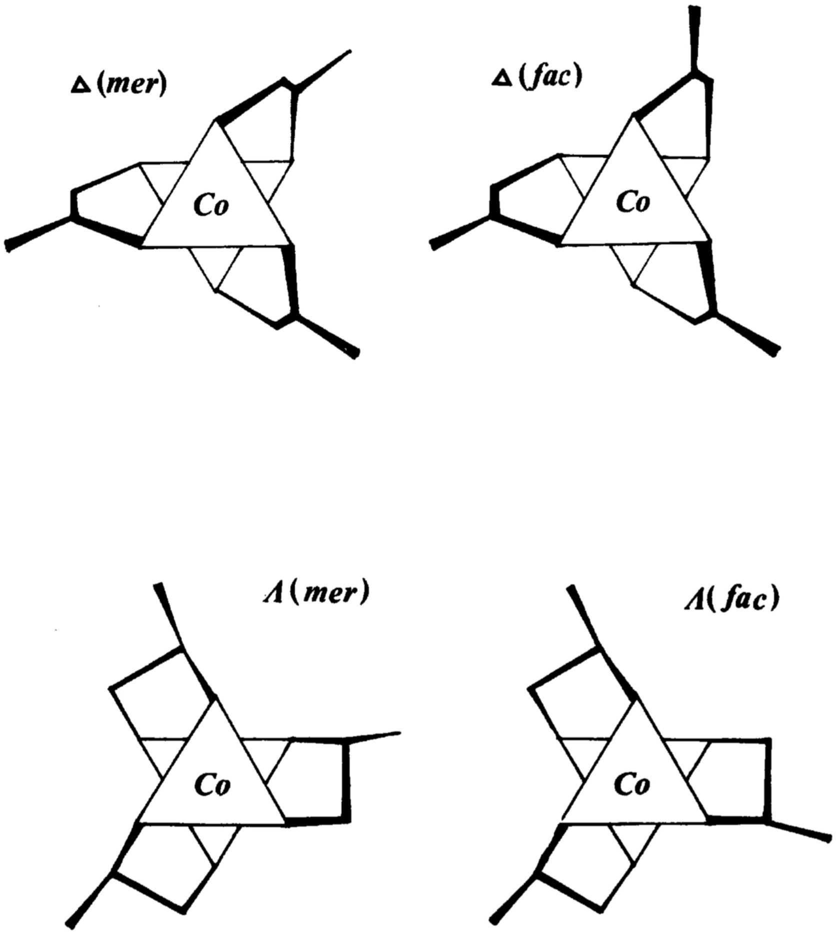


Fig. 1

Cobalt-59 nuclear magnetic resonance spectra were recorded with JEOL JNM-WB-30 spectrometer operating at 13.5550 MHz. All the measurements were carried out at room temperature (25°C). Spectra were obtained by field sweep, and 0.10 gauss of modulation widths.

The cobalt-59 chemical shift data are shown in Table I with line widths. It is remarkable that there are much greater differences of chemical shift in ob-lel isomerism than that in mer-fac isomerism. The origin of these difference for such alike complex ions should be attributed to the difference of the energy separation of the first excited state (d-d excitation), because the other possible contribution to the chemical shift difference might be estimated to be negligible, considering the very slight change of line widths in each (ob and lel) isomer pair, which suggests that the dipolar or quadrupolar interaction in these complexes are not so much different. The change of chemical shift of cobalt-59 of 10 ppm for these complexes should correspond to the change of 10 Dq of about 4 cm^{-1}, or the wavelength of the first absorption maxima of 0.086 $nm^{8)}$, which can be hardly observable.

