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On ^{13}C NMR Spectra of *lel*- and *ob*- Conformations in Tris(diamine)-cobalt(III) Complexes

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The inert tris(diamine)cobalt(III) complexes with their puckered and flexible rings are often used as test-compounds for the study of theoretical and experimental aspects of conformational analysis.

One well-known stereochemical detail in these compounds is the occurrence of *lel*- and *ob*-rings (Fig. 1).¹

In the present communication we wish to draw attention to a possibility of distinguishing *lel*- and *ob*-conformations of certain five-membered rings on the basis of proton-decoupled ^{13}C NMR spectra.

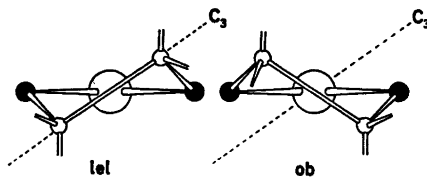


Fig. 1. A chelate ring, $\overline{\text{C}-\text{N}-\text{M}-\text{N}-\text{C}}$, viewed perpendicular to the C_3 -axis (or pseudo C_3 -axis) of a tris-complex.

In the following it is assumed that the reader is familiar with the IUPAC nomenclature for conformations and configurations.²

A family of complexes, $[\text{Co}(\text{en})_x(\text{lbn})_{3-x}]\text{Cl}_3 \cdot n\text{H}_2\text{O}$ ($x=0, 1, 2$), where en is 1,2-ethanediamine and lbn is $(-)_D$ -(*R,R*)-1,2-dimethyl-1,2-ethanediamine, has been separated and resolved by descending paper chromatography.³

It is reasonable to assume that the chelated lbn ligand is forced to have the energetically favoured λ -conformation with two equatorially oriented methyl groups.⁴ This assumption together with the knowledge of the absolute configuration of lbn makes it possible to deduce if an lbn ligand will adopt a *lel*- or an *ob*-conformation in a tris-complex, where the absolute configuration about the central atom is known.

This possibility of predicting ring conformations makes lbn complexes particularly suited for the present study.

The lbn conformations in complexes I–VI are given in Table 1.

The proton-decoupled 22.63 MHz ^{13}C NMR spectra of the six complexes with known lbn-ring conformations were measured in D_2O solution. The characteristics of the lbn patterns are presented in Table 1.

Two spectral features seem to mark a difference between *lel*- and *ob*-rings.

The linewidths of the methyl peaks from *lel*-conformations are broader than from *ob*-conformations. The half linewidths lie in the two separate intervals 14–26 Hz and 6–10 Hz, respectively. Both categories of peaks appear in the graphical representation as bands without structure and have a chemical shift of ca. 18.3.

The chemical shifts of the CH-resonances are different, the position of *lel*-ring peaks being 0.9–1.2 ppm downfield relative to the *ob*-ring peaks. The linewidths are all 2–4 Hz.

These findings are in accordance with a study of 1-propylenediamine complexes by Kojima and Yamasaki.⁵ These authors observed that the methyl half linewidths in *fac*- Δ - $[\text{Co}(\text{lbn})_3\text{lel}]_3^+$ and *fac*- Δ - $[\text{Co}(\text{lbn})_3\text{ob}]_3^{2+}$ were ~ 27 and ~ 7 Hz, respectively,⁶ and that the shift difference between the CH carbon atoms was 1.3.

Table 1. Information on lbn rings.

	Conformation	Half linewidth of CH ₃ -peaks (Hz)	Chemical shift ^a of CH-resonances
I. Δ -[Co(en) ₂ (lbn)] ³⁺	<i>ob</i>	6	57.6
II. Δ -[Co(en) ₂ (lbn)] ³⁺	<i>lel</i>	14	58.7
III. Δ -[Co(en)(lbn) ₂] ³⁺	<i>ob</i> ₂	7	57.6
IV. Δ -[Co(en)(lbn) ₂] ³⁺	<i>lel</i> ₂	14	58.5, 58.8 ^b
V. Δ -[Co(lbn) ₃] ³⁺	<i>ob</i> ₃	10	57.4
VI. Δ -[Co(lbn) ₃] ³⁺	<i>lel</i> ₃	26	58.6

^a Dioxane (δ 67.40) was used as internal standard. ^b Double peak.

We have at present no satisfactory explanation of the remarkable differences in the linewidths of the methyl resonances.

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