Carbon-13 Nuclear Magnetic Resonance of Tris(diamine)-cobalt(III) Complexes

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In our study of conformations in five- and sixmembered metal-diamine rings we have applied the technique of Fourier transform ^{13}C-NMR to a series of tris(diamine)cobalt(III) complexes.

In the only previous ^{13}C-NMR study [1] of diamagnetic diamine complexes known to us it was reported that at 15.1 MHz the ^{13}C chemical shifts between some free 1,2-diamines and the same diamines coordinated to cobalt(III) were negligible within the experimental uncertainty of 5 ppm. This finding might suggest that constancy of chemical shifts would limit the structural information that could be obtained by the technique.

Furthermore, it is known that the ^{1}H-NMR spectra of tris(diamine)cobalt(III) consistently exhibit broad, rather unresolved bands (Fig. 1) due to spin-spin coupling over three bonds of the protons with ^{59}Co ($I = 7/2$, 100 % natural abundance); ^{59}Co decoupling is necessary to get sufficient resolution for accurate analysis.[2] A similar complication might arise in the ^{13}C-NMR spectra, especially because only two bonds separate the cobalt nucleus from its nearest carbon atoms.

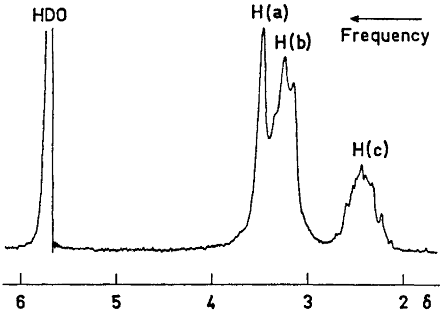

Fig. 1. 60 MHz ^{1}H NMR spectrum of [Co(en)(tn)$_2$]Cl$_3$.

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

[Co(en)$_2$(i-bn)]$^{3+}$ was prepared by reacting *trans*-[Co(en)$_2$Cl$_2$]$^+$ with i-bn. All other complexes were obtained by the general procedure described earlier [3] for preparation and chromatographic separation of "mixed" tris-complexes.

The carbon skeletons of the ligands involved and the letter indices used are shown in Fig. 2.

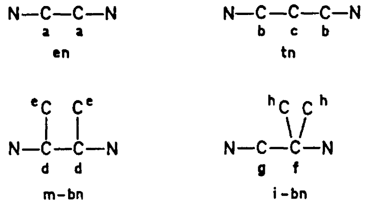

Fig. 2.

Fig. 3 illustrates the quality of the spectra obtained. The experimental uncertainty of peak positions is *ca.* 0.1 ppm.

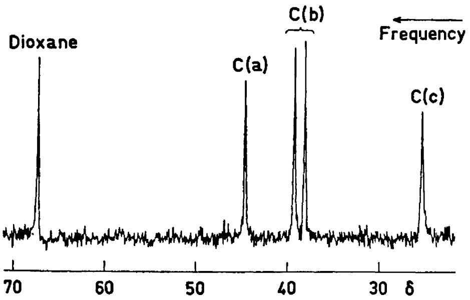

Fig. 3. Illustrative example of the 22.63 MHz ^{13}C NMR spectra. 0.246 g [Co(en)(tn)$_2$]Cl$_3$ and 20 μl dioxane in 1.3 ml D$_2$O. (4000 pulses, 4K input data points, 1 s sampling time.)

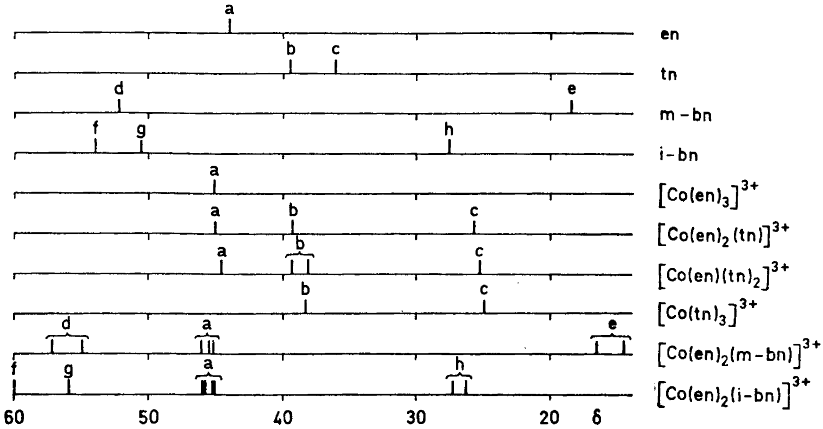

Fig. 4. Diagrammatic representation of the ^{13}C NMR spectra, showing the positions of resonance lines on a δ-scale.

In contrast to the ^{1}H spectrum (Fig. 1) the ^{13}C spectrum exhibits well-resolved and sharp lines, and thus ^{13}C-^{59}Co spin-spin coupling does not significantly influence the resolution.

Assignments and chemical shift data are outlined in Fig. 4.

It appears that chelation of the diamines causes distinct chemical shifts, and characteristic patterns for the different complexes result.

The ^{13}C-resonances of both the CH_3 (e) and CH (d) moieties in $[Co(en)_2(m\text{-}bn)]^{3+}$ are split into two lines, and this is consistent with the presence of both an equatorial and an axial methyl group on the puckered fivemembered Co-m-bn ring.[4] Similarly $[Co(en)_2(i\text{-}bn)]^{3+}$ contains an equatorial and an axial methyl group, but in this case they are bound to the same carbon atom, and this causes a smaller chemical shift difference between the two CH_3 lines (h).

The methylene groups bound to nitrogen in the sixmembered Co-tn rings in $[Co(en)(tn)_2]^{3+}$ give rise to two peaks (b). This is tentatively explained by assuming that different conformations, *e.g.* chair and skew-boat forms,[5,6] of the Co-tn rings are present.

Clearly, ^{13}C-NMR spectroscopy offers new possibilities for conformational studies of chelate diamine rings in diamagnetic complexes.

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