Tehan, and K. Voorhees for their assistance in the synthesis of the complexing agent.

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Cobalt-59 Nuclear Magnetic Resonance Study of Optical and Geometrical Isomerism in Tris((±)propylenediamine)cobalt(III) Complexes

Sir:

A large number of optical and geometrical isomers may be formed in tris-chelate metal complexes of chiral, bidentate ligands containing nonequivalent donor atoms. Tris((±)propylenediamine)cobalt(III) chloride, for example, forms eight optical isomers[1] each of which may form both cis and trans geometrical isomers[2] resulting in a total of 24 distinguishable structures. Conformational isomerism may also occur in a five-membered chelate ring in which the carbon–carbon bond is aligned either parallel or perpendicular to the threefold axis of the complex. The methyl groups preferentially adopt an equatorial configuration in propylenediamine complexes[3] so that the conformation of the chelate ring is determined by the optical configuration of the ligand. This preferential orientation in turn determines the distribution of optical isomers formed in a tris(pn) complex, since the λ conformation of the chelate is preferred in the Δ complex and the δ conformation preferred in the Λ complex.

The optical isomers of $Co((\pm)pn)_3^{3+}$ are easily separated chromatographically;[1] however, this technique leaves the geometrical isomers unresolved. The existence of the cis isomer has been demonstrated by an X-ray analysis of Δ-$[Co((-)pn)_3]Br_3$.[4] Attempts to prove the existence of *trans*-Δ-$Co((-)pn)_3^{3+}$ by X-ray analysis of nine different salts were unsuccessful because of the formation of insufficiently ordered crystals.[5]

Proton nuclear magnetic resonance has been a useful technique for the investigation of diastereomers of tris-chelate metal complexes.[6] Cobalt-59 decoupling is necessary in order to obtain high-resolution proton spectra of cobalt complexes;[7] however, even under these conditions no splitting due to the cis and trans isomers is observed in the pmr spectrum of Δ-$[Co((-)pn)_3]Cl_3$ at 100 MHz. On the other hand, at 251 MHz additional fine structure is observed[8] that can be attributed to the presence of the geometrical isomers; however, the presence of many nonequivalent pn ligands prevents a simple interpretation of this spectrum or an estimation of relative abundances.

Cobalt-59 nmr signals of cobalt(III) complexes occur over an extremely large frequency range;[9] therefore the ^{59}Co resonance is very sensitive to subtle details of the cobalt environment. For example, separate cobalt-59 nmr signals are observed for the geometrical isomers of complexes such as $Co(en)(NH_3)_2(OH)_2^+$ [10] and for $Co(en)_3^{3+}$ complexes with different degrees of N deuteration.[8] This sensitivity is utilized in the present work, in which separate cobalt-59 resonances are resolved for the optical and geometrical isomers of a tris-chelate complex, $Co((\pm)pn)_3^{3+}$. The existence of *trans*-$Co(pn)_3^{3+}$ is proved and relative intensities of the nmr signals are used to determine equilibrium ratios of the various isomers.

$[Co((\pm)pn)_3]Cl_3$ was prepared as described by Jenkins and Monk.[11] *Anal.* Calcd for $CoC_9H_{30}N_6Cl_3$: C, 27.88; H, 7.80; N, 21.68. Found: C, 28.03; H, 7.73; N, 21.29.[12] This complex was chromatographically separated into three fractions as described by Dwyer, Sargeson, and James.[1] (−)pn was resolved from (±)pn by the method of Dwyer, Garvan, and Shulman[13] and chromatographically pure Δ-$[Co((-)pn)_3]Cl_3$ was obtained as described by Dwyer, MacDermott, and Sargeson.[14] *cis*-Δ-$[Co((-)pn)_3]Br_3$ was crystallized according to the procedure described by MacDermott.[2]

The cobalt-59 nmr spectra were obtained on a Varian DP-60 nmr spectrometer equipped with a Varian V-4210A variable frequency rf unit which operated at 14.2 MHz. The spectrometer system included a Princeton Applied Research Model 121 lock-in amplifier which was operated at a frequency of 1500 Hz with the phases adjusted to display the first audio side band as an absorption mode signal. The field was swept with a Varian Fieldial Mark II using a 5 G sweep width and calibrated from the side band separation. The samples were contained in 15-mm o.d. test tubes and measured at the temperature of the magnet gap of 27 ± 2°. Relative integrated intensities of the peaks were measured with a planimeter, and errors are given as the mean deviation from the mean of four separate measurements.

The cobalt-59 nmr spectrum of aqueous $[Co((\pm)pn)_3]Cl_3$ is shown in Figure 1A. Figures 1B, C, and D show the cobalt-59 spectra of the three fractions of diastereomers obtained by chromatographic fractionation of $[Co((\pm)pn)_3]Cl_3$. Fraction 1 (Figure 1B) contains Δ-$Co((-)pn)_3^{3+}$ and Λ-$Co((+)pn)_3^{3+}$ and fraction 2 (Figure 1C) contains Δ-$Co((-)pn)_2((+)pn)^{3+}$ and Λ-$Co((+)pn)_2((-)pn)^{3+}$. The Δ and Λ configurations in these cases correspond to mirror image species and will exhibit identical nmr spectra. Fraction 3 (Figure 1D) consists of the remaining four racemic pairs. By inspection of Figure 1, peaks d and e are readily assigned to fraction 1, peaks b and c to fraction 2, and peak a to fraction 3. From relative integrated intensities of these lines, the ratios a:(b + c):(d + e) are

