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PARAMAGNETIC SHIFTS IN SOLUTIONS OF CIS-AND-TRANS-1,2-CYCLOHEXANEDIOL AND COBALT(II) ACETYLACETONATE

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Recently the use of paramagnetic ions in the interpretation of pmr spectra of complex organic molecules has been reported by a number of investigators. Zaev et al. (1) have made assignments in the spectra of some substituted pyrazoles on the basis of contact shifts induced by $NiBr_2 \cdot 3H_2O$. Changes induced by metal ions in the spectra of biologically important molecules such as lysozyme (2) and cholesterol (3) have also been described. In this laboratory $Co(acac)_2$ (acac = acetylacetonate) has been used to simplify and aid in the interpretation of the pmr spectra of a wide variety of alcohols (4,5). With saturated alcohols it has been found that the signals for hydroxyl groups broaden and shift at very low cobalt concentrations; however, the magnitude and direction of the shifts vary unpredictably. Signals due to α-CH_n groups always move downfield quite rapidly as the cobalt-alcohol ratio increases, whereas the signals for β-, γ-, etc. CH_n groups usually shift to slightly higher field. Some broadening of the lines occurs also as $Co(acac)_2$ is added, an effect that has been found to be attenuated along the molecule. These studies are being extended to cyclic polyhydric alcohols, including carbohydrate derivatives; we report now some preliminary results with cis-and-trans-1,2-cyclohexanediol.

The perturbation of the pmr spectrum of trans-1,2-cyclohexanediol by $Co(acac)_2$ is shown in Figure 1. The spectra were measured on a Varian T-60 spectrometer in chloroform-d (0.2 M) with tetramethylsilane as internal standard. In the spectrum of the diamagnetic solution (a), the eight methylene protons appear in the region τ7.78-9.04 as a broad multiplet; the narrow signal at τ6.39 and the band at τ6.68, each corresponding in intensity to two protons, have been assigned to the hydroxyl protons and methine protons, respectively. It is seen that the α-CH and OH resonances shift downfield as $Co(acac)_2$ is added. Moreover, the signal for the hydroxyl groups broadens at very low cobalt concentrations, and the signals for the methylene protons appear as three bands of integrated intensity 4:2:2 at a high cobalt-diol ratio (spectrum e). The α-CH resonance shifts at about the same rate as that of ethanol (using equal hydroxyl-group concentrations) (4,5).