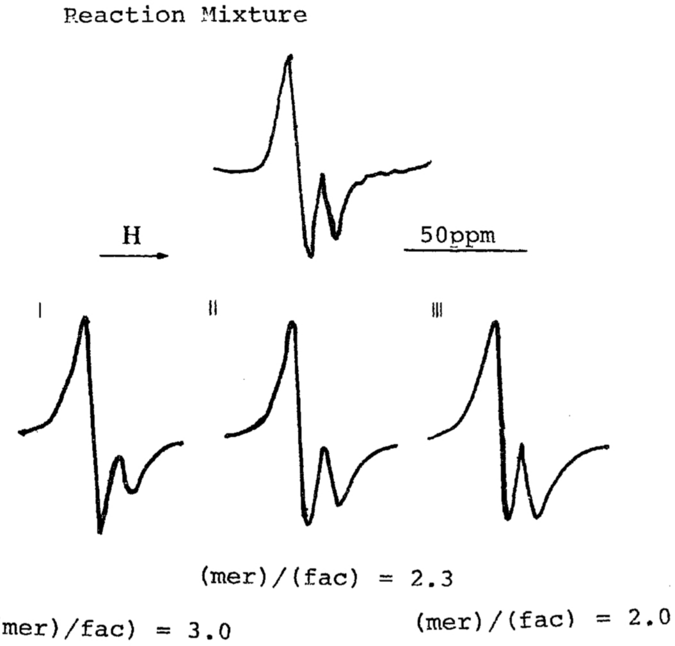
The effect of counter ions on the chemical shift is also observed. The presence of sulfate ions causes the downfield shift of about 50 ppm. This relatively large downfield shift might be attributed to the ion-pair formation such as $[Co(pn)_3 \cdots SO_4]$. For tris(ethylenediamine)cobalt(III) complex, about 60 ppm downfield shift has been reported.$^{6)}$

The relative formation ratio of Δ(mer) and Δ(fac)-isomers were also determined by spectrum simulation. The nuclear magnetic resonance spectra of the reaction mixture of **cobalt(II)** chloride and l-propylenediamine were simulated with four parameters, i.e., line widths for two Lorentzian curves, chemical shift, and the ratio of populations for two isomers. Calculation were performed on a Hitac 8700/8800 computer at Computer Centre, The University of Tokyo. (The simulation program was coded by Dr. Hiroshi Ozawa.) The best-fit parameters show that the relative population of Δ(mer) and Δ(fac) are 2.3 : 1(see Fig. 2), **which is slightly different from the theoretical value (3 : 1) assuming entirely statistical distribution.**

The change of nuclear magnetic resonance spectra through multiple recrystallizations is shown in Fig. 3. The most insoluble fraction (namely well-crystallized) fraction is Δ(fac), and corresponds to the most-high field spectra. This isomer$^{13)}$ has been characterized by X-ray crystallography.

The reaction mixture from aerial oxidation of **cobalt(II)** salts under the presence of racemic propylenediamine in place of l-propylenediamine shows much complicated spectra. Only the doublet of most high-field side (A and B in Fig. 4) can be assigned to the Δ(fac)-(lll)(and Λ(fac)-(ddd)), and Δ(mer)-(lll) (and Λ(mer)-(ddd)), respectively. Further investigations are in progress.

Fig. 2



(mer)/(fac) = 2.3

(mer)/fac) = 3.0

(mer)/(fac) = 2.0

Fig. 3

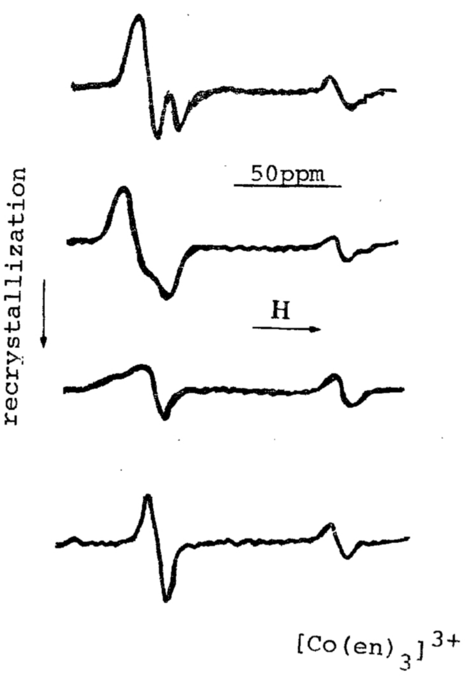
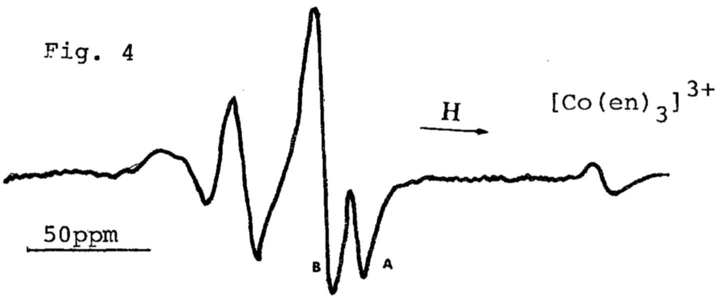


Fig. 4



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