BULLETIN OF THE CHEMICAL SOCIETY OF JAPAN, VOL. 48 (3), 1093 (1975)

The Carbon-13 Nuclear Magnetic Resonance Spectra of Isomers of the Tris(*l*-propylenediamine)cobalt(III) Ion

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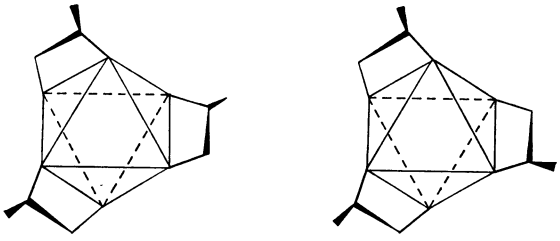
(Received August 22, 1974)

Synopsis. The proton-decoupled carbon-13 NMR spectra were measured for the *mer*-*Λ*(*ob*), *facial*-*Λ*(*ob*), and *facial*-*Δ*(*lel*)[Co(*l*-pn)$_3$]$^{3+}$ ions using the Fourier transform technique. There was a clear difference between the *Λ* and *Δ* configurations. However, no appreciable difference was observed between the *mer* and *facial* isomers of *Λ*(*ob*)-[Co(*l*-pn)$_3$]$^{3+}$.

Since the proton NMR spectra of tris(diamine)-cobalt(III) complexes are broad as a result of the spin-spin coupling of protons with ^{59}Co (I=7/2, 100% natural abundance), ^{59}Co decoupling is necessary to get a sufficient resolution for accurate analysis and to detect, for instance, the *mer* and *facial* isomers of the *Δ*(*lel*)-[Co(*l*-pn)$_3$]$^{3+}$ ion.[1] We have separated the *mer* and *facial* isomers of *Λ*(*ob*)-[Co(*l*-pn)$_3$]$^{3+}$ by column chromatography on SP-Sephadex (Fig. 1) and measured the 100 MHz PMR spectra in DMSO-d_6; the spectra were similar for these two isomers except for the amine-proton signals.[2]

As recent developments in the carbon-13 NMR technique have made valuable contributions to the analysis of conformations[3] and to the determination of stereochemical structures,[4] this method has been applied to these isomers. Figure 2 shows an illustrative example of the 22.63 MHz ^{13}C-NMR spectra, including the assignment of the signals. Table 1 gives the results, together with that of *facial*-*Δ*(*lel*)-[Co(*l*-pn)$_3$]Br$_3$. As the uncertainty of peak positions is about 0.1 ppm, there is a clear difference between the *δ*-positions of the *Λ* and *Δ* isomers. The *facial* isomer has a three-fold axis of rotation and its chelate rings are equivalent, whereas the chelate rings of the *mer* isomer are non-equivalent (*cf.* Fig. 1). Consequently, three signals can be expected for each carbon atom of the latter. The spectrum obtained, however, showed only one signal for the *mer* isomer as well as for the *facial* isomer (Fig. 2). Therefore, neither the ^{13}C-NMR nor the 100 MHz PMR technique is effective in distinguishing the *mer* isomer from the *facial* isomer of *Λ*(*ob*)-[Co(*l*-pn)$_3$]$^{3+}$. The cobalt-59 NMR spectra, however, showed a difference in chemical shift in the *mer-facial* isomerism.[5]



mer *facial*

Fig. 1. Geometric isomers of *Λ*(*ob*)-[Co(*l*-pn)$_3$]$^{3+}$.

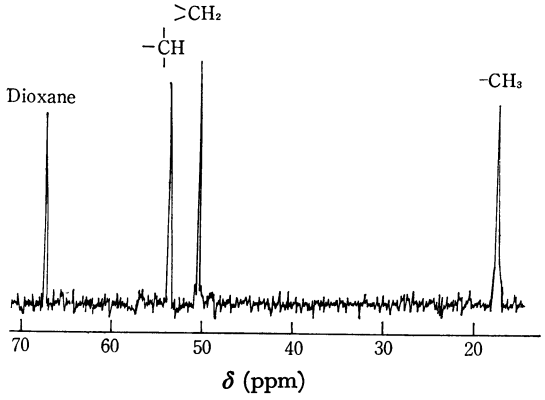


Fig. 2. ^{13}C-NMR spectrum of *mer*-*Λ*(*ob*)-[Co(*l*-pn)$_3$]Cl$_3$·4H$_2$O.

Table 1. ^{13}C-NMR Chemical shifts of the isomers of [Co(*l*-pn)$_3$]$^{3+}$ (in *δ* ppm)

Complex	–CH$_3$	>CH$_2$	–CH
mer-*Λ*(*ob*)-[Co(*l*-pn)$_3$]Cl$_3$·4H$_2$O	17.5	50.4	53.7
facial-*Λ*(*ob*)-[Co(*l*-pn)$_3$]Cl$_3$·3H$_2$O	17.6	50.2	53.7
facial-*Δ*(*lel*)-[Co(*l*-pn)$_3$]Br$_3$	17.8	50.7	55.0

Experimental

Measurement of the ^{13}C-NMR Spectra. The proton-decoupled 22.63 MHz ^{13}C-NMR spectra were obtained by means of a Bruker WH 90 spectrometer, using the Fourier transform technique, which allows the measurement of samples with ^{13}C in natural abundance (1.1%). The solvent was D$_2$O, and the spectra were run at an ambient temperature. Dioxane (*δ*=67.40) served as an internal standard; the *δ*-values are given relative to TMS.

The ^{13}C-NMR spectra were measured by Dr. Sven Bagger and Prof. Woldbye, Chemistry Department A, The Technical University of Denmark. We wish to express our deep gratitude for their kindness.

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