The Use of Paramagnetic Transition-metal Ions in the Interpretation of Nuclear Magnetic Resonance Spectra of Complex Alcohols and Amines

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Summary Addition of paramagnetic transition-metal ions to solutions of complex alcohols and amines causes changes in their n.m.r. spectra which are useful in interpreting the spectra.

THE effects of paramagnetic transition-metal ions on line positions and widths in ^1H n.m.r. spectra have been recognized for several years.[1] Unusually large contact shifts in the ^1H n.m.r. spectra of organic ligands co-ordinated, for example, to the metals vanadium, cobalt, and nickel have been observed,[2] the spectra being reasonably well-resolved because of favourable electronic relaxation times. In the case of labile complexes such as those of Co acac$_2$ and Ni acac (acac = acetylacetonate) with various O-, N-, and P-donor ligands,[3] the observed spectra are time-averaged, the difference in chemical shift of a given ligand proton in diamagnetic and paramagnetic environments, $\Delta\nu$, being proportional to the mole fraction of the ligand complexed.

In spite of the large chemical shifts which often result when organic molecules are co-ordinated to paramagnetic metal ions, there have only been scattered reports in the literature of attempts to use contact shifts to analyse the ^1H n.m.r. spectra of complex organic molecules.[4] We have found that the presence of very low concentrations of paramagnetic metal ions can be of great help in simplifying the ^1H n.m.r. spectra of complex biological compounds such as carbohydrates, and we now report some preliminary results of a comprehensive investigation involving a large number of model compounds containing hydroxy-groups.

The solutions of the hydroxy-compounds varied in concentration from 0·2 to 1M in CDCl$_3$, although in any one system the concentration was kept constant. As a paramagnetic metal ion, Co acac$_2$ (concentration range

3×10^{-3}—0·3M) has mostly been used. Under these conditions, the cobalt complex probably exists primarily as the very labile species *trans*-Co acac$_2$L$_2$ (L = alcohol),[5] and the observed chemical shifts of the protons on L are the weighted averages of those of free and complexed L. On adding increasing amounts of Co acac$_2$ to a solution of a saturated alcohol in CDCl$_3$, quite drastic and systematic changes take place in the n.m.r. spectrum, both in the chemical shifts and in the resolution. The signals for hydroxy-groups generally broaden and move upfield at very low cobalt concentrations, although both the magnitude and direction of the shifts vary rather unpredictably; deuteriated samples are used whenever possible. Signals due to α-CH$_n$ groups always move downfield quite rapidly as the cobalt–alcohol ratio increases, the CH$_2$ resonance of a 1M-ethanol solution being more than 5 p.p.m. below the diamagnetic position in the presence of 0·3M Co acac$_2$. As expected, $\Delta\nu$ is proportional to the cobalt concentration and thus, in principle, the line position of the α-CH$_n$ group in a complex molecule can be determined by extrapolation to zero cobalt concentration. Although it had been expected that the signals for β-, γ-, *etc.* CH$_n$ groups would also shift downfield, the relative shifts being in some inverse relationship to their distance from the co-ordinating OH group,[6] it was found that these resonances usually shift to slightly higher field. Thus contact shifts can be used only to assign CH$_n$ groups α to the hydroxy-group(s). A second important change in the n.m.r. spectra of alcohols as Co acac$_2$ is added is broadening of the lines, an effect which *is* attenuated along a saturated organic molecule. This broadening has the effect of destroying the fine structure of the α-CH$_n$ resonance and changing it to a broad band at such low cobalt concentrations that the spectrum of the rest of the molecule is still quite well resolved. As the cobalt concentration is increased, the β-CH$_n$ resonance loses its fine structure, then that of the γ-CH$_n$ group, and so on.

It has been found that ketones, ethers, and sulphoxides do not interact significantly with Co acac$_2$; very little line broadening is observed, with either no contact shifts or shifts to slightly higher field.

As an example of the usefulness of the method, the change in the n.m.r. spectrum of a 0·2M-solution of 2-hydroxymethyltetrahydropyran in the presence of 2×10^{-3}, 4×10^{-3}, and 6×10^{-3}M Co acac$_2$ has been studied. In the spectrum of the diamagnetic solution, an intense multiplet centred at τ 8·5 can be assigned to the protons at C-3, C-4, and C-5; these signals do not shift significantly as Co acac$_2$ is added. The signal for the hydroxy-group at 7·9 broadens and moves to lower field as Co acac$_2$ is added. The signals for the methylene protons of the hydroxymethyl-group and the protons at C-2 and C-6 appear in the region τ 5·8—6·9 as a multiplet, which collapses and divides into two bands as Co acac$_2$ is added. The band which shifts to lower field corresponds in intensity to two protons. It should thus be possible to determine the number of protons α to the hydroxy-group(s) in a compound.

Some selectivity can also be gained by varying the paramagnetic complex. Although amines interact quite strongly with both Co acac$_2$ and Cu(ethylacetoacetate)$_2$, alcohols appear to interact very little with the latter. Thus while a 1M-solution of ethanol is relatively unaffected by a 10^{-2}M-solution of Cu(ethylacetoacetate)$_2$, the methylene quartet of a 1M-solution of diethylamine is broadened (although not shifted) by a 10^{-3}M-solution of Cu(ethylacetoacetate)$_2$ to such an extent that it cannot be observed. The methyl triplet, on the other hand, is still well resolved.

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