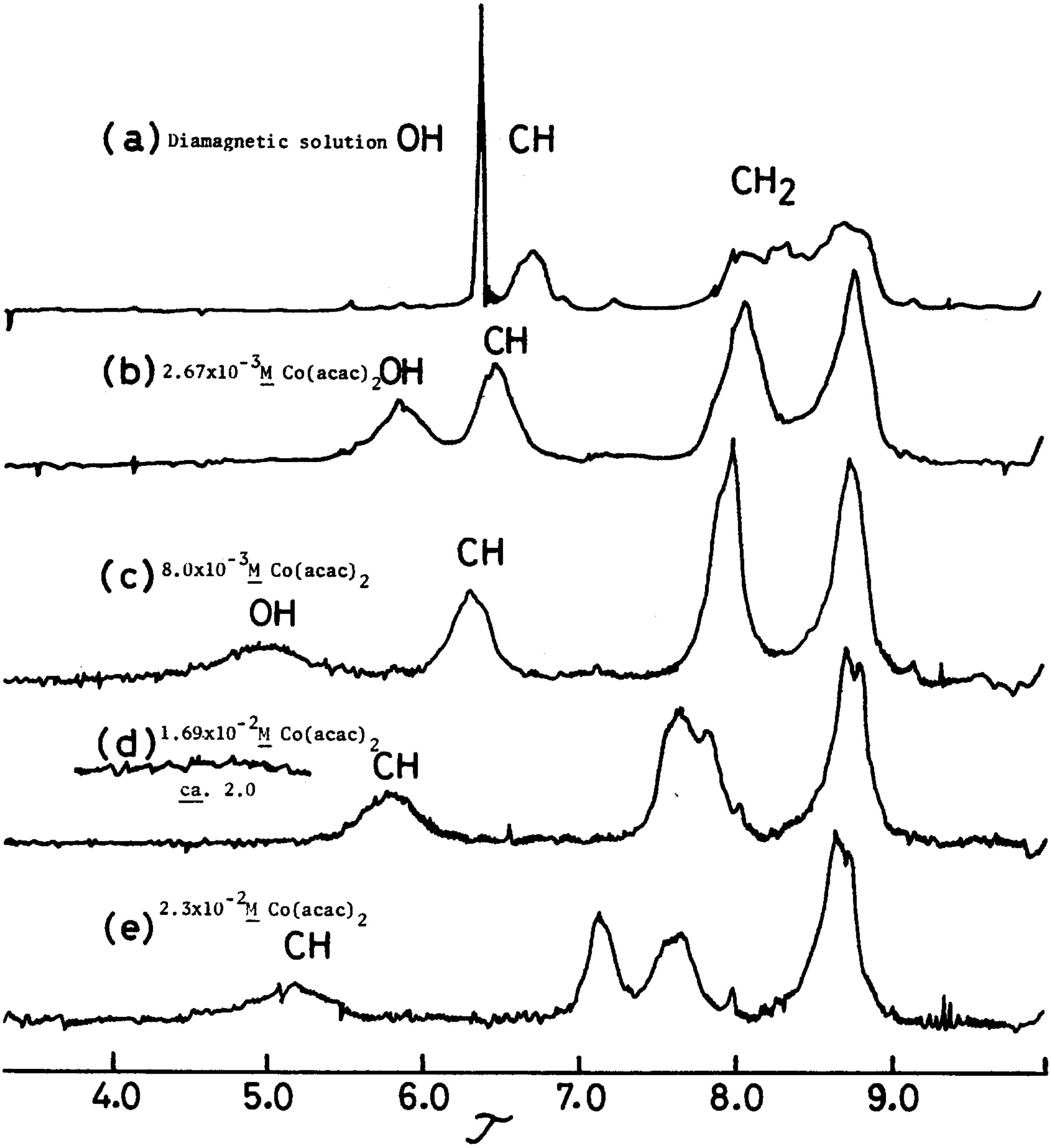

FIGURE 1

The pmr of *cis*-1,2-cyclohexanediol is very similar to that of the *trans* isomer; as $Co(acac)_2$ is added the signals for the methine and hydroxyl groups shift downfield. Significantly, however, the signals for the *cis* isomer shift at considerably faster rates than the corresponding signals for the *trans* isomer. When the concentration of $Co(acac)_2$ is $2.67 \times 10^{-3} \underline{M}$, the methine resonances of $0.2\underline{M}$ solutions of the *cis* and *trans* isomers are 0.33 and 0.21 ppm, respectively, below the diamagnetic positions. With $2.67 \times 10^{-2} \underline{M}$ $Co(acac)_2$ the shift for the *cis* isomer is 2.41 ppm, whereas that for the *trans* isomer is only 1.54 ppm with $2.3 \times 10^{-2} \underline{M}$ $Co(acac)_2$.

In the presence of an alcohol, the cobalt complex probably exists as the labile species *trans*-$Co(acac)_2L_2$ (L = alcohol) (6).

$$Co(acac)_2 + 2L \rightleftharpoons Co(acac)_2L_2 \qquad (1)$$

Since the exchange of ligands L between complexed and uncomplexed sites is rapid on the nmr time scale, the spectra are time-averaged, the various proton resonances being shifted from their normal diamagnetic values by an amount which is proportional to the concentration of the paramagnetic compound. Thus as $Co(acac)_2$ is added to a solution of a potential ligand (an alcohol), the proton resonances of L shift towards the resonance positions of the complex $Co(acac)_2L_2$. The relatively large contact shifts of the 1,2-cyclohexanediols are probably a result of chelate formation. It is well known (7) that ligands which can coordinate to a metal ion by way of two donor atoms form more stable complexes than those which coordinate through only one donor atom. Whether the diols actually form a *cis*-$Co(acac)_2$(diol)-type complex or whether the two hydroxyl groups of a monodentate diol exchange on the same site in a *trans*-$Co(acac)_2(diol)_2$-type complex, the result will be that the equilibrium constant for equation 1 will be larger than for a compound of similar structure with only one hydroxyl group.

The much larger contact shift in the case of *cis*-1,2-cyclohexanediol than for the *trans* isomer is noteworthy, since it implies that the interaction of the cobalt with the *cis* isomer is much stronger than that with the *trans*. The distance in an undistorted chair between vicinal equatorial hydroxyl groups (*trans*) is the same as between an axial and an equatorial hydroxyl group (*cis*). It is known (8), however, that reactions involving formation of a five-membered ring fused to a six-membered ring generally prefer the *cis* geometry. *Cis*-1,2-cyclohexanediol, for example, forms a cyclic ketal with acetone under certain conditions when the *trans* isomer does not (9). Another familiar example is the faster rate of oxidation of *cis*- as compared to *trans*-1,2-cyclohexanediol with lead tetraacetate (10) and with periodate (11); for most glycol oxidations with these reagents five-membered cyclic intermediates of Pb(IV) (10,12) and iodine (13) have been proposed. Thus, it is reasonable to expect that, in the present work, the cobalt would form a more stable complex with the *cis* isomer, with a corresponding larger contact shift.

The results obtained in this work demonstrate further the utility of $Co(acac)_2$ as a shift reagent, and suggest its application to conformational studies of cyclic polyhydric compounds such as carbohydrates and inositols.

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