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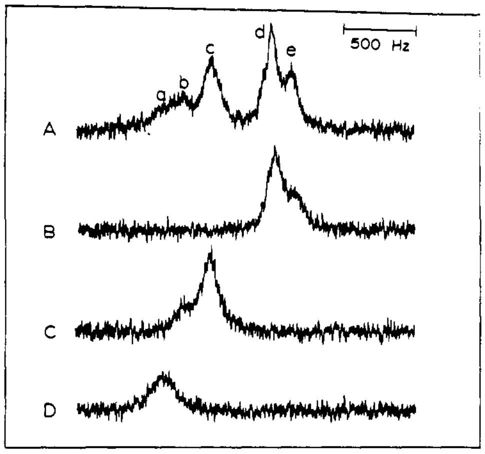

Figure 1. Cobalt-59 nmr spectra of aqueous (A) 0.41 *m* $[Co((\pm)\text{-}pn)_3]Cl_3$, (B) 0.15 *m* $[Co(pn)_3]Cl_3$ from fraction 1 described in the text, (C) 0.15 *m* $[Co(pn)_3]Cl_3$ from fraction 2, and (D) 0.08 *m* $[Co(pn)_3]Cl_3$ from fraction 3.

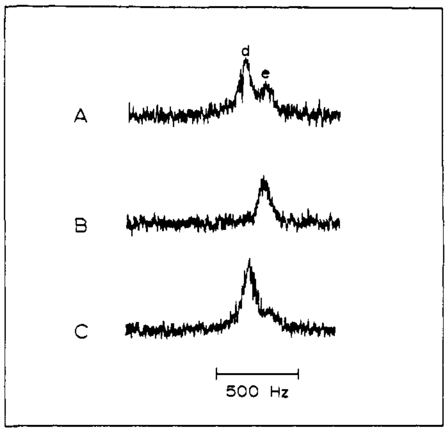

Figure 2. Cobalt-59 nmr spectra of aqueous (A) $\Delta\text{-}[Co((-)pn)_3]Br_3$ and $\Lambda\text{-}[Co((+)pn)_3]Br_3$, [Co(III)] = 0.07 *m*, (B) 0.03 *m* *cis*-$\Delta\text{-}[Co((-)pn)_3]Br_3$, and (C) supernatant liquid from crystallization of *cis*-$\Delta\text{-}[Co((-)pn)_3]Br_3$, containing primarily *trans*-$\Delta\text{-}[Co((-)pn)_3]Br_3$ and a small amount of the cis isomer.

calculated to be 1:(3.9 ± 0.3):(4.9 ± 0.2). These ratios are 1:(2.5 ± 0.3):(2.1 ± 0.1) for $[Co((\pm)pn)_3]Cl_3$ prepared in the presence of charcoal. The latter ratios compare favorably with the 1:2.1:2.1 values determined previously by Dwyer, *et al.*[1] The different relative isomer abundances obtained for different preparations of $Co((\pm)pn)_3{}^{3+}$ show that the presence of the charcoal catalyst establishes a different equilibrium distribution of diastereomers, producing a greater abundance of energetically less favored but statistically more probable species.

Figure 2A shows the cobalt-59 nmr spectrum of the enantiomers from fraction 1 after conversion to the bromide salts. Figure 2B shows the cobalt-59 spectrum of the cis geometrical isomer isolated from $\Delta\text{-}[Co((-)pn)_3]Br_3$, and Figure 2C is the spectrum of the supernatant liquid separated from the cis crystals. The different intensities are due to different cobalt(III) concentrations. Figure 2 clearly permits an unambiguous assignment of peaks e and d in Figure 1 to the cis and trans geometrical isomers of $\Delta\text{-}Co((-)pn)_3{}^{2+}$ and $\Lambda\text{-}Co((+)pn)_3{}^{3+}$, respectively. Similarly, peaks b and c can be assigned to the geometrical isomers present in fraction 2. Trans to cis ratios (3.4 ± 0.3):1 and (2.9 ± 0.3):1 are calculated from the relative integrated intensities of these peaks (the ratios of c:b and d:e). These correspond to the expected 3:1 statistical distribution. Actually, fraction 2 contains a mixture of eight distinguishable isomers. For example, in the Δ complex only one cis isomer may be formed but three distinguishable trans isomers may be formed. If all four of these diasteriomers exist, four separate cobalt-59 signals could exist. The resolution of only two peaks does not distinguish between the possibilities that only one trans isomer is formed or that all three trans isomers are formed but have very similar chemical shifts. The possibility that peak b could be assigned to one of the trans isomers rather than to the cis isomer must also be considered. However, the c:b intensity ratio of 3:1 strongly suggests that a statistical distribution of geometrical isomers also occurs in fraction 2.

This work demonstrates the advantages of using cobalt nmr rather than pmr for the detection of optical and geometrical isomerism in cobalt complexes. Proton shifts in diamagnetic complexes are relatively small, whereas cobalt shifts in the same complexes may be quite large, providing better resolution. The lack of resolved spin coupling with protons simplifies assignments in cobalt spectra and allows a straightforward estimation of relative abundances. Because of the excellent resolution, isomerism in complexes formed from unresolved ligands may be investigated directly. There is currently much interest in the stereoisomerism of tris-chelate metal complexes.[7,15] In view of the utility of cobalt-59 nmr for the detection of optical and geometrical isomers of cobalt complexes, cobalt-59 nmr should be a valuable tool for the investigation of stereoisomerism in tris-chelate cobalt complexes.

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Virtual Coupling in Carbon-13 Nuclear Magnetic Resonance Spectra with Off-Resonance Continuous Wave Proton Spin Decoupling

Sir:

Continuous wave proton spin decoupling (CWSD) has become a routine procedure for assignment of carbon-13 resonance absorptions.[1] An intense CW rf field several hundred hertz upfield from the proton resonances is used to irradiate the proton transitions. The resulting carbon-13 spectrum retains the nuclear